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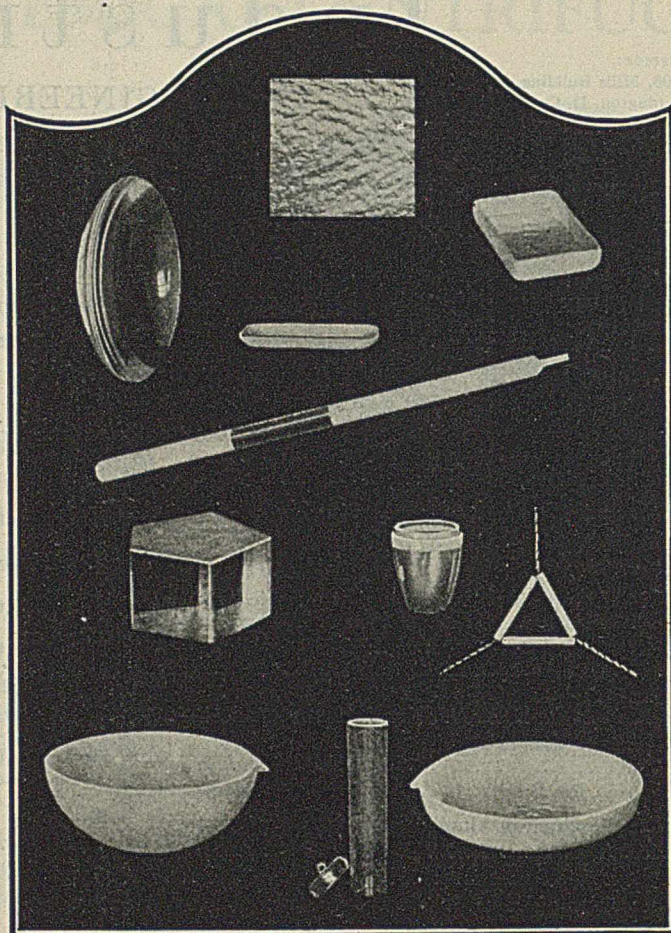
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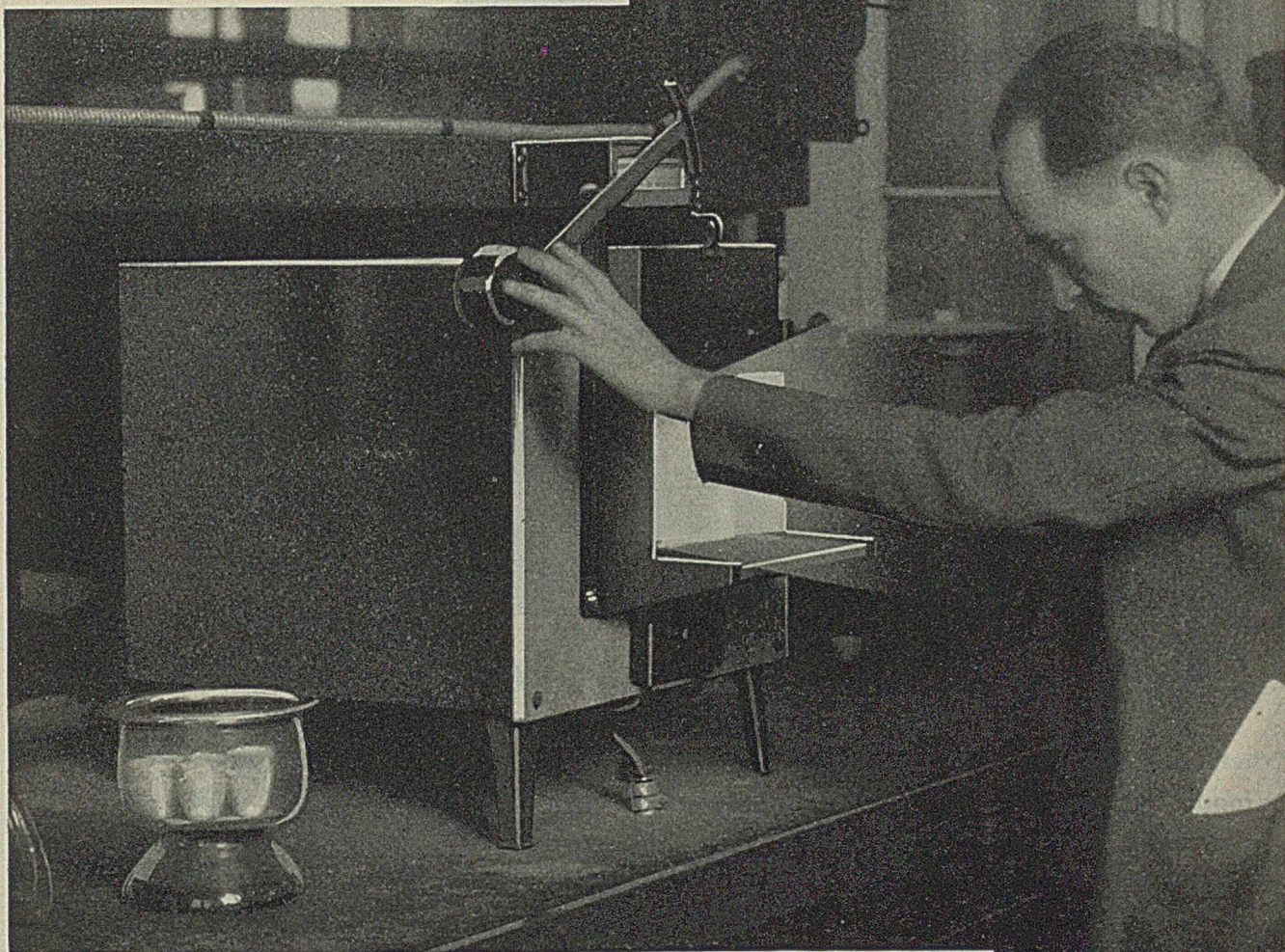
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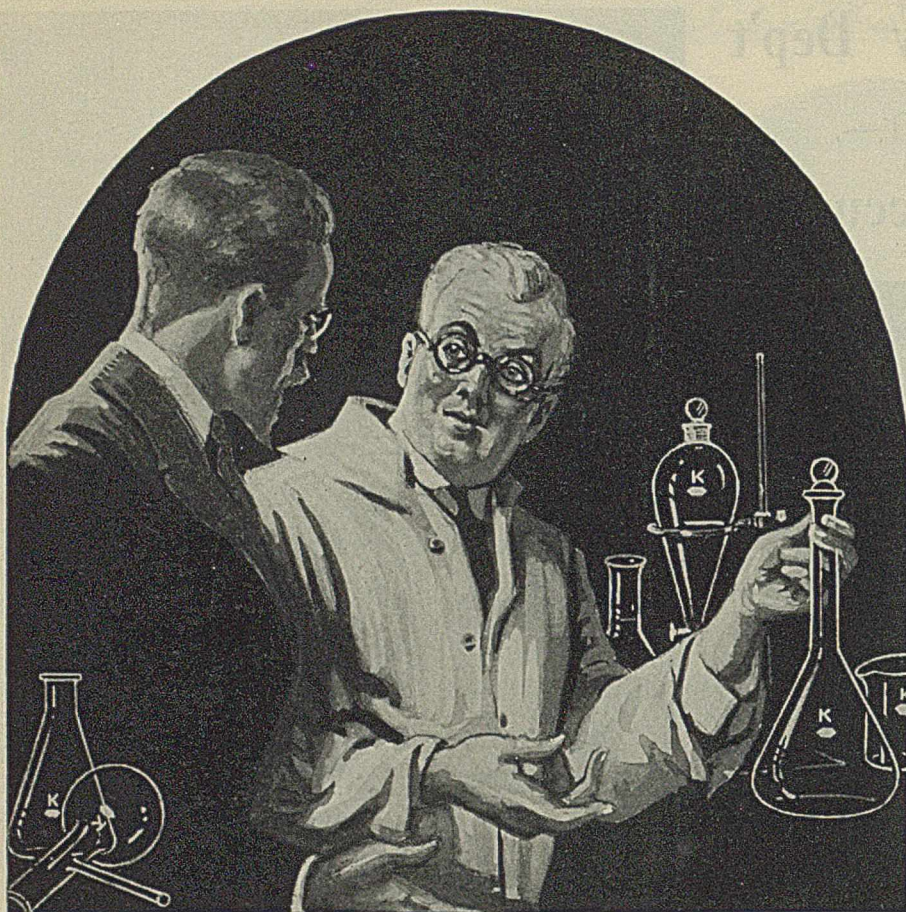
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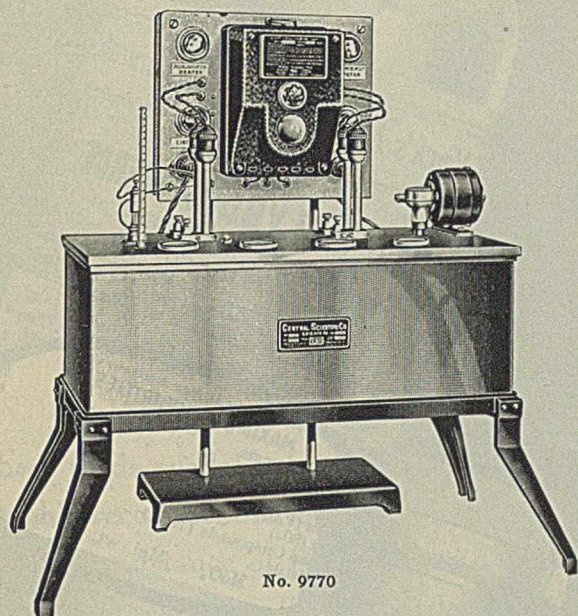
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Estimation of Small Amounts of Iron in Copper

BART PARK, Michigan College of Mining and Technology, Houghton, Mich.

SOME time ago the author was requested to determine the percentage of iron in some copper in the form of turnings which appeared clean, bright, and free from dust and oil. Ten-gram samples were dissolved in nitric acid, the solutions neutralized with ammonium hydroxide, and a slight excess added. The solutions were boiled, allowed to stand on a hot plate for several hours, the precipitated ferric hydroxide was filtered out, washed, and dissolved in dilute hydrochloric acid (1 to 15), and, after the addition of 5 cc. of bromine water, reprecipitated with ammonium hydroxide and washed free from copper. The precipitates were again dissolved in dilute hydrochloric acid, and the iron was estimated by the salicylic acid colorimetric method described by Yoe (1), which consists essentially of adding salicylic acid to a neutral solution of ferric iron and comparing the color with that of a standard sample treated in the same way.

The results were very discordant. In six runs the percentages were 0.0045, 0.0065, 0.0031, 0.0049, 0.0035, and 0.0039. No trouble was experienced in checking the colorimeter readings against standard solutions containing approximately the same amount of iron.

The estimation of minute amounts of such a widespread element as iron requires special precautions to avoid contamination from outside sources. The beakers, funnels, etc., used were thoroughly cleaned and then boiled out with concentrated hydrochloric acid and washed with distilled water. Blanks were run and corrections were made, where necessary, for the iron present in the reagents.

An investigation of other possible causes of such erratic results showed that most of the iron was on the copper and not in it.

Two hundred grams of turnings were treated with 500 cc. of water and 50 cc. of hydrochloric acid in the cold for about 2 hours. The turnings were filtered off and washed free from acid. A very little copper dissolved during the treatment, approximately 0.5 gram. Iron was determined in the filtrate. One 200-gram sample gave 0.0046 and another gave 0.0066 per cent iron. (All results are based on the weight of copper.) Duplicate 10-gram samples of the acid-washed copper were treated as before, and the iron found in the acid-washed turnings was 0.00086 and 0.00084 per cent, a satisfactory check.

The manner of contamination of the surface was next investigated. The cutting tool offered a possible source of

contamination and, in order to determine whether or not an appreciable amount of iron rubs off and contaminates the sample, the following experiment was performed.

A piece of copper wire bar was cleaned and placed on a clean lathe. The outside layer, about one-eighth inch (0.32 cm.) was turned off with a stellite cutting tool and discarded. A sample was turned off with the stellite tool and caught on a clean piece of paper. Then a sample was cut with a regular high-speed steel tool. Stellite was employed again, the two tools were alternated until about 3 pounds (1.36 kg.) of turnings had been collected. Each time the stellite was used a small amount of surface was turned off and discarded before starting to collect turnings. In this manner two samples were obtained from the same wire bar, one cut with stellite and the other with high-speed steel.

Two hundred grams of each sample were treated with dilute hydrochloric acid, as previously described. The first washing from the high-speed steel turnings yielded 0.00016 per cent iron, and those from the stellite turnings only 0.00006 per cent.

The samples were treated with another wash of 500 cc. of water and 50 cc. of hydrochloric acid, and after standing for 2 hours this was removed and a third wash put on them. Iron was estimated in each of the wash solutions. In both the second and third washings the amount of iron found was too small to allow comparison in a colorimeter, but was estimated to be about 0.00001 per cent. This corresponded to the amount found by running a blank on the hydrochloric acid. The first washing, therefore, must have removed all of the iron on the surface of the copper.

Fifty-gram samples of the washed and unwashed turnings were dissolved in nitric acid, and the iron determined as before, with the following results:

Stellite unwashed	0.00069%	High-speed steel unwashed	0.00080%
Stellite washed	0.00063%	High-speed steel washed	0.00063%

The source of the iron in the washings from the stellite turnings is not apparent. The stellite itself contained very little iron, less than 5 per cent. With copper in the form of turnings, a fairly large surface is exposed, and a small amount of the iron in the copper undoubtedly dissolves in the hydrochloric acid wash. This could hardly be 10 per cent of the iron present in the copper, however. Even though pains were taken to prevent incidental contamination, the author is

inclined to think this the most probable source of the greater part of the iron found in the washings.

Whether or not the cutting tool plays an important part in adding iron to the sample depends upon the extent of contamination from other sources. The following results, obtained from analysis of a piece of blister copper, serve as an illustration:

NATURE OF SAMPLE	IRON	
	Unwashed %	Washed %
Surface turnings, stellite	0.035 ^a	0.00074
Inside turnings, stellite	0.0016	0.00083
Inside turnings, high-speed steel	0.0019	0.00083
Washings from inside high-speed steel turnings		0.00104
Washings from inside stellite turnings		0.00077

^a Weighed as Fe₂O₃.

Here again the washings from the steel-cut sample yielded more iron than those from the one cut with stellite. The amount, however, is so small in comparison with the difference between the percentages found in the washed and unwashed turnings as to be negligible.

The above results indicate that it is advisable to wash samples of copper with dilute hydrochloric acid when an accurate determination of iron is desired.

LITERATURE CITED

- (1) Yoe, "Photometric Chemical Analysis," Vol. I, p. 243, Wiley, 1928.

RECEIVED November 10, 1930.

Specification of Color on Dyed Fabrics by Spectroanalysis

E. M. SHELTON¹ AND ROBERT L. EMERSON, Cheney Brothers, South Manchester, Conn.

THE files of a textile manufacturer contain many thousands of samples of dyed fabrics, either retained as standards for color lines or in connection with dyeing formulas which they illustrate. As standards for commercial production, such samples are frequently open to suspicion of having become soiled or faded, and a permanent record of the original condition of a sample would prevent occasional disputes from this cause. Since commercial matches usually deviate in some degree from the standard, some numerical measure of the discrepancies would be of great value in establishing tolerances. Moreover, a numerical record defining a color should be of value in systematic filing of the samples.

A spectrophotometric analysis of the light reflected from the colored sample is to the physicist the most satisfactory record and definition of the appearance of the sample. Whether the interpretation and use of such data by a textile manufacturer would be practicable has been open to question, but the time-consuming and expensive methods of color analysis which until recently were the only ones available prohibited any extensive practical trials. The invention of automatic recording color analyzers, notably one by Professor Arthur C. Hardy at Massachusetts Institute of Technology, subsequently developed and marketed by the General Electric Company, has radically simplified the task of preparing the spectrophotometric curves.

The purpose of this paper is to describe the experience at the laboratory of Cheney Brothers in recording the colors of fabric samples in terms of spectrophotometric curves using the General Electric recording color analyzer with modifications noted below.

The recording color analyzer has been described elsewhere by Hardy (2), and a general description will not be repeated. The machine, as delivered to Cheney Brothers' laboratory in January, 1930, was arranged to view an area of the sample about 1 mm. wide and 18 mm. long. The sample was held in a fixed position. It was found at once that this band of

By a modification of its sample holder, the General Electric recording color analyzer has been made applicable to analysis of color on fabrics. A program of work for applying spectroanalysis to color on fabrics is described, covering recording of color produced by individual dyestuffs, standard color lines, commercial matches, loss of color during fastness tests, and calculation of dye formulas.

illumination was too narrow to give a representative view of a fabric sample, for marked shifts in the recorded curve occurred with changes in the position of the sample. This was particularly serious in a fabric with a distinct rib effect such as a bengaline, but it was found that even in comparatively smooth weaves the surface irregularities were sufficient

to cause noticeable shifts in the position of the curve corresponding to changes in brightness with slight rotary shifts in the position of the sample in the sample holder. The manufacturer changed the optical system so as to increase the width of the area illuminated to approximately 3 mm., effecting some improvement. There still remained difficulty in obtaining reproducible readings because of vertical shifts in the curve resulting from slight rotation of the sample when replaced in the holder. Figure 1 illustrates the curves obtained from a sample of fabric when viewed in two positions 90 degrees apart. In the case of a satin this difference has been observed to be as much as 55 per cent.

ROTARY SAMPLE HOLDER

Following a preliminary demonstration of an experimental rotary sample holder by the General Electric Company, an inexpensive sample holder of this type was constructed and has proved highly satisfactory. Its construction is shown in Figure 2. A circular sample of fabric about 25 mm. in diameter is cut out with a die and placed behind a glass window in the holder which is mounted on the end of the shaft of a small motor. To correct for possible error due to viewing the sample through glass, the magnesium carbonate standard is cut in the shape of a thin disk which may be slipped into the sample holder behind the same glass window. The motor is so mounted in the cabinet of the color analyzer that the light strikes the sample at 90 degrees and is taken off at 45 degrees exactly as in the original fixed sample holder, the only difference being that the sample is rotated continuously. Experiments showed that the speed of rotation may vary over a wide range, and it is only necessary to avoid certain critical speeds at which synchronism with the flicker

¹ Since February 15, 1932, research chemist for the Tannin Corporation, 100 E. 42nd St., N. Y. C.

wheel occurs and a stroboscopic effect results. When this occurs, it is at once evident from the motion of the recording pen and can be stopped by a change in speed of the motor. A rheostat is installed in the motor circuit for this purpose. Motor speeds between 3000 and 10,000 r. p. m. were tried, and the lower speeds were found satisfactory.

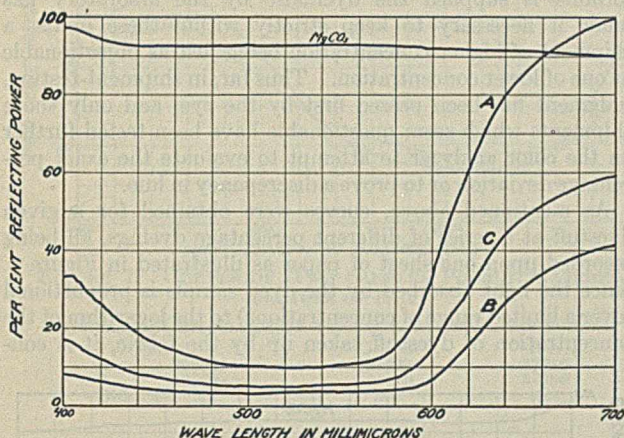


FIGURE 1. CURVES FOR A SAMPLE VIEWED IN TWO POSITIONS 90 DEGREES APART

- A. Warp vertical in stationary sample holder
B. Warp horizontal in stationary sample holder
C. Sample rotated

Referring again to Figure 1, there is shown the curve for a rotated sample as compared with curves obtained for the same sample viewed in two fixed positions 90 degrees apart. Figure 3 shows curves of samples of a satin and a crepe which were taken from goods accepted as a commercial color match. These illustrate the difficulty of comparing curves obtained with samples held in a fixed position and the good agreement of curves obtained from rotating samples. This confirms our assumption that the practical color matcher, when called upon to match fabrics of strikingly different construction, consciously or unconsciously matches the average appearance of one sample to that of the other with practically the result obtained by rotation in the color analyzer.

CALIBRATION OF COLOR ANALYZER

The color analyzer is calibrated and its correct adjustment is checked not only by running curves for magnesium carbonate, but by transmission curves for two glasses of known transmission values, one blue and one red. It has been the practice to make these tests once a day, keeping a permanent file of the curves obtained. All measurements made upon samples submitted are dated so that they may at any time be compared with the calibration curves for that day. Ex-

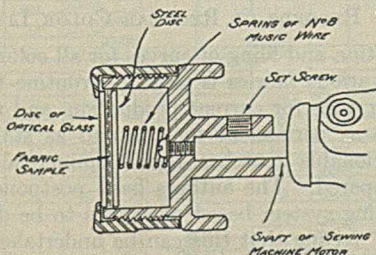


FIGURE 2. ROTATING SAMPLE HOLDER

perience has shown that the calibration curves do not shift appreciably during any one day, so it has not been necessary to run them for each fabric sample tested. For convenience in subsequent calculations, the curve for magnesium carbonate is generally recorded on the sheet with those of samples analyzed.

PREPARATION OF FABRIC SAMPLES

It will be appreciated that satisfactory results depend not only upon the performance of the color analyzer but also upon the preparation of the sample. In trying to define a dyestuff, not in terms of a sample of the dyestuff as obtained from the manufacturer but in terms of its color value when applied to a sample of fabric, the dyeing technic is exceedingly important. In dyeing silk, perfect exhaustion does not usually occur in the laboratory and is seldom obtained in plant practice. Reproducibility of dyeings depends, therefore, upon exceedingly accurate standardization of the dye-bath and the whole procedure for dyeing.

In spite of marked improvement in dyeing technic acquired through the necessity for reproducibility and the evidence shown by the color analyzer of frequent deviations in dyeing uniformity, it is believed that at present the limiting factor in accuracy in these experiments is in application of the dyestuffs to the fabric rather than in the measurements obtained with the color analyzer. It is safe to say that one by-product of real value from the experience in this laboratory

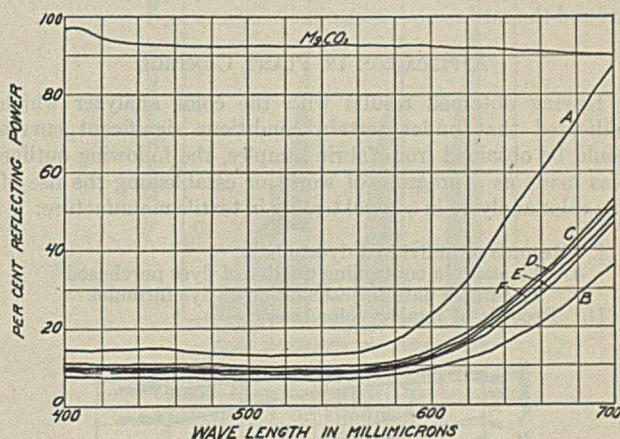


FIGURE 3. COMPARISON OF COLORS ON SATIN AND CREPE SILKS

- A. Satin with warp vertical
B. Satin with warp horizontal
C. Satin rotated
D. Crepe with warp vertical
E. Crepe with warp horizontal
F. Crepe rotated

with the color analyzer has been the growth of a consciousness of the possibility of more exact reproduction of dyeings and a resulting general improvement in laboratory practice.

In the case of samples of fabrics obtained from mill production or from outside trade, there has been a limitation in the application of the color analyzer owing to the area of sample required for examination. Not only is a circular sample 25 mm. in diameter used in the present sample holder, but several thicknesses of the material have been necessary to avoid errors due to the light passing through the sample. In the case of thin goods such as voiles, as many as sixteen thicknesses have been found necessary, although in most fabrics three or four layers are sufficient. Printed designs seldom offer large enough areas of a given color to furnish the necessary samples. In piece dyed goods there is no trouble provided sufficient material has been submitted for test.

At the time of this publication, although some measurements of color on yarn samples have been made, a completely satisfactory method of mounting the yarn sample has not been developed. The construction of the sample holder made it convenient to pack the space behind the glass with small bits of fiber clipped from the sample, but it was demonstrated that the curve obtained varied with the fineness of cutting of the yarn, and a more representative curve would be had if all the yarn fibers could be stretched smooth and flat behind the glass of the sample holder. With a larger sample holder

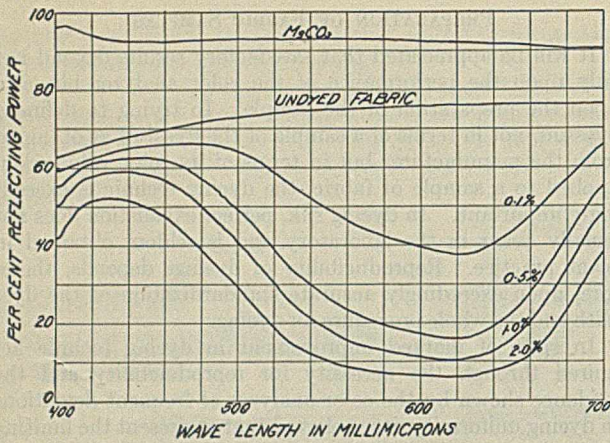


FIGURE 4. FAMILY OF CURVES FOR BRILLIANT WOOL BLUE FFR APPLIED ON SILK CREPE

in which a square card could be mounted, this condition could readily be obtained using several layers of yarn wound around the card.

APPLICATION IN PLANT CONTROL

Having obtained results with the color analyzer which indicated that under certain conditions significant curves could be obtained from fabric samples, the following outline was made as a program of work for establishing the use of the color analyzer in control testing in textile manufacture:

- I. Records of individual dyestuffs
 - a. To assist in controlling quality of dyes purchased
 - b. To furnish data for calculation of dye formulas
- II. Records of regular color lines

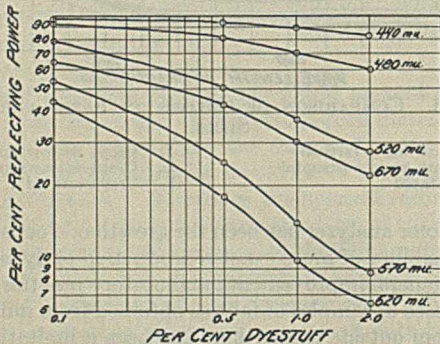


FIGURE 5. DATA FOR BRILLIANT WOOL BLUE FFR REPLOTTED FROM CURVES OF FIGURE 4 AFTER CORRECTING FOR MAGNESIUM CARBONATE AS 100 PER CENT REFLECTION AND FOR COLOR FROM UN-DYED FABRIC

- III. Records of matches obtained in commercial production
 - a. To accumulate data for tolerances in deviations from standard color lines

- IV. Records of wash tests and light tests on individual dyestuffs and standard color lines

- a. To accumulate data on which to establish tolerances for loss of color during these tests

- V. Calculation of formulas in terms of two or more dyestuffs required to produce a color on fabric from which a given spectrophotometric curve will be obtained

I. RECORDS OF INDIVIDUAL DYES

For this purpose dyeings were made on a crepe fabric with each of the commonly used dyestuffs. Dyeings were made in each case with a series of percentages of dye (calculated, as is customary in dyeing practice, on the weight of the fabric sample). The values taken were 0.1, 0.5, 1.0, 2.0, and 4.0

per cent. Of this series the 2.0 per cent dyeing was chosen as a standard of comparison for shipment testing.

As a rule, a shipment of dyestuff which is within 5 per cent of the concentration guaranteed by the manufacturer is satisfactory provided the hue is correct. The increasing application of standardized dyeing in which a definite dyeing formula is supplied the dyehouse by the laboratory has made it necessary to keep strictly within these limits, a shipment of higher concentration being just as objectionable as one of lower concentration. Thus far, in shipment-testing, judgment has been passed first by the eye, and only those shipments which seem questionable have been tested further on the color analyzer to attempt to evaluate the exact percentage deviation or to prove a discrepancy in hue.

As mentioned above, curves were obtained for a given dyestuff at a series of different percentage dyeings, all being recorded upon one sheet of paper as illustrated in Figure 4. Since the light absorbed by the dyed sample is proportional (over a limited range of concentrations) to the logarithm of the concentration of dyestuff taken up by the fabric, it is con-

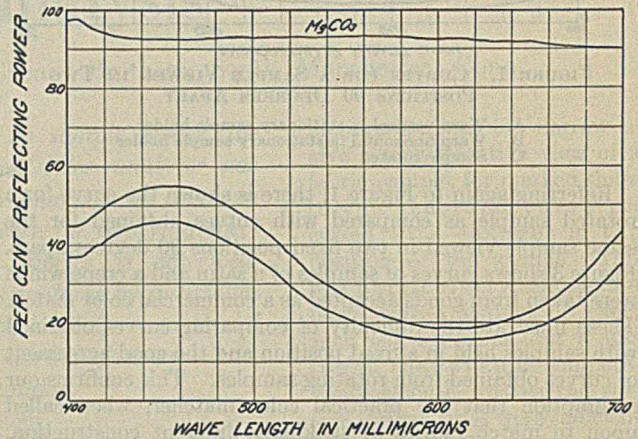


FIGURE 6. CURVES OF TWO SAMPLES OF POOR MATCH WITH DIFFERENCE IN BRIGHTNESS, NOT HUE

venient for purposes of interpolation to plot this data over on another sheet as illustrated in Figure 5. In order to include the range of values most conveniently, log concentration has been plotted against log reflection. In Figure 5 each curve represents the reflection at any concentration at a given wave length. The curves thus obtained are used in interpreting deviations in color-analyzer curves in terms of per cent dyestuff involved, applying both in estimations on faulty shipments of dyes and in calculation of dye formulas to correspond to given spectrophotometric curves.

II. RECORDS OF REGULAR COLOR LINES

The collection and filing of curves for all colors offered for sale in the various fabrics is largely a routine type of test. This is being done for current production, and the resulting curves serve as permanent records and as standards with which questionable matches from commercial production may be compared. The authors have postponed trying to develop a filing system based on values to be derived from these curves, feeling that this can be undertaken most conveniently when a large number of measured samples has been collected. The simplest system to suggest itself consists of designating each color by a number derived from the ordinates of the curve at a number of arbitrarily chosen wave lengths. (The present practice is to designate colors in the manufactured line by numbers which have no significance whatever.) A numerical expression in terms of three excitation factors calculated from the curve would be still more sig-

able discrepancy appears greater when the difference is one of brightness than when hue is involved. It must be appreciated that the severity or laxity of the inspector in judging matches is a direct indication of the tolerance allowed by the trade. The consistent use of the color analyzer to assist the inspector in passing doubtful lots would do much to establish a more uniform standard for color matches.

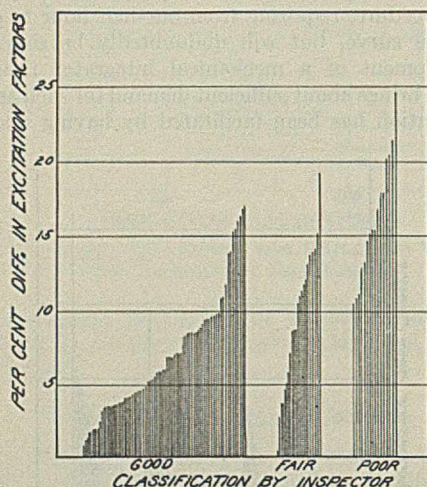


FIGURE 10. GRAPHIC CORRELATION OF COLOR MATCHES WITH PREDOMINATING HUE DIFFERENCES

The use of the color analyzer has proved especially valuable in comparing goods of radically different construction in which individual persons frequently disagree as to whether or not a satisfactory match has been obtained. Attempts have been made to use measurements of dyed yarns to compare with measurements of the color in the fabric obtained from the yarns, but a completely satisfactory method of mounting the yarn sample has not been obtained.

IV. RECORDS OF SAMPLES AFTER FASTNESS TESTS

WASH TESTS. Good washability of fabrics has come to be more and more expected by the customer, and in the case of silks very marked improvement in washability has been shown within the last 5 years. Standard methods of making wash tests have been fairly generally adopted, but the decision as to the degree of loss of color through the washing operation has been left to estimation by eye.

Since the change in appearance of a properly dyed fabric after washing is chiefly one of brightness, it is comparatively simple to apply the color analyzer to obtain a numerical expression for the loss of color during this test. Typical curves from samples before and after wash test are shown in Figure 11. It is only necessary to express the change in terms of per cent difference in reflectance at any one wave length. It should of course be kept in mind that the color analyzer can give only a numerical value to the change that takes place during such a test, and the trade will establish the tolerances based upon commercial practice. However, a tolerance which can be expressed in numerical values is certain to become more uniform and less likely to lead to misunderstanding and disputes.

LIGHTFASTNESS TESTS. Experiments on the fastness of the dyed samples to light were based on exposures to a carbon arc light in the Fade-Ometer. These curves are not so simply interpreted as those for wash tests, since in some cases there is a change in brightness, but more commonly the action of the light causes a distinct change in hue. Typical curves are shown in Figure 12. The same calculation for comparing curves for commercial matches may be applied to curves before and after light exposure.

V. CALCULATION OF FORMULAS FROM CURVES

This section has been included in the outline for a program for application of the color analyzer to textile manufacture, but, because the preceding steps obviously needed to be developed first and because at this time the ability to calculate the dye formula from the curve is of less practical than theoretical interest, there are no data to report here.

In one instance, however, in which goods are dyed by a continuous method (the Cohoe process) ordinary experience in dye application was not adapted to establishing the continuous feed bath required. A study of the substantivity of individual dyestuffs using the color analyzer has proved a solution for this problem and is reported in a paper by W. P. and E. R. Cohoe (1).

SPECIAL APPLICATIONS

For development work in the laboratory where experiments may be carried out under controlled conditions, the color analyzer is invaluable. A simple illustration of a laboratory use has been the establishing of a test for the tarnishing action of velvets intended for the jewelry box trade. The color of a

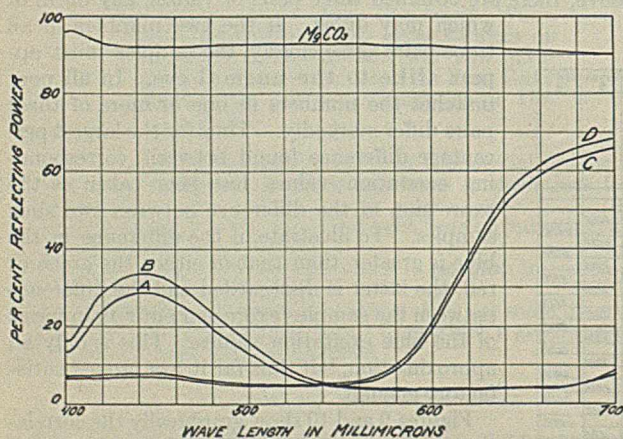


FIGURE 11. CURVES OF SAMPLES BEFORE AND AFTER WASH TESTS

- Victoria Blue B before washing
- Victoria Blue B after washing, showing unsatisfactory fastness
- Erie Scarlet 3B before washing
- Erie Scarlet 3B after washing, showing satisfactory fastness

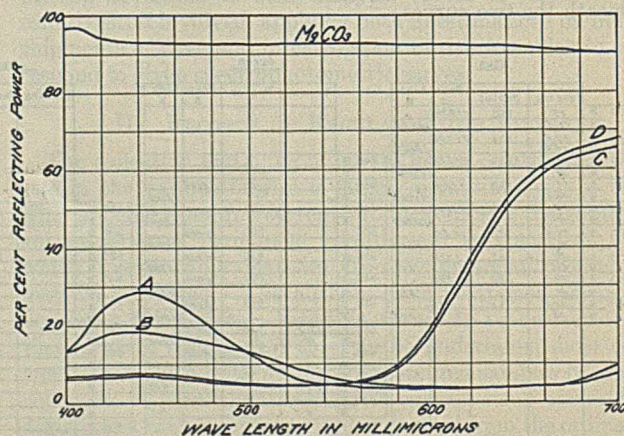


FIGURE 12. CURVES OF SAMPLES BEFORE AND AFTER LIGHT EXPOSURE

- Victoria Blue B before exposure
- Victoria Blue B after 5 hours in Fade-Ometer, showing objectionable change
- Erie Scarlet 3B before exposure
- Erie Scarlet 3B after 25 hours in Fade-Ometer, showing good fastness

disk of silver is recorded in the analyzer before and after a standard exposure in contact with the velvet sample, and from the two curves obtained there may be calculated a numerical grading of the tendency of the velvet to tarnish the metal.

CONCLUSION

The work described in this paper is still in progress, but since this program of development may be applicable in other fields and of greater general interest than any detailed and final results, the authors have felt justified in publishing this work at this stage. The expense of the color analyzer and the necessity of an operator with somewhat specialized training will probably limit its use in a plant dyehouse where a simpler form of color comparator is better adapted if and when it is

necessary to supplement the trained eye of the dyer. Special laboratory applications and the use of the analyzer in mill control, particularly in establishing tolerances in commercial matches and for loss of color after wash and light tests, should justify a general recognition of spectrophotometric analysis in the textile industry in the near future.

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RECEIVED December 28, 1931. Presented before the Division of Dye Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Automatic Apparatus for Determination of Small Concentrations of Sulfur Dioxide in Air. III

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EARLIER papers of this series (1, 2) describe the development of a completely automatic apparatus for the determination of traces of sulfur dioxide in air. This apparatus has now been improved and its application extended to the continuous analysis and recording of (1) small concentrations of sulfur dioxide in the field, with a range of 0.01 to about 7.0 p. p. m.; (2) higher concentrations up to about 6 per cent in flue gases which are low in sulfuric acid but contain appreciable amounts of carbon dioxide; and (3) the absorption of sulfur dioxide by plants in laboratory fumigation experiments in the range from less than 0.1 p. p. m. to 50 p. p. m. This paper describes the apparatus for the three purposes mentioned above, and submits confirmatory analytical data on the absorption of the gas by plants.

The machines are built on an angle iron framework and are driven by a small motor operating through the appropriate commercial reduction gears. Steady suction is obtained by means of a small Crowell pump, and the air volume is measured in a wet test meter, which may be provided with an electrical contact on the 1-cubic foot dial, so that the air volume can be recorded on the chart with the sulfur dioxide analysis. Steel cams, 5 inches (12.7 cm.) in diameter, operate the poppet valves as previously described (2). The valves are made from 0.635-cm. (0.25-inch) brass angle valves, as illustrated in Figure 1, and are mounted in solder permanently on a steel plate, care being taken to secure good alignment for the valve rods which are connected with the cam followers through universal joints. The valves have functioned perfectly over a period of more than 2 years. The heavy-wall flexible red rubber bellows will last more than 1 year, and can readily be replaced. The apparatus is connected by block

The application of the acid-hydrogen peroxide method to the continuous analysis of traces of sulfur dioxide in air, as well as higher concentrations in smelter flue gases, is described, and its application to fumigation studies for the absorption of the gas by plants is compared with analyses of the plants themselves for total sulfur, with results which indicate that these analytical machines are capable of a high degree of precision in evaluating the concentration of sulfur dioxide in air.

tin tubing, which is unaffected by the solutions employed. The mercury valves described in the first paper (2) have been replaced by these poppet valves.

Slightly acidulated hydrogen peroxide solution is used as absorbent. In the first and third of the uses for which the apparatus was designed, this solution contains about 0.003 per cent hydrogen peroxide and 0.0005 per cent sulfuric acid.

In the second it contains more peroxide. The increased conductance of the solution, as indicated by a recording Wheatstone bridge, gives a measure of the amount of SO₂ absorbed. A typical assembly is shown in Figure 2, which is a photograph of a laboratory machine. The solution is fed from a large supply bottle, 1, into a constant-level bottle, 2, whence it is measured in a 100-ml. pipet, 3, and placed in an absorber, 4. While the solution in one absorber is being aspirated, the solution in the other is replaced with fresh absorbent. The photograph also shows the motor and reduction gears, 5, the gas meter, 6, the cams, 7, and an assembly of 14 valves, 8.

FIELD MACHINE

The field apparatus is installed in a small well-insulated house, and the gas sample is drawn through a tin tube through the roof, the opening being provided with a screen to exclude insects. The room is provided with a thermograph and in the winter is thermostated.

The field apparatus aspirates each solution for 20 minutes, drawing about 15 liters of air per minute and recording each cubic foot on the chart. This large volume of air causes an appreciable evaporation of the absorbing liquid, with attendant cooling, two factors which tend to compensate each other. The absorbers are mounted snugly in heavy copper

pipes, which reduce the cooling effect so that the latter offsets almost exactly the evaporation of the absorbing liquid. Temperature compensation is obtained with a large volume of

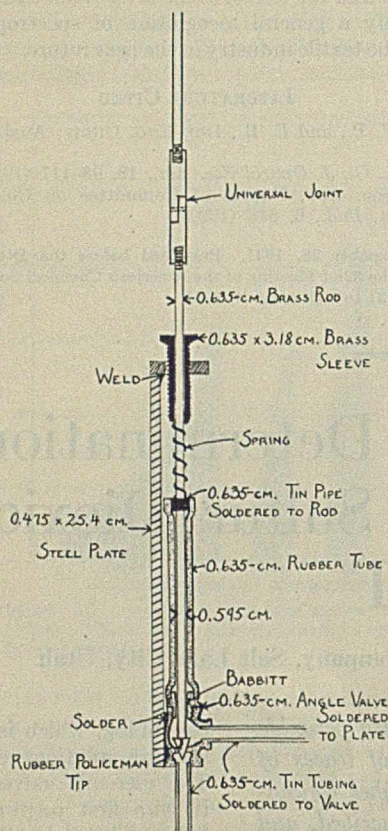


FIGURE 1. SECTION OF MOUNTED POPPET VALVE

approximately 0.002 *N* sulfuric acid in series with the variable temperature rheostat of the recording Wheatstone bridge. By means of a double-pole double-throw switch, this compensating solution can be checked against the regular temperature compensator provided on the recorder. The record shows the concentration over each 20-minute period, but peak concentrations during intervals as small as 1 to 2 minutes can readily be calculated from the slope of the conductance curve.

The apparatus has been used during the past 3 years to determine the sulfur dioxide content of the air near three smelters of the American Smelting and Refining Company, and a number of machines have also been used by investigators of the United States Department of Agriculture and the Canadian National Research Council.

FLUE-GAS MACHINE

It has been demonstrated that the method is applicable to much higher concentrations of sulfur dioxide than occur in the field, and that the presence of carbon dioxide does not interfere appreciably with the determination. An apparatus especially adapted for the analysis of the flue gases has therefore been installed at the El Paso Smelting Works. This machine is provided with two 600-cc. aspirator bottles and a 0.32-cm. copper pipe for drawing the gas sample from the flue. The electrodes in the conductivity cell have a constant of about 2 reciprocal centimeters, so as to permit the measurement of higher concentrations of sulfuric acid. The apparatus operates on a 10-minute schedule, and has been checked against the iodine method of flue-gas analysis.

LABORATORY MACHINE

The laboratory apparatus as finally constructed is particularly well adapted for the study of the absorption of sulfur dioxide by plants in both day and night fumigations, with either high or low concentrations. The absorption is determined by measuring the change of sulfur dioxide concentration of an air stream of known velocity on passing through a fumigation cabinet. The machine operates on a 2-minute schedule. This time period is sufficiently short so that samples from intake and outlet positions in the cabinet may be considered to have been taken virtually simultaneously, unless the concentration in the cabinet is fluctuating rapidly. In very short fumigations, of the order of 15 minutes or less, it is necessary to use two machines in order to get reliable absorption data. For our purpose it is desirable to be able to measure the difference of concentra-

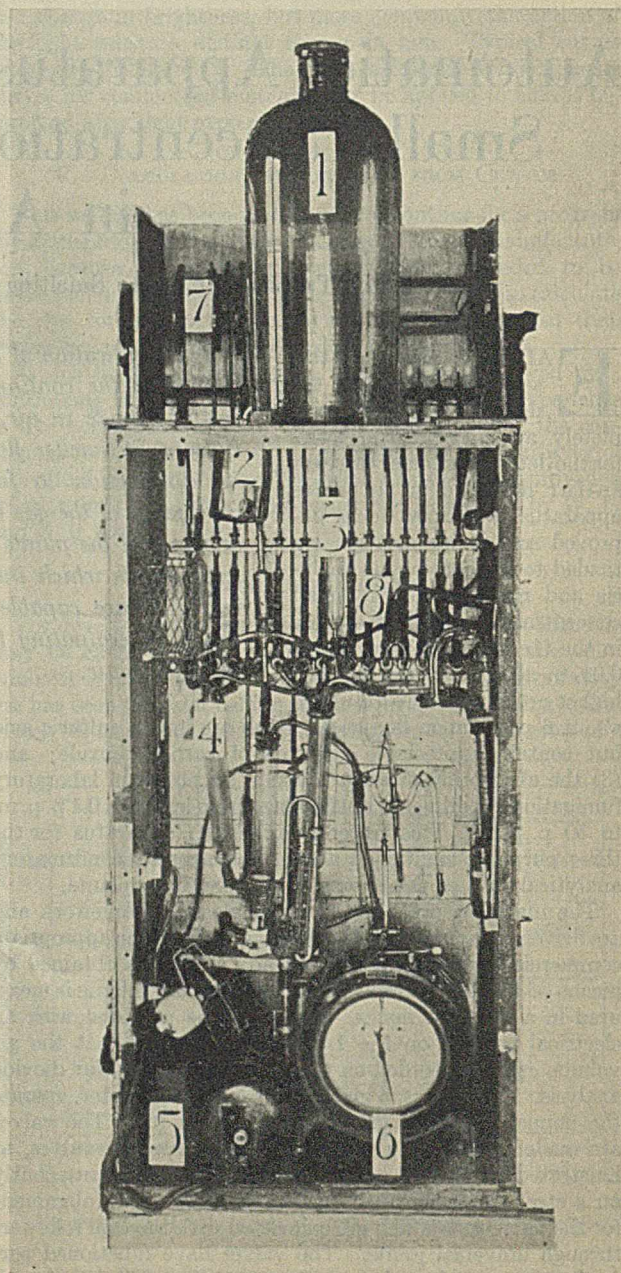


FIGURE 2. LABORATORY PORTABLE SULFUR DIOXIDE AUTOMETER

tion between the intake and outlet positions with an accuracy of at least 1 per cent of the total concentration.

As it is difficult to adjust the two absorbers to register exactly the same concentration under identical conditions of operation, it is necessary to alternate the source of the sample for each absorber so that any machine difference between the two absorbers can be eliminated by averaging the indicated concentrations for each absorber sampling from both intake and outlet. This alternation of the source of the sampling can of course be accomplished by hand in short fumigations, but with long fumigations it is necessary to do it automatically. The laboratory machine (Figure 2) has therefore been provided with a second cam shaft, placed directly underneath, and geared to the first with a reduction of speed of 16 to 1 to operate a system of valves so that each absorber draws one blank sample from the outside air and 7 subsequent samples from either intake or outlet points in the fumigation cabinet before drawing another blank sample, and reversing the source of the sample. The slower moving cam shaft is also provided with four cams, which, when the corresponding cams above are inactivated by raising the nuts on the valve rods, recharge the absorbers only after eight consecutive aspirations, thus permitting the accumulation of the absorbed gas so that concentrations as low as 1 part in 10 million can be measured with a high degree of accuracy.

Although not absolutely necessary to the operation of the machine, the blank aspiration has been found to be useful in calculating the data. The omission of one-eighth of the absorption curve has not often been of any consequence, since the gas concentration is usually uniform.

The whole apparatus is inclosed with light wooden panel and provided with thermostatic control.

ABSORPTION DATA

During the past season a number of fumigations of alfalfa plots have been carried out, using two laboratory machines operating simultaneously and sampling from the same two positions in the fumigation cabinet. The latter is a light metal framework 1.98 by 1.98 by 1.52 meters, covered with sheets of celluloid and mounted in a heavy felt pad on a galvanized iron base. A mixture of sulfur dioxide and air, made uniform by baffle plates in the line, is blown in at the top of the cabinet through a 15.2-cm. pipe and led out through a 20.3-cm. pipe in the base. The sulfur dioxide is supplied from a bottle of the liquid and is controlled by a needle valve and capillary flowmeter. This apparatus is thermostated to yield a steady flow of gas. The air blower can deliver 1400 liters of air per minute, but the volume actually employed is modified by a shutter on the intake, according to the amount of vegetation on the plot.

The concentrations observed in these fumigations are

recorded in Table I, which indicates a very close concordance between the two machines, both as to total concentration and the difference of concentration between intake and outlet positions. In general the concordance in the latter case is better than 1 per cent, the two cases in which this difference is exceeded being in fumigations in which there was an appreciable fluctuation of the concentration in the cabinet.

TABLE I. SULFUR DIOXIDE CONCENTRATION AT INTAKE AND OUTLET OF FUMIGATION CABINET

(Determined by two analytical machines sampling simultaneously from same points)

PLOT	MACHINE	DURATION OF EXPT. Min.	SO ₂ CONCENTRATION		DIFF. %
			Intake P. p. m.	Outlet P. p. m.	
5-14	1	56	6.60	5.70	13.6
	2		6.59	5.58	15.3
5-13	1	58	6.17	5.24	15.1
	2		6.19	5.23	15.5
5-1	1	65	6.17	5.65	8.5
	2		6.21	5.65	9.0
5-2	1	73	6.50	6.10	6.2
	2		6.48	6.05	6.6
4-9	1	70	6.79	6.34	6.6
	2		6.81	6.36	6.6
6-7	1	60	7.02	6.34	9.7
	2		7.00	6.32	9.7
2-7	1	70	5.23	4.60	11.2
	2		5.17	4.59	12.0
3-5	1	125	0.555	0.541	2.5
	2		0.553	0.534	3.3
3-5	1	330	0.276	0.251	10.0
	2		0.270	0.244	9.6
3-5	1	375	0.232	0.213	8.4
	2		0.236	0.216	8.7
3-5	1	120	0.220	0.202	8.2
	2		0.231	0.208	9.9

The volume of air which is sent into the fumigation cabinet is measured by anemometers in both the intake and outlet pipes. The reading of the outlet instrument is usually about 10 per cent lower than the other, and the average of the two readings is taken as the correct volume, on the assumption that about equal portions of gas at both intake and outlet concentrations escaped from the cabinet without going through the outlet pipe. The absorption of sulfur dioxide by the walls of the cabinet is determined by a blank fumigation with the soil completely covered by sheets of celluloid.

The weight of leaves on the plot is found by harvest a few days subsequent to fumigation, allowance being made for additional growth during this period and the percentage of leaves being determined by samples taken at the time of fumigation. The stems are ignored in this calculation, since it has been found that they contain only about 5 to 10 per cent of the added sulfur, even in the case of the two long fumigations in which part of the increase in sulfur in the plants may

TABLE II. ABSORPTION OF SULFUR DIOXIDE BY ALFALFA

(Determined by analysis of SO₂-air mixture and the leaves)

PLOT	DATE 1931	TIME	DURATION OF FUMIGATION Min.	AIR VOL. L./min.	WT. OF SO ₂ Mg./cc.	CONC. SO ₂ INTAKE P. p. m.	SO ₂ ABSORBED BY:			TOTAL S IN DRY LEAVES		S ABSORBED FROM ANALYSIS OF:			
							Cabinet and plants %	Plants		Before fumigation %	After fumigation %	Air P. p. m.	Leaves P. p. m.		
								%	Mg. of S					Mg.	
4-14	8/21	12-1 P. M.	56	8700	2.14	6.60	14.5	13.5	465	310	1.350	1.480	1500	1300	
5-13	8/25	12-1 P. M.	58	8500	2.14	6.18	15.3	14.3	465	450	1.353	1.497	1030	1440	
5-1	9/3	3-4 P. M.	65	8250	2.14	6.19	8.8	7.8	278	472	1.310	1.390	590	800	
5-2	9/1	5-6 P. M.	73	8500	2.19	6.49	6.4	5.4	238	604	1.150	1.210	394	600	
4-9	8/28	6-7 P. M.	70	8500	2.23	6.80	6.6	5.6	253	402	1.130	1.210	630	800	
6-7	9/9	11:30 A. M. to 12:30 P. M.	60	8500	2.24	7.01	9.7	8.7	348	310	1.145	1.290	1120	1450	
2-7	10/3	12-1 P. M.	70	8500	2.24	5.20	11.6	10.6	368	350	1.265	1.410	1050	1450	
3-5	9/22 to 9/25	Continuous	4110	8600		0.384				900	300	1.170	1.450	2900	2800
			12770	8600		0.320				2400	330	1.170	1.877	7050	7070
3-3	10/8 to 10/27	Continuous	26900	8500		0.202			4920	400	1.200	2.380	12300	11800	

have come from the soil. This effect is probably small, however, because samples of leaves taken from a nearby check plot during the fumigation period of plot 3-5 showed no appreciable change of sulfur content.

The absorption values have been checked by analysis of the leaves for total sulfur using the Burgess-Parr sulfur bomb. The leaf samples are taken in large rubber-stoppered test tubes, weighed fresh, then frozen in salt and ice, and allowed to dry in air for about 24 hours before grinding. Analyses are run on 0.7-gram air-dried samples. The procedure is carefully standardized, particularly as to the amounts of reagents and the volume and acidity of the liquid before precipitation with barium chloride. Ten milliliters of 0.1 *N* sulfuric acid are added to each solution as a true blank and the precipitate is allowed to stand 2 to 3 days, with occasional agitation, before filtration.

Table II shows a fairly satisfactory concordance between the sulfur absorbed, as indicated by the analysis of the gas

and the analysis of the leaves. The latter value is in most cases somewhat higher than the former, probably because the absorption took place unevenly on the plants, and there was doubtless a tendency to take as the leaf sample more of the active leaves near the top of the plants, which probably had absorbed more gas than the less active leaves lower down. The uncertainty in the sulfur analysis of the leaves is of the order of several hundred parts per million, owing principally to sampling errors, but also partly to analytical errors. These errors were both minimized by taking at least two samples before and after fumigation and running a number of duplicate analyses on each sample.

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RECEIVED December 21, 1931.

Methods for Microanalysis of Extremely Hygroscopic Substances

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DURING the regular course of analysis, certain series of compounds were found to be so extremely hygroscopic that the existing methods of keeping the material free from water were found to be inadequate. New methods were therefore developed for the analysis of these compounds.

MICRO-DUMAS METHOD

While investigating some extremely hygroscopic derivatives of choline chloride, it was found that a solid micro sample would become liquid in an interval from 10 to 100 seconds. According to the regular method of Pregl (*1*), the material was weighed in a small weighing tube about 3 mm. in diameter, fitted with a ground-glass stopper. The material, however, became sticky from absorbed water and could not be shaken from the tube properly. The material which was shaken into a shaking bottle became liquid and could not be quantitatively transferred to the combustion tube. The nitrogen values on these compounds ran consistently low and were never within the 0.3 per cent limit of error.

Very good results were obtained, however, by a modification of the Pregl method. A glass-stoppered weighing bottle or "piggie" as described by Pregl, having a diameter of 10 mm. and a length of 40 mm., was cut down to a length of 15 mm. The sample was easily placed in the bottle with great speed. The bottle was then placed in a vacuum desiccator for about 20 minutes. After it had been dried in this way it was stoppered, placed in the balance, and weighed within 5 minutes. Then the stopper was removed and the sample was transferred quickly to the shaking bottle which contained dry powdered copper oxide. The stoppered weighing bottle was weighed at once. The sample in the shaking bottle was mixed with the copper oxide immediately so that the material would not become sticky and adhere to the glass. The vacuum desiccator was situated near the balance so that the weighing tube was kept at the same temperature as the balance. The air which was admitted to the desiccator was passed slowly over magnesium perchlorate trihydrate. Results obtained by this method were quite constant and were only slightly below theory.

ANALYSIS FOR CARBON AND HYDROGEN

Certain compounds of the type $B \cdot 3H_2O$ gave off the exact amount of water ($3H_2O$) as determined by drying experiments on a macro scale. The analysis of B, however, always indicated that the material still held at least 1 H_2O . The material B apparently picked up water very rapidly, as all methods of keeping the sample dry were found to be inadequate. The analyses for carbon in B were seldom within 1 per cent of theory, and the analyses for hydrogen were always high. The material appeared to be very hygroscopic and could not be exposed to the air even for a very few seconds without absorption of moisture. Therefore, the material was dried and analyzed in the following manner: The air-dried material which had been previously analyzed as $B \cdot 3H_2O$ was weighed in a platinum boat and placed in the combustion tube in the same manner as for regular carbon and hydrogen determination. Previously weighed absorption tubes were placed in the usual position to determine the amount of water driven off and to show any decomposition which might take place. Nitrogen was then passed through the tube by way of the regular preheater and drying train at a rate of 5 cc. per minute. The material was heated to 100° to 105° C. by means of a Pregl heating block. The nitrogen was passed over the material for a period of about 90 minutes. The apparatus was then swept out with air for 20 minutes, and the absorption tubes were removed and weighed to determine the results of the drying. When the amount of water was very small it was found necessary to correct for the dehydrite absorption tube which picked up water over the 2-hour period. The weights of the ascarite absorption tubes were very constant, showing little or no decomposition. The absorption tubes were then attached to the combustion tube, and the carbon and hydrogen analysis was carried out in the usual manner. The results were very satisfactory for the material B when entirely free from water.

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Determination of Hydroxyl Number of Oils, Fats, and Waxes

An Accurate, Rapid Method

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THERE is an obvious need for improved technic in the determination of those constituents of the fatty oils and waxes which are reactive with acetic anhydride, inasmuch as the current procedures which serve that purpose are laborious and uneconomical of time and materials and, as applied to rancid materials, inaccurate. The present method of the Association of Official Agricultural Chemists (2) for accomplishing these ends, referred to as the acetyl number, finds its origin in the studies of Benedikt and Ulzer (3) who, proceeding on the theory that the consumption of acetic anhydride is a function of the hydroxyl group to the exclusion of the carboxyl, recommended that the fatty acids of the oil be used as the point of departure. Lewkowitsch, after demonstrating experimentally that anhydrides of the fatty acids are formed in consequence of the dehydrating action of the acetic anhydride when it is used in excess, eventually developed (8) a procedure in which the quantity of acetic acid liberated from the acetylated oil serves as the index of the hydroxyl content of the parent oil. Finally André (1) and then Cook (4), without disturbing the technic of Lewkowitsch but utilizing the stoichiometrical relationships involved in the change in saponification numbers of the oil before and after acetylation, derived a mathematical expression whose application materially simplified the whole operation.

The variable results which are sometimes obtained in the determination of the acetyl number of the same oil by the foregoing procedure are frequently due to the fact that the operator does not arrive at the correct saponification number. For instance, a corn oil showing an initial saponification number of 191.2, after having been subjected to exactly the same washing procedure as for its acetylated product, then possessed a lower value, or 189.7. The percentage error involved in neglecting this situation with reference to oils of low acetyl value, when the latter is calculated with the André-Cook (4) formula, is appreciable. In other instances the presence of soluble, volatile acids, which are lost by washing and drying the acetylated oil, also introduces an error. Hydrolysis of the former in the operation of washing out the excess of acetic anhydride tends towards low results. In fact, this was demonstrated experimentally with a sample of rancid corn oil whose initial acetyl value dropped from 18.93 with five successive washings, each time with 2 liters of hot water and a 15-minute boiling period, to 18.58, 17.01, 16.09, 14.92, and 14.25, respectively. Furthermore, it is not unusual to find a group of operators working in collaboration on the same oils unable to agree among themselves (5, 7) for the same reason, a

The hydroxyl number, defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of fat, oil, or wax, may be determined with economies of sample, reagents, and time if the reaction is carried out in a sealed tube in the presence of acetic anhydride. Upon completion of the acetylation, the excess of acetic anhydride is hydrolyzed and then determined as acetic acid by titration with 0.5 N potassium hydroxide solution. In contradistinction to the current procedure for determining the acetyl number, the entire process is carried out in the presence of the acetylated product except in the case of such samples as contain free soluble acids when filtration, prior to titration, is necessary.

situation which has in the past given rise to the criticism that the chief difficulty of the procedure appears to be in the decomposition and complete removal of the excess of active anhydride (as acetic acid) over that required for the acetylation without causing more or less hydrolysis of the acetylated fat (6). Another criticism of the process is that the fundamental reaction herein involved will not proceed smoothly because excessive amounts of acetic anhydride are made to react with the material under examination for too long a time at the elevated temperatures employed. Undesirable side

reactions, such as aldehyde formation, for example, are thereby made possible.

It appears, then, in the light of the above, that far too many steps are necessary for the determination of this value. The method here offered, serving the same ends as the foregoing one, is simple and accurate, it involves but few operations, and is far from being time-consuming. It is the result of the experiences gained and the information obtained in a critical study of the effect of varying the several major factors which direct the course of most reactions in organic chemistry—time, temperature, and concentration of reactants.

REAGENTS AND APPARATUS

1. Freshly distilled acetic anhydride, 90 per cent purity or better. It should be stored in glass-stoppered amber bottles. Under these conditions it has been found that its keeping qualities are excellent with the result that standardization once a month is sufficient. This operation is carried out in triplicate on 1.5-gram \pm 0.01 samples in the same manner as the determination of the hydroxyl number itself. Its strength should be expressed in terms of milligrams of potassium hydroxide per milligram of reagent. The standardizations should check within 0.0008 mg. of each other.

2. Carbon dioxide-free 0.5 N \pm 0.01 potassium hydroxide solution. It should be adjusted to this strength so that the 50 cc. which are added prior to hydrolysis of the acetic anhydride will be within the proper range.

3. Distilled water. Whenever reference is hereinafter made to water, it should be understood that carbon dioxide-free water is meant.

4. Indicator solutions. Either phenolphthalein or thymol blue may be used, although the latter is preferable.

5. Reaction tubes may be made from 10-mm. soft glass tubing by constricting 300-mm. lengths at the middle and then breaking them at that point. The large end of each tube is then sealed off, thus making two tubes.

PROCEDURE

The sample weight and quantity of acetic anhydride are controlled by the order of magnitude of the probable hydroxyl number as follows:

HYDROXYL NUMBER	ACETIC ANHYDRIDE Grams	SAMPLE Grams
0-50	1.5 ± 0.01	5.0
50-100	1.5 ± 0.01	2.5
100-200	2.0 ± 0.01	2.5

By means of a calibrated capillary pipet introduce the acetic anhydride into a tared tube, weigh accurately the amount taken, add the sample, and re-weigh. Solids may be added in pellet form. Seal off the tube, place it in an oven at 120° C. for 10 minutes, shake, and then return to the oven leaving it there at rest in a horizontal position for one hour. (Carrying out this reaction under pressure as herein recommended offers no unusual hazards to the operator, for the total pressure within the tube will not exceed 2 atmospheres. Over three hundred acetylations were made during the course of this study without a single accident.)

Open the tube after it has cooled and pour its contents into a 500-cc. Erlenmeyer flask containing 50 cc. of water. Rinse the tube several times, first with cold and then with hot water, finally completing the volume to approximately 200 cc. Now swirl the flask and add exactly 50 cc. of 0.5 *N* potassium hydroxide solution, throw in a few glass beads, attach a reflux condenser, and bring almost to boil over a moderate free flame. (The acetic anhydride is completely hydrolyzed in this operation, the acetic acid being taken up by the water layer.) Rinse down the condenser with 50 cc. of water, wash off the tip of the condenser tube, swirl, cool, and, titrating in the presence of either 10 drops of phenolphthalein or twice as much thymol blue indicator solution, complete the addition of the hydroxide solution.

Solids, such as waxes, which should preferably be heated with the acetic anhydride for 2 hours at 120° C. or 1 hour at 130° C., are best treated as follows: Break the sealed tube in the middle and place it in an Erlenmeyer flask containing 200 cc. of water.¹ Gently warm the mixture until the acetylated wax has melted, swirl, cool, add the 50 cc. of the standard alkali solution, and finally boil the mixture very gently under reflux. Cool and titrate, repeating the process until neutrality is reached. Blanks are run similarly.

Blank determinations are unnecessary in the case of normal samples, but those containing free soluble acids or those highly rancid require filtration prior to titration, the material on the filter paper being thoroughly washed with hot water. In making a blank determination, a weighed amount of the unacetylated oil is thoroughly washed with hot water on a moistened filter paper and the washings titrated.

CALCULATION

Convert all buret readings to their equivalents in terms of milligrams of potassium hydroxide. To find the quantity of the latter involved in this reaction, subtract that required to neutralize the excess of acetic anhydride (as acetic acid) from that equivalent to the amount of the former taken for acetylation of the sample. Then the hydroxyl number, which is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of fat, oil, or wax, is calculated as follows:

$$\frac{\text{mg. KOH involved}}{\text{weight of sample}} = H$$

If desired, the acetyl number also may be calculated from these data by means of the following formula:

$$\frac{\text{hydroxyl number}}{1 + 0.00075 H} = \text{acetyl number}$$

The value 0.00075 represents the stoichiometrical relationships involved in the increase in molecular weight of the material under examination because of the exchange of the hydrogen atom of the hydroxyl group for an acetyl radical.

In the development of this method for determining the hydroxyl content of fatty oils and waxes, many data were obtained in the search for a suitable method for hydrolyzing the excess of acetic anhydride and its quantitative estimation as acetic acid. Space does not permit of a detailed discussion, nor does one seem to be particularly necessary. Of peculiar interest, however, are the data pertinent to the time-temperature-concentration factors in the acetylation of the material under examination. Typical data, illustrative of the manner in which these variables affect, respectively, the hydroxyl number of oils of high and low acetyl values, are presented in Table I.

TABLE I. EFFECT OF VARIATIONS IN TIME, TEMPERATURE, AND CONCENTRATION UPON HYDROXYL NUMBER

OIL	APPROX. CONCENTRATION OF REACTANTS		TEMPERATURE ° C.	TIME Hours	HYDROXYL NUMBER
	Oil Parts	Acetic anhydride Parts			
Castor	1.0	1.0	100	1	129.5
	1.0	1.0	100	2	149.2
	1.0	1.0	100	4	163.9
	1.0	1.0	100	6	164.5
	1.0	1.0	100	10	164.4
	1.0	1.0	110	1	162.2
	1.0	1.0	110	2	164.8
	1.0	1.0	110	4	164.4
	1.0	1.0	110	10	164.7
	1.0	1.0	120	1	164.5
	1.0	1.0	120	2	164.3
	1.0	1.0	120	4	164.9
	1.0	1.0	120	6	164.2
	1.0	1.0	120	10	164.7
	1.0	1.0	130	10	164.3
	1.0	1.0	140	10	164.6
	1.0	1.0	150	10	164.0
	2.5	2.0	120	1	164.3
	2.5	1.5	120	1	163.3
	2.5	0.9	140	2	163.6
Olive	1.0	1.0	100	1	4.7
	1.0	1.0	100	2	4.9
	1.0	1.0	120	1	4.9
	1.0	1.0	120	2	5.3
	1.0	1.0	120	6	4.5
	1.0	1.0	140	2	5.0
	2.5	1.0	140	2	5.0
	5.0	0.2	140	2	4.2
	5.5	1.5	120	1	5.0
	5.0	1.0	120	1	4.8
	5.0	0.7	120	1	4.6

In the interaction of acetic anhydride and castor oil, for all practical purposes here typifying ricinolein, is seen an example of the statement that reaction rates are doubled for every 10-degree rise in temperature, since the same stage in the equilibrium of this reaction, as indicated by the hydroxyl number, was reached in 4 hours at 100° C., in 2 hours at 110° C., and in 1 hour at 120° C. In much the same way this condition obtained in the case of olive oil. It was from the information gained by the mode of procedure suggested by the data recorded in Table I that the optimum ratios of sample weights to acetic anhydride, and time and temperature considerations, were selected.

The stability of the acetylated product when prepared as herein described from normal, nonrancid material is seen—taking castor oil as an example—in the fact that the reaction product can be boiled without fading of the end point after neutralization of the excess acetic anhydride (as acetic acid). On the other hand, the acetylated product from a rancid oil—the corn oil cited in the introductory paragraphs serves as an example—will behave in quite a different manner. In this case, acid will be liberated every time the solution is boiled following a period of rest. The quantity of acid set free on

¹ An alternative procedure is to use purified chloroform in removing the acetylated product, in which case, however, the solvent must be removed before the final titration. The possibility of losing acetic acid in this operation must not be overlooked.

hydrolysis of the reaction products will gradually diminish. The source of this hydrolysis is evidently not traceable to acetyl derivative of hydroxy acids, for the behavior of the castor oil belies such an assumption, nor is it brought about by the breaking down of mixed anhydrides. Rather it appears to be due to the presence of either unstable acetylated mono- and diglycerides, or some acetylated oxidation products of the fatty acids. The observed instability of an acetylated mono-*n*-valerin under the above conditions (it was found that the acetyl number of the parent compound cannot be determined at all by the official method (2) and only approximately by the proposed one) supports the former view.

A very important step in the determination of the acetyl number under the present mode of procedure (2) is that excessive washing of the reaction mixture be avoided. In fact, Lewkowitsch (9) cautioned against more than three applications of wash water. Yet, even when this precaution is observed, it is necessary to use at least 1.5 liters of wash water. No such situation arises, however, in carrying out this determination under the proposed procedure, for when conditions are such as to make a blank determination desirable (see description of method), the volume of water necessary to hydrolyze the anhydrides of the soluble fatty acids which have been formed is small; in fact it is not enough to cause a measurable hydrolysis of the major acetylated product. The presence of insoluble (higher) fatty acids does not introduce an error, for the action of acetic anhydride upon them is such as to form their corresponding anhydrides (9). These are very stable, even on continued boiling. Since equivalent quantities of acetic acid are formed in this reaction, none of its anhydride is actually consumed, a condition which would make a blank determination unnecessary in this case.

By way of comparison of the two methods for determining acetyl numbers, there is included in this report a set of typical data (Table II). It will be observed that there is a satisfactory agreement in results when the necessary correction for

interfering substances has been applied. Hydroxyl and acetyl numbers are practically the same in the bracket below twenty.

TABLE II. COMPARISON OF OFFICIAL AND PROPOSED METHODS FOR DETERMINATION OF ACETYL NUMBER

MATERIALS	ACETYL NUMBER		HYDROXYL NUMBER
	Official method	Proposed method	
Oils:			
Olive	5.0	4.9	4.9
Cottonseed	5.9	5.5	5.5
Sesame	3.3	3.8	3.8
Tobacco seed (extracted)	9.0	8.6	8.7
Tobacco seed (expressed)	4.8	5.3	5.3
Peanut	5.4	5.1	5.1
Rye germ	20.2 ^b	21.0 ^a	21.5 ^a
Corn	16.7 ^b	17.7	17.9 ^c
	15.4 ^b	18.1	18.3 ^d
Castor	146.3	146.4	164.5
Waxes:			
Beeswax	24.2 ^e	26.3	26.8
Carnauba	44.7	44.7	46.2

^a Analyses by Albert W. Stout.
^b Values calculated from saponification number of washed original sample. They will be several points lower if carried out by official method.
^c Filtered before titration, correction for blank was applied.
^d Titrated in presence of acetylated product. No blank applied.
^e Some constituents apparently lost along with coloring matter which dissolved in acetic anhydride during the process of acetylation. Original product was bright yellow; final a pure white.

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Determination of Small Amounts of Methyl Chloride in Air

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IN CONDUCTING an investigation of the toxicity of small amounts of methyl chloride in air, it was necessary to check the computed concentrations by chemical analyses. Of the various methods (1, 4, 5, 6) reported in the literature, none of them appeared suitable for the purpose at hand. Attempts were made, therefore, to develop a method which would be satisfactory for the conditions outlined, and thus a procedure which proved satisfactory was devised.

Allison (1) determined methyl chloride by absorption in glacial acetic acid and also by burning with an excess of oxygen in an Orsat gas apparatus. McKee (4) and Niellou (5) also used a combustion method similar to that of Allison. Roka and Fuchs (6) heated methyl chloride with methanol and sodium iodide in a pressure flask to form methyl iodide, which they distilled into silver nitrate. It is obvious that none of these methods would be suitable for small amounts of methyl chloride in air—as, for example, 50 p. p. m. by volume (3).

BUREAU OF MINES METHOD

The procedure adopted is very similar to the Referees method for determining total sulfur in fuel gases. The air

containing the methyl chloride is mixed with natural gas and burned in a microburner. The halogen products formed combine with ammonia obtained from ammonium carbonate cubes placed around the burner, and also with ammonium hydroxide formed by the ammonia from the ammonium carbonate and the water in the products of combustion of the gas. The chlorides produced are collected and determined by the Volhard method.

APPARATUS. Figure 1 shows the apparatus. The methyl chloride-air mixture is added as the primary air supply to burner *a*, shown in detail in Figure 2 and described later. Secondary air enters around the base of the burner. The products of combustion of the fuel gas, the methyl chloride and excess secondary air, are carried by convection up through the trumpet tube *b* and are impregnated with ammonia which emanates from the ammonium carbonate cubes piled around the burner (Figure 2). In the presence of the water vapor some of the halogen reacts with the ammonia and is deposited on the walls of the upper part of the trumpet tube. The remainder enters a glass marble-filled absorption tower, *c*, where the surfaces are wet with ammonium hydroxide formed by the condensation of water vapor in the presence of am-

monia. This absorbs additional halogen products of combustion. The excess condensate drips from the tower into a beaker. The effluent vapor from the tower is led through a Cottrell precipitator which collects any halogen-bearing smoke or fog that escapes the tower. The precipitator is made by sealing a platinum wire concentrically in a glass tube, *d*, which has a side outlet at each end. The outside of the tube is wrapped with tin or copper foil to within about 4 inches of each end, and the foil is bound in place with friction tape. A wire wound around the foil with one end protruding through the tape serves as one terminal and the platinum wire as the other, both being connected to the secondary of a Ford spark coil, *e*. The current for the spark coil is obtained from a 110-volt 60-cycle lighting circuit through a toy transformer, *f*, adjusted to give 6 volts. It is obvious that other designs of electrical precipitators may be used, providing they readily permit a washing out of the precipitate.

Figure 2 is a detailed sketch of the burner. It is constructed by placing a glass T tube tightly over the burner stem of an ordinary laboratory microburner, *g*, and sealing the primary air intake with wax, *h*. A piece of platinum gauze, *i*, is fused onto the burner tip to stabilize the flame. The connection between the stem and the arm of the T tube is made gas-tight by means of a rubber tubing collar. The fuel gas enters at *j* and the methyl chloride-laden air at *k*. Secondary air enters between the trumpet tube wall *l* (shown in entirety in Figure 1) and a cork base, *m*, which supports ammonium carbonate cubes, *n*.

The cork is covered with a sheet of asbestos, *o*. This cork is smaller than the base of the trumpet tube in order to permit secondary air to be drawn by convection or the stack-effect of the trumpet tube and tower above.

The above burner design, and in fact much of the other equipment described, was an assembly of parts readily available in the laboratory. Other designs and parts which will carry out the principle of the method will be satisfactory. This also applies to the fuel, which may be any combustible gas not containing an appreciable amount of halogen compounds. A blank determination using the fuel employed must, of course, be made.

EXPERIMENTS MADE TO TEST METHOD

The accuracy of the method was tested by making a series of determinations of carefully measured amounts of methyl

A method for the determination of small amounts of methyl chloride in air is described. The apparatus and procedure are in many respects similar to the Referees method for total sulfur in fuel gases. Tests of the method using amounts of methyl chloride ranging from 12.36 to 30.74 mg. have shown the error to be less than 2 per cent of the amount present for the lower, and less than 1 per cent for the upper limits of the range used. In developing the method, a range of concentrations from 200 to 1600 p. p. m. or 0.02 to 0.16 per cent by volume was used. The method has also been used for the determination of dichlorodifluoromethane vapor in air, and is suggested for the determination of other organic halide gases and vapors.



the microburet was measured at atmospheric pressure and the prevailing temperature, after which it was corrected to 0° C. and 760 mm. Hg. A minimum of stopcock grease was used.

CHEMICALS AND REAGENTS USED. The methyl chloride used was obtained from the Roessler and Hasslacher Chemical Co., and according to specifications was 99.5 per cent pure. The silver nitrate solution used was approximately 0.025 *N* and was standardized against standard hydrochloric acid. The hydrochloric acid was standardized using sodium carbonate prepared by heating sodium bicarbonate. The potassium sulfocyanate was standardized against the silver nitrate. Ferric alum was used as an indicator. Calibrated burets were used in making all titrations.

DILUTION AND BURNING OF SAMPLE. The methyl chloride which was confined in the microburet was forced into a stream of air by opening the stopcock at the top of the buret and slowly displacing with mercury. The air was measured and the rate controlled by means of a dry meter, and the mixture led through glass tubing to the microburner previously described. All connections were glass-to-glass held in place by rubber tubing. The volume of the samples varied from approximately 5.5 to 13.5 cc. of methyl chloride. The air was admitted through the meter at the rate of about 20 liters per hour. The time of burning for the 13.5-cc. samples was approximately 1 hour, for the 10-cc. samples from 20 minutes to 1 hour and 20 minutes, and for the 5.5-cc. samples from 45 minutes to 1 hour and 30 minutes. This gave a range of concentrations varying from about 200 to 1600 p. p. m. by volume, or 0.020 to 0.16 per cent. Blank determinations were made on room air and gave an average titration of 0.05 cc. of silver nitrate, the equivalent of which was 0.07 mg. of methyl chloride. This blank titration was subtracted from the silver nitrate values in the determinations.

DETERMINATION OF CHLORIDES. The chlorides were washed from the trumpet tube, Cottrell precipitator, and absorption tower until the washings gave a negative test for chlorides. It was found that this was best accomplished in the tower by quickly pouring 4 or 5, 50-cc. portions of water over the beads. This procedure prevented channeling and produced a solid column of water which resulted in more efficient scrubbing. The washings were added to the condensate which collected and dropped from the tower during the combustion, and the chlorides were then determined by the Volhard method. The silver chloride was removed by filtration through a Gooch crucible prior to the sulfocyanate titration.

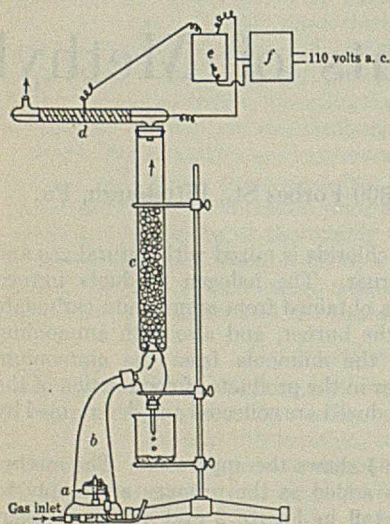


FIGURE 1. APPARATUS FOR DETERMINING METHYL CHLORIDE IN AIR

chloride introduced into a stream of air.

APPARATUS AND PROCEDURE FOR MEASURING METHYL CHLORIDE. The methyl chloride was measured with a calibrated gas microburet which used dry mercury as the displacing liquid. The buret was surrounded by a water jacket equipped with a thermometer, the water being kept in circulation by bubbling air through it. A by-pass was arranged so that the buret could be flushed with methyl chloride, and the waste gas conducted from the room to prevent contamination of the atmosphere which was used as the secondary air supply to the burner. The sample of methyl chloride in

TABLE I. DETERMINATIONS WITH KNOWN AMOUNTS OF METHYL CHLORIDE

VOL. OF CH ₂ Cl ₂ (99.5% AT 0° C. 760 MM.)		CH ₂ Cl ₂ TAKEN	VOL. OF AIR	AVERAGE CONCEN. P. p. m.	AgNO ₃ TITRATION	CH ₂ Cl ₂ RECOVERED	RECOVERY %	ERROR %
Cc.	Mg.							
13.43	30.12	22.5	600	21.14	30.00	99.6	-0.4	
13.71	30.74	22.5	610	21.87	31.03	100.9	+0.9	
13.67	30.68	19.0	710	21.53	30.56	99.7	-0.3	
13.51	30.32	20.0	670	21.37	30.32	100.0	0.0	
9.95	22.32	7.0	1250	15.85	22.47	100.6	+0.6	
10.07	22.60	6.3	1600	16.00	22.68	100.3	+0.3	
10.07	22.60	24.7	410	15.85	22.47	99.4	-0.6	
10.02	22.48	10.7	940	15.79	22.39	99.6	-0.4	
5.60	12.57	13.5	370	9.02	12.70	101.5	+1.5	
5.60	12.57	19.0	290	8.81	12.46	99.2	-0.8	
5.58	12.52	17.2	330	8.79	12.43	99.4	-0.6	
5.52	12.38	27.5	200	8.87	12.54	101.3	+1.3	
5.51	12.36	19.0	290	8.79	12.43	100.5	+0.5	

RESULTS. The results of the determination, given in Table I, show that the accuracy of the method with amounts of methyl chloride ranging from about 20 to 30 mg. is in the neighborhood of 0.5 per cent, being at least within 1 per cent in all cases. When amounts as low as 12 mg. are determined, the accuracy is nearer 1 per cent, being better than 2 per cent in all cases.

The equivalent of 0.1 cc. of the silver nitrate solution used was 0.14 mg. of methyl chloride. A titration error of 0.1 cc. would cause an error of approximately 1 per cent in samples weighing about 12 mg. Therefore, the per cent error of the method depends primarily on the weight of methyl chloride in the sample taken rather than on the concentration. This fact should be borne in mind in any attempt to extend further the range or accuracy of this method.

PROCEDURE USED FOR ROOM ATMOSPHERES CONTAINING METHYL CHLORIDE. The above method has been used in this laboratory to check concentrations of methyl chloride ranging from 50 to 600 p. p. m. by volume in air which were used for toxicity experiments with animals. The atmosphere to be analyzed was taken from the animal exposure chamber with a small rotary air pump and delivered through a dry meter to the burner. A by-pass between the blower and the meter permitted the excess air from the blower to return to the chamber. The rate of burning and size of flame depended upon the concentration of methyl chloride in the air, a slower rate and smaller flame being used for higher concentrations. The above procedure gave results which were within 5 per cent of the values computed from flowmeter measurements of the volume of methyl chloride and air used in the mixture that entered the gas chamber. The results were always lower than the computed values and, aside from flowmeter errors and control, may be partially explained by the fact that the Cottrell precipitator was not used in this particular set-up of apparatus.

TABLE II. ABSORPTION OF METHYL CHLORIDE (from a 1 per cent methyl chloride-air mixture) BY CONTACT WITH DISTILLED WATER IN GAS-ANALYSIS PIPET

NO. OF PASSES INTO PIPET	ABSORPTION OF CH ₂ Cl ₂ , ACCUMULATIVE			BLANK, USING ROOM AIR ACCUMULATIVE ABSORPTION
	Sample 1 %	Sample 2 %	Sample 3 %	
1	5	5	5	0.04
2	5	5	5	0.03
5	15	5	6.5	-0.01
10	26.5	20	19.5	-0.01
20	45	40	35.0	a
30	50	46	45	a
40	55	57.5	a	a
50	a	65	62.5	a
60	a	75	66.5	a
70	a	75	71.5	a
80	a	75	72.5	a
90	a	a	72.5	a
100	a	a	72.5	a

a Not determined.

The sampling procedure, as described, may be modified in accordance with other common procedures for sampling gases. For example, it is obvious that samples of atmospheres

may be taken by air displacement in containers of suitable size and delivered to the apparatus by sweeping into the burner with a stream of air; or if the samples are relatively small they may be delivered to the apparatus by mercury displacement. Owing to solubility of methyl chloride in water, the use of water as a displacing medium should be avoided, though if absolutely necessary, it may be used if care is taken to avoid operations that facilitate solution of the gas in the liquid. If the water is not agitated a great deal or left in contact with the gas-laden air, it is possible to use it without vitiation of the results for practical health investigations. Experiments were made in which methyl chloride-air mixtures were passed from a mercury-filled buret into distilled water contained in a Haldane type gas-absorption pipet at room temperatures (2). Table II gives the results of these experiments.

The practical use of water as a displacing liquid was also studied. Three determinations were made using 19-liter samples of 600 p. p. m. methyl chloride-air mixture obtained in and delivered from a 20-liter aspirating bottle by use of distilled water as the displaced and displacing medium. The results obtained were 98, 95, and 96 per cent, respectively, of the calculated amount of methyl chloride in the air. The surface of the water was disturbed very little, but no special precautions were used to prevent motion other than removing and admitting water under the water surface.

The line to the burner was flushed by drawing a few liters of room air into the aspirating bottle and then forcing this air to the burner.

In judging the size of samples, the allowable per cent error and the probable error of method must be considered.

USE OF METHOD FOR OTHER ORGANIC HALIDE GASES AND VAPORS

The same apparatus has been used to determine dichlorofluoromethane, and dichlorodifluoromethane in concentrations of 2 and 20 per cent, respectively. In dealing with these relatively high concentrations, the samples were taken over mercury and diluted with air prior to combustion. The results agreed well with other methods of analysis, and point to the applicability of this method to the determination of other organic halide gases and vapors in air.

ACKNOWLEDGMENT

The development of the method described in this report was a necessary part of an investigation of the response of animals to methyl chloride in air which was conducted cooperatively by the Roessler and Hasslacher Chemical Company and the Bureau of Mines. The development was carried out at the Pittsburgh Experiment Station of the Bureau of Mines under the direction of its chief surgeon, R. R. Sayers.

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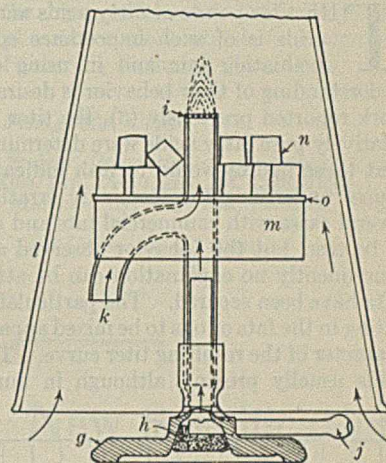


FIGURE 2. DETAIL OF BURNER

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Some Titer Points of Mixed Fatty Acids

II. Mixtures of Pure Fatty Acids

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THE titer points of fatty acids and of mixtures of fatty acids is of such importance commercially, both in evaluating fats and in using them, that a better understanding of their behavior is desirable. Continuing the work reported previously (3), the titer points of mixtures of relatively pure fatty acids were determined. It was expected that these figures would furnish indications, at least, of the causes underlying the seemingly erratic results obtained in several cases with commercial fats and oils. This was found to be true, but the behavior observed needs elucidation and consequently no explanation can be attempted until further data have been secured. The particular fatty acids predominating in the fats or oils to be mixed apparently determined the character of the resulting titer curve. The several other fatty acids usually present, although in much smaller amounts,

influence the curve somewhat, but to just how great an extent has not yet been determined.

The four fatty acids selected for this work were lauric, myristic, palmitic, and oleic. The selection was determined principally by the fact that mixtures of the glycerides of these (together with that of stearic acid) in varying proportions form the majority of the commonly occurring nondrying oils and fats. The other acids, such as caproic, caprylic, capric, linoleic, etc., are present in much smaller quantity.

The lauric, myristic, and palmitic acids were the specially purified grade of the Eastman Kodak Company. The oleic acid was purified in the laboratory, using a high-grade commercial red oil as the source, by the lead salt-ether method with subsequent fractionation under reduced pressure.

That none of these acids was strictly chemically pure is recognized. It is a very difficult matter to effect the absolute separation of the fatty acids from one another (2), especially when acids close to each other in the series are under consideration, and for the present purpose strict chemical purity is not essential. The acids used were, however, of a relatively high degree of purity.

The titer point is not a value of as high an order of accuracy as are some of the other physical constants. It varies within certain limits according to the method employed in determining it, the exact technic exerting considerable influence upon the result. The amount of fatty acid used, the method of stirring, the differential in temperature of fatty acid and surrounding bath, and the number of times the titer has been read on the same portion of fatty acid are a few only of the variables which must be standardized because no particular method can be considered the only correct one. Because of this factor of inherent variability in the titer itself, absolute purity of the fatty acids was not considered essential.

PROCEDURE

The fatty acids were kept dry and, just before determining the titer point, were weighed out carefully in the desired proportions in a 50-cc. glass beaker; they were heated to about 115° C., thoroughly mixed, and, after cooling somewhat, were transferred to the titer tube. Determination of the titer from this point on was in accordance with the method of the Fat Analysis Committee of the AMERICAN CHEMICAL SOCIETY (1).

The results are reported in the form of curves which are plotted with the titer points as ordinates and the percentage composition of the mixed fatty acids as abscissas.

DISCUSSION OF RESULTS

As it was desired to learn in the first place the effect of mixing two acids adjacent to each other in the same homologous series (considering only acids with an even number of carbon atoms), lauric and myristic were selected. The curve resulting

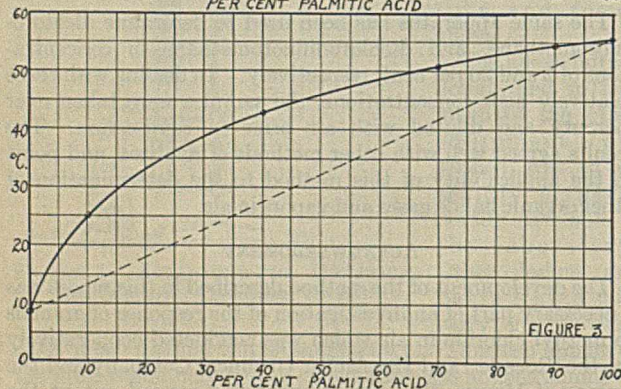
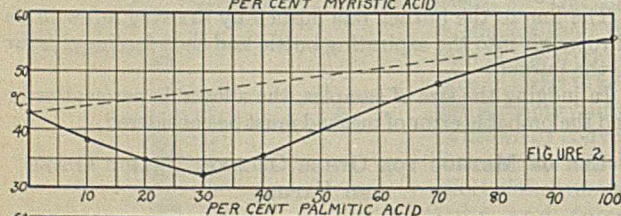
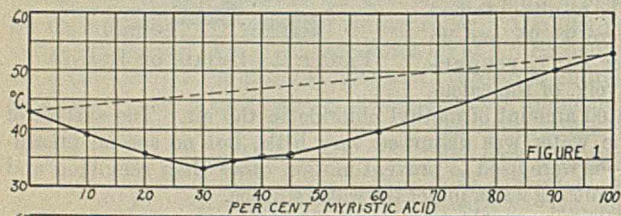


FIGURE 1. TITER CURVE FOR MIXTURES OF LAURIC AND MYRISTIC ACIDS

FIGURE 2. TITER CURVE FOR MIXTURES OF LAURIC AND PALMITIC ACIDS

FIGURE 3. TITER CURVE FOR MIXTURES OF OLEIC AND PALMITIC ACIDS

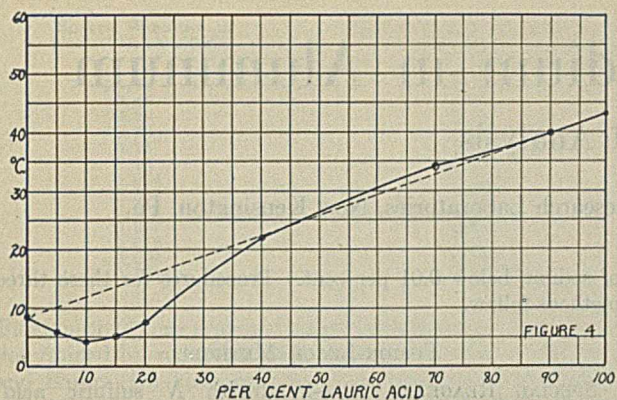


FIGURE 4. TITER CURVE FOR MIXTURES OF OLEIC AND LAURIC ACIDS

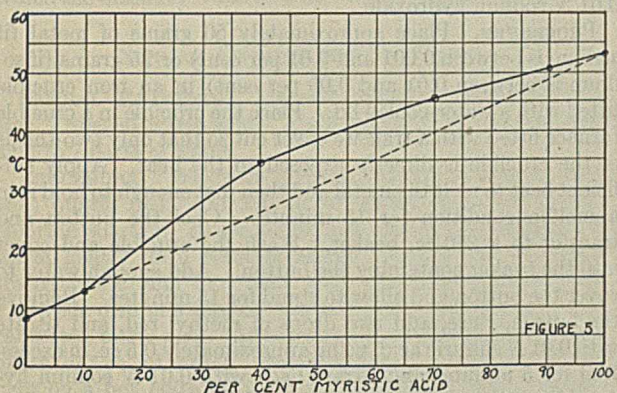


FIGURE 5. TITER CURVE FOR MIXTURES OF OLEIC AND MYRISTIC ACIDS

(Figure 1) shows the depressing effect upon the titer of the addition of a higher titered material. This is similar to the effect upon the melting point observed in general when two materials similar chemically are mixed, but in the case of fatty acids no generalization can be made. The lowest point was reached with the mixture containing 30 per cent myristic acid.

Mixtures of lauric and palmitic acids (Figure 2) give a curve similar to Figure 1, but distinguished by the fact that palmitic acid, although having a higher titer, exerts a greater depressing effect upon the titer than does myristic acid. The low point, however, is reached at the mixture containing 30 per cent palmitic acid, just as 30 per cent myristic acid gave the low point in Figure 1. At approximately 60 per cent lauric acid the two curves cross each other and from there on the mixtures containing palmitic acid have the higher titer. At the point of greatest depression the titer of the mixture of lauric and palmitic acids is almost 15°C . below the "mean line." This is the line connecting the titers calculated arithmetically from the titers of the two pure acids involved (3).

Mixtures of saturated acids with an unsaturated acid were tried next. Because its glyceride is a constituent of so many different naturally occurring oils and fats, oleic acid was selected as the unsaturated acid. Figure 3 shows that the addition of a high titered acid (palmitic) raises the titer of the mixture even from the beginning, contrary to the effect observed in the two previous cases. The rise is abrupt and remarkable, reaching in one portion of the curve a point 16°C . above the mean line.

Figure 4 shows the effect of mixing lauric acid with oleic. Instead of raising the titer of the mixtures, as did palmitic acid, it depresses it sharply at the beginning, and not until

44 per cent is present does the titer reach that on the mean line. At no place is the curve much above this line.

As might be expected in view of the two preceding results, the addition of myristic acid (intermediate in position in the series between lauric and palmitic) to oleic, as shown in Figure 5, gives a curve intermediate in form between that for lauric and palmitic acids. The titers of all mixtures are either on the line or above it, but there is no abrupt or great rise in any portion.

That it is not possible to generalize about the behavior of the titer of mixtures of other acids until further data have been secured is apparent in view of the results obtained with these four acids. Mixtures of several other saturated acids, both with a less and with a greater number of carbon atoms, must be tried, and these acids in turn mixed with oleic. Another unsaturated acid—linoleic—present in corn oil, cottonseed oil, etc., as well as in the drying oils such as linseed, must be used before any attempt can be made to explain or predict the behavior of mixtures of naturally occurring oils and fats.

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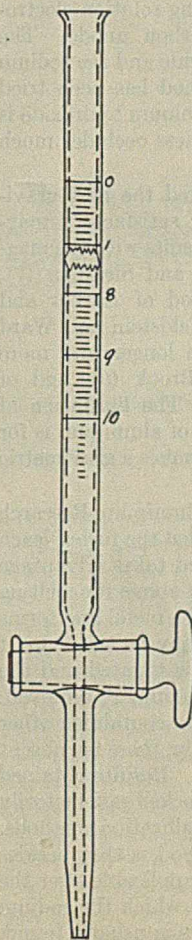
New Specification for Burets

WITHROW MORSE, Röhm and Haas Co., Bristol, Pa.

BY MEANS of a few marks representing tenths of cubic centimeters below the lowest graduation of a buret, many exasperating errors of passing this mark can be obviated. Few chemists have escaped these experiences, owing to diverted attention, defective eyesight, poor light, or other cause. The added graduations should be shorter than the standard marks to insure against mistaking them for divisions of the lowest cubic centimeter of the buret.

Frequently the buret is used as a large pipet of the Mohr type. In such a case the additional marks serve a useful function where a few tenths of a cubic centimeter are demanded beyond the decimal aliquot (10 cc., 50 cc., 100 cc.). Refilling the buret to accommodate a fraction of a cubic centimeter is obviated.

The Arthur H. Thomas Company kindly prepared a buret to this specification.



MARKED BURET

RECEIVED March 2, 1932.

Determination of Sodium in Aluminum

I. Chemical Analysis

R. W. BRIDGES AND M. F. LEE, Aluminum Research Laboratories, New Kensington, Pa.

THE problem of determining sodium in aluminum is not a new one. As early as 1859, Sainte-Claire Deville (24) developed a leaching method for the determination of sodium. He converted the aluminum to nitrate, ignited at low temperature, and leached the alkalis with water. This method has been used or modified by Diehl (8), Richards (23), Hunt, Langley, and Hall (14), Moissan (18), Jean (15), Seligman and Willott (26), Kohn-Abrest (16), Belasio (3), Bhattacharyya (5), Pattison (22), Villavecchia (27), and Bertiaux (4). Handy (13) dissolved aluminum in hydrochloric acid and nitric acid, ignited gently, and applied the J. Lawrence Smith method to the oxides formed. Allen (1) dissolved aluminum in hydrochloric acid, made an ammonium hydroxide separation, and determined alkalis in the filtrate. Nicolardot (19) proposed to disintegrate the aluminum with mercuric chloride, filter, and determine alkalis in the filtrate. When small amounts of sodium and large amounts of aluminum are present, these methods do not achieve quantitative recovery of the sodium.

An electrolytic method has been proposed by Gaith (12) in which the aluminum is dissolved in hydrochloric acid, the excess acid neutralized with calcium carbonate, the copper group removed as sulfides, and the resulting solution electrolyzed with a mercury cathode and carbon anode. The amalgam is decomposed with sodium chloride and the sodium hydroxide formed is titrated. This method has been tried by several workers without success. Aluminum hydroxide is formed during the electrolysis, and doubtless occludes much sodium.

The uranyl acetate method is considered the best gravimetric procedure. Difficulty in securing satisfactory magnesium acetate has led to unsatisfactory results with the magnesium uranyl acetate method of Caley and Sickman (7). However, the zinc uranyl acetate method of Barber and Kolthoff (2) gives satisfactory results. Feldstein and Ward (10) used nickel uranyl acetate. Of the longer and more tedious methods, those of Fairlie and Brook (9), and of Schürman and Schöb (25) are feasible. The limitation of these methods is that the sodium content of aluminum is for the most part 0.01 per cent or less, which makes a gravimetric determination very difficult.

From a qualitative test used in the Aluminum Research Laboratories, a quantitative procedure called the fusion-leach method has been developed. This method takes advantage of the fact that when aluminum is held just above the melting point the sodium comes to the surface of the metal and forms sodium compounds which, after cooling, may be leached out with water. The alkalinity so produced is titrated and the fusion and leaching repeated until the sodium is removed. The method cannot be applied to aluminum containing other alkali or alkaline earth metals. Fortunately, these are absent as a rule or present in negligible amounts. Results obtained with the fusion-leach method have been checked satisfactorily with the uranyl acetate and nitrate crystallization methods. One good feature of the fusion-leach method is that besides being the shortest chemical method, it is applicable over the range of 0.001 to 0.05 per cent sodium, in which the sodium content of aluminum and aluminum alloys is usually found. The uranyl acetate method is not applicable for determination

of sodium below 0.01 per cent. Procedures for these three methods follow.

FUSION-LEACH METHOD

SPECIAL REAGENTS. One-hundredth *N* sulfuric acid; 0.01 *N* sodium hydroxide.

PROCEDURE. Place approximately 50 grams of metal (if sodium is between 0.001 and 0.01 per cent) or 25 grams (if sodium is between 0.01 and 0.05 per cent) in an iron crucible fitted with a water-cooled lid. Place the crucible in a crucible furnace fitted with a transite cover cut so that only two-thirds of the crucible is directly exposed to the heat. Apply sufficient heat to melt the metal and then just enough to hold it in a molten condition for 15 minutes. Cool the button and transfer to a 250-cc. beaker. Wash the crucible and cover into the beaker containing the button. Add enough water to cover the button and allow to stand for 15 minutes. Remove the button, rinse, add two drops of methyl red, and titrate with 0.01 *N* sulfuric acid, using approximately 0.5 cc. in excess. Boil for 5 minutes and titrate back with 0.01 *N* sodium hydroxide, and repeat the fusion and leaching until the net titration falls to 0.5 cc. or less. The number of leachings necessary will depend on the sodium content.

$$\text{Per cent sodium} = \frac{\text{net titration in terms of 0.01 } N \text{ sulfuric acid} \times 0.023}{\text{weight of sample}}$$

URANYL ACETATE METHOD

SPECIAL REAGENTS

SOLUTION A		SOLUTION B	
	Grams		Grams
Uranyl acetate	10	Zinc acetate	30
Acetic acid	6	Acetic acid	3
Water to make	65	Water to make	65

Mix solution A with solution B and allow to stand for at least 24 hours. Filter before using.

PROCEDURE. Dissolve 1 gram of sample in a minimum amount of 1 to 1 hydrochloric acid, filter, and evaporate to a volume of 5 cc. Add 100 cc. of zinc uranyl acetate solution, stir for 45 minutes with a mechanical stirrer, and allow to stand overnight. Filter through a Gooch or sintered-glass crucible. Wash first with reagent, then twice with ethyl alcohol and six times with acetone. Dry for 30 minutes at 105° C. and weigh as sodium zinc uranyl acetate. A blank must be carried through in parallel with the determination.

$$\text{Sodium} = \text{sodium zinc uranyl acetate} \times 0.01495$$

NOTE. Instead of weighing the sodium zinc uranyl acetate precipitate, its sodium content may be calculated from a volumetric determination of the uranium by the following procedure: Dissolve the washed precipitate with hot water, add 15 cc. of 1 to 1 sulfuric acid, and weak potassium permanganate until pink. Add a few zinc shot, warm gently for 15 minutes, cool, filter through a cotton plug into a beaker containing 100 cc. of cold water, and titrate with potassium permanganate of suitable strength (0.07 *N* and 0.02 *N* have been used). A blank must be carried through with the determinations.

A comparative study of the gravimetric method and the volumetric method has been made and the results obtained are given in the following table:

SODIUM WEIGHED AS NaZn(UO ₂) ₂ Ac ₂ ·6H ₂ O %	SODIUM DETD. VOLUMETRICALLY BY TITRATION OF URANIUM %
0.44	0.44
0.45	0.45
0.29	0.29
0.30	0.30
0.15	0.14
0.15	0.14
0.074	0.074
0.074	0.074
0.037	0.037
0.037	0.036
0.015	0.014
0.008	0.008
0.0016	0.0017

Blenkinsop (6) has proposed a method in which the uranium is determined by reduction with titanium chloride. McCance and Shipp (17) have introduced a colorimetric method in which the uranium is determined with potassium ferrocyanide.

NITRATE CRYSTALLIZATION METHOD

SPECIAL REAGENTS. Mercuric chloride, saturated solution. Special nitric acid. Eight parts of 70 per cent nitric acid to 7 parts of water.

PROCEDURE. Weigh on a rough balance an 8-inch (20.32-cm.) quartz dish, add 250 cc. of water, 10 cc. of mercuric chloride solution, 30 grams of fine aluminum drillings, and warm gently until reaction starts. Add 10 cc. of concentrated nitric acid and heat until vigorous reaction starts. Place the dish in a cooling pan and slowly add 390 cc. of concentrated nitric acid. If the mass becomes viscous, add another 100 cc. of water. When apparent action has ceased, heat on a hot plate until the solution of the sample is complete. If the weight of the liquid falls below 600 grams before solution is complete, add special nitric acid. Finally evaporate the solution to 600 grams, cool, with continual stirring, in a water bath, and, when dish and contents are cold, allow to stand for 1 hour or more. Filter the crystals formed through a 5-inch (12.7-cm.) Büchner porcelain funnel, using suction to dry the crystals. Press well with a flattened rod, and, when dry, wash with 50 cc. of concentrated nitric acid. Allow the wash acid to stand on the crystals for a few minutes before suction is again applied. Receive the filtrate in a 4.5-inch (11.43-cm.) quartz dish. Evaporate the solution until a hot saturated solution is obtained, crystallize, and allow to stand as before. Filter through a quartz funnel,

receiving the filtrate in a 3.25-inch (8.25-cm.) quartz dish. Wash with 10 cc. of concentrated nitric acid, add 2 cc. of concentrated sulfuric acid, evaporate to dryness and bake until no more fumes are evolved, cool, add 10 cc. of ammonium hydroxide, and allow to stand overnight. Warm, filter into a platinum dish, return the paper to the dish, add 5 cc. of concentrated hydrochloric acid, macerate the paper, warm, and precipitate with ammonium hydroxide. Filter, and wash with hot, slightly ammoniacal 2 per cent ammonium chloride solution. Combine the filtrates and evaporate to approximately 25 cc., add 10 drops of concentrated sulfuric acid, pass in hydrogen sulfide gas, filter, and evaporate the filtrate to dryness. Ignite to drive off ammonium salts, add a few cubic centimeters of water and 2 cc. of saturated ammonium carbonate solution, filter, evaporate to dryness, and ignite for 30 minutes at 500° C., cool, and weigh. Add a few drops of water, 2 drops of ammonium hydroxide, warm, filter, ignite the paper at 500° C., cool, and weigh. The loss in weight is sodium sulfate. The filtrate should be examined for magnesium.

Return the crystals from the first and second crystallizations to the 8-inch (20.32-cm.) quartz dish, add 150 cc. of concentrated nitric acid and 50 cc. of water, evaporate to 580 grams, cool, and recrystallize. Repeat the procedure outlined above. Deduct a determined reagent blank.

$$\text{Sodium} = \text{sodium sulfate} \times 0.3238$$

Some results obtained by the foregoing methods are as follows:

SAMPLE	FUSION-LEACH METHOD	NITRATE CRYSTALLIZATION	URANYL ACETATE
	%	%	%
1	0.040	0.040	
2	0.016	0.015	
3	0.009	0.010	
4	0.008	0.009	
5	0.040		0.038
6	0.017		0.016

ACKNOWLEDGMENT

The authors wish to acknowledge the contributions made by W. I. Sivitz, formerly of Aluminum Research Laboratories, and P. M. Budge, chief chemist of the Fairfield Works Laboratory, toward the development of the fusion-leach method.

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II. Spectrographic Analysis

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THE determination of sodium in aluminum may be made by means of the spectrograph, and the results agree with chemical analysis within satisfactory tolerances. Chief among the advantages of the spectrographic determination, as contrasted with chemical determinations, is the rapidity with which a series of results can be reported. Eight to ten specimens may be examined within 2.5 hours, or an average of not more than 20 minutes per sample. The presence of other alkalis or alkaline earths does not interfere with the determination and, at the same time, the presence or absence of such impurities is established.

Methods using both the direct current arc and the condensed spark have been investigated. Solution of the metal in acids with subsequent arc excitation of the dry salt, as used by Nitchie (20) in the analysis of zinc, was not entirely successful because of the relatively low solubility of aluminum and the strong continuous spectrum of the graphite electrodes in the region of the sensitive sodium lines. The sodium con-

tent of the solvents is also to be considered. Sparking the metal did not seem sensitive enough to warrant an attempt at development, as the smallest amounts could not be detected and the intensity gradient was not well marked for the higher amounts.

The method which seems most applicable for determining sodium in aluminum is arc excitation of the metal itself between electrodes of graphite. Papish and O'Leary (21) determine chromium in fused alumina by the arc. Fesefeldt (11) uses a similar method for determining beryllium in aluminum oxide. Metallic aluminum cannot be used very successfully as electrodes with the arc because of its relatively low melting point and the formation of a heavy crust of oxide on the tips which is nonconducting and nonvolatile. However, the metal burns readily in the graphite arc and, when used in this way, the continuous spectrum of the graphite is practically eliminated.

Since solutions have not been found successful for this

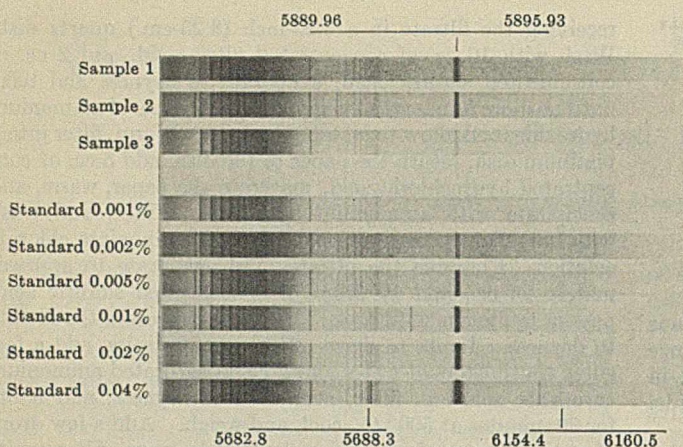


FIGURE 1. DETERMINATION OF SODIUM IN ALUMINUM BY FIRST METHOD

Sample 1, 0.008%; sample 2, 0.005%; sample 3, 0.0015%

determination, synthetic standards are necessarily eliminated. Therefore, the standards used are samples of aluminum which have been carefully analyzed by the available chemical methods. A series of these standardized metals containing 0.000, 0.001, 0.002, 0.005, 0.01, 0.02, and 0.04 per cent sodium have been prepared and are used for all spectrographic determinations.

Sodium in aluminum is estimated by four of its lines, the *D* lines at $\lambda\lambda$ 5889.97 and 5895.93, and the green lines at $\lambda\lambda$ 5682.68 and 5688.22. The *D* lines serve for amounts up to 0.02 per cent. The green lines are just visible at 0.02 per cent and are more valuable for estimating amounts between 0.02 and 0.04 per cent, as they show a gradation of intensity which is more apparent to the eye than that of the *D* lines (Figure 1). The sensitive ultra-violet doublet at λ 3303, al-

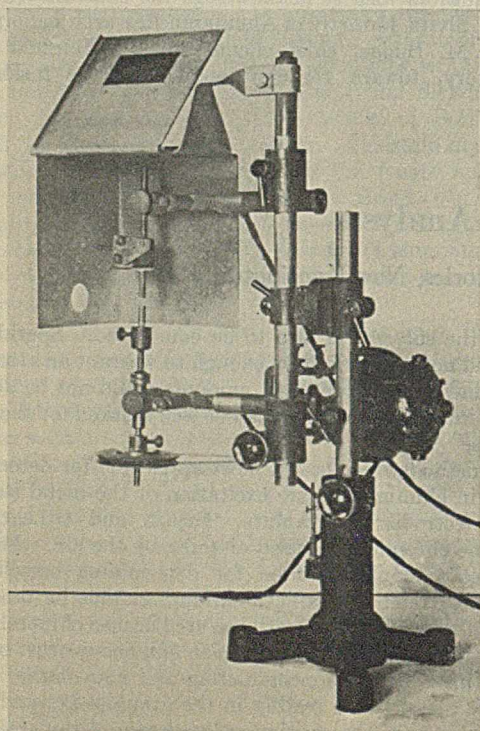


FIGURE 3. ARC STAND WITH ROTATING ELECTRODE HOLDER AND MOTOR

though more sensitive than the green pair, is in general not so valuable, as aluminum sometimes contains a small amount of zinc, and in such cases the sodium lines are rendered useless by the zinc lines at λ 3303. For this reason, no attempt has been made in these laboratories to utilize the ultra-violet sodium lines. A Littrow auto-collimating spectrograph with a quartz optical system is used for the determination. Eastman process panchromatic plates are used for photographing the spectra.

PROCEDURE. Two 1.25-inch (3.18-cm.) lengths of 0.25-inch (0.64-cm.) diameter round Acheson graphite rods are used for the electrodes. (A separate set is necessary for each sample photographed.) Drill a $\frac{7}{32}$ -inch (0.56-cm.) hole in one end of one of the pieces about 0.25 inch (0.64 cm.) deep. This piece serves as the lower and positive electrode and supports the metal. The upper electrode is used solid. Place the two pieces of graphite in the steel holders of the arc stand and give them

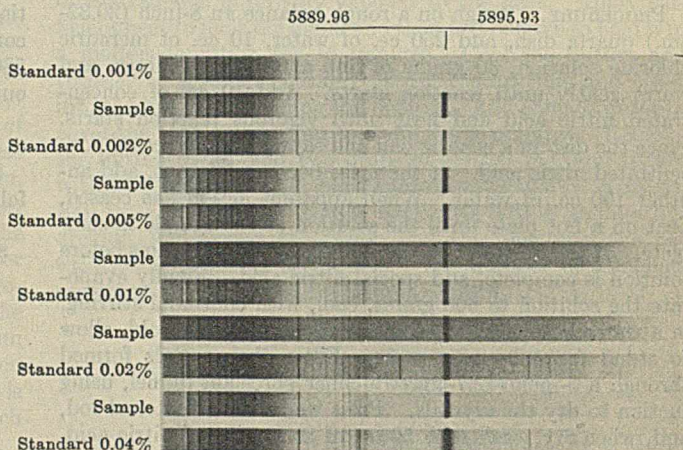


FIGURE 2. DETERMINATION OF SODIUM IN ALUMINUM BY SECOND METHOD

Sample alternated with standards; sodium estimated as 0.01%

a preliminary burn for about a minute with a current of 6 amperes. This step is to volatilize any sodium in the electrode tips or any which may have been placed there by handling. Saw or shear from the specimen a section about $\frac{3}{16}$ inch (0.48 cm.) square by $\frac{3}{8}$ inch (0.95 cm.) long. Place this piece of metal in a small beaker or crucible and cover with strong nitric acid. Place on a hot plate and heat near boiling for 4 or 5 minutes. Remove the metal from the acid with forceps, wash with distilled water, and dry. Place in the cavity of the lower electrode. With the spectrograph in correct adjustment, strike the arc and give an exposure of 1.5 minutes, with a current of 6 amperes at about 50 volts. The voltage is maintained as nearly constant as possible by focusing the images of the tip of the upper electrode and the image of the sample on two horizontal lines ruled on the slit diaphragm. This procedure keeps a constant distance between the two electrodes which is about all that is necessary to insure constant voltage. The samples for analysis and the standard samples are exposed under conditions as nearly identical as is possible.

Comparison with standards is accomplished in either of two ways, one possessing the advantage of requiring less time, the other that of being somewhat more accurate. The two methods are illustrated in Figures 1 and 2, respectively. In both schemes, intensities are matched visually without the aid of a measuring device such as a densitometer. The first

method consists of photographing all the samples, in duplicate if desired, on one portion of the plate, and then adding all the standards on another portion of the plate, as in Figure 1. The second method alternates each sample with the standards so that the spectrum of the sample is always between two standards. Obviously, a better opportunity is offered for matching intensities, as shown in Figure 2. Small differences in sodium produce such noticeable differences in intensity that the second method is rarely used, the first being considered accurate enough for ordinary requirements.

This method of analysis is based on the assumption of a constant exposure with an excess of metal always in the arc. To assist in accomplishing this end, a rotating holder for the lower electrode and a timing device are used. The rotating electrode holder shown in Figure 3 is made of steel with a fiber pulley, and is driven by a small motor mounted on the arc stand. Rotating the metal during the exposure keeps the image of the flame centered on the slit. Without this feature, the flame has a tendency to wander around the edges of the specimen or the graphite, often being shifted laterally enough to be thrown off the slit entirely. Accurate timing is controlled by means of a specially built device actuated by a Telechron motor. The apparatus is wired as an auxiliary circuit through a system of relays which allows the Telechron motor to run only when the arc is burning. As soon as the predetermined interval is complete, the timer opens the main contractor in the arc circuit and extinguishes the arc. A similar appliance is mentioned by Nitchie (20). Control of the exposure by some such means is very desirable when accurate timing is essential, as in this determination. The arc may be extinguished several times in a single exposure because of an oxide film, a draft of air, or other reasons. With such a device to record the successive intervals as they occur, the total exposure will be the same in time, regardless of the number of interruptions.

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Mineral Composition of Dates

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THE chemical composition of the date is of interest because of the widespread use of this fruit as a human food. In the date-producing countries of the Orient and northern Africa it is a principal component of the diet. France and Italy import many dates from their colonies across the Mediterranean. In England the annual consumption is 3 pounds per capita, whereas in Canada and the United States it is respectively 1 pound and 0.43 pound. The date industry in California and Arizona is important and is growing rapidly, the present production being over 3,000,000 pounds per year. The American-grown dates, however, furnish only a small fraction of those consumed, for approximately 54,000,000 pounds of dates are imported annually, principally from Iraq.

Although there are many varieties of dates, only a few are of commercial importance. The Deglet Noor is the principal American-grown variety, while the Hallowi, Sayer, and Khadrawi comprise the greater part of the annual import. The present paper is concerned particularly with the more important imported varieties, Hallowi and Sayer.

PROXIMATE COMPOSITION

Numerous proximate analyses of dates have been reported in the literature. However, to show the general composition

of dates, proximate analyses of packaged samples of Hallowi and Sayer varieties purchased on the market were made and are presented in Table I. These samples were grown in Iraq and were packed by the Hills Brothers Company of New York.

TABLE I. PROXIMATE COMPOSITION OF EDIBLE PORTION OF IRAQ DATES

	HALLOWI %	SAYER %
Moisture	19.0	18.0
Ash	2.22	1.59
Protein (N × 6.25)	1.72	2.16
Fat (ether extract)	1.90	0.31
Reducing sugars as invert	73.50	..
Total carbohydrates other than crude fiber	73.67	76.14
Crude fiber	2.17	1.90
Sucrose	None	..

The moisture content of bulk dates varies from 12 to 21 per cent, about 17 to 20 per cent being that of a palatable date. It may become considerably less in storage. As the date dries out, the dextrose crystallizes. Sugared dates are considered inferior both by the trade and by the public, but they can be restored to a suitable moisture content by treatment with moist steam. Dates with a moisture content below 23 per cent will keep satisfactorily, because the high sugar concentration inhibits the growth of microorganisms.

The high percentage of sugar, approximately 75 per cent, gives the high calorific value of 1420 calories per pound (3). In this respect dates are practically on a par with figs and raisins, but higher than prunes.

The percentage of protein is low, approximately 2 per cent. In the date-producing countries of the Orient and northern Africa the natives unknowingly compensate for this in their diet of dates and milk.

Sucrose, as the table indicates, is lacking in the Hallowi date. Slade (4) was the first to note that there are two types of dates: the invert type, possessing at maturity a large amount of invert sugar and little or no sucrose; and the cane sugar type, possessing at maturity practically all of its sugar in the form of sucrose. The imported varieties, Hallowi and Sayer, are of the invert type, while the principal American-grown variety, the Deglet Noor, is of the cane sugar type.

The percentage of ash is high and is comparable to that of other dried fruits.

The ratio of edible portion to pit is variable in different varieties of dates, but at a definite moisture content is relatively constant for a given variety. Thus at 18 per cent moisture the Hallowi yielded on an average 89.6 per cent of flesh and 10.4 of pit; Sayer yielded 91.2 and 8.8 per cent.

MINERAL COMPOSITION

The amount and composition of the ash are shown in Table II. Methods of analysis of the Association of Official Agricultural Chemists (2) were used in obtaining the data presented in this table, with the exception of the data for iron and copper. Iron was determined by means of the thiocyanate method as modified by Stugart (5), and copper by the method of Ansbacher and his associates (1), using xanthate colorimetry. Each of the values given is the average of results from the analysis of two samples, one representative of a 72-pound case of Iraq dates from the 1929 crop, the other representative of a similar case from the 1930 crop.

The percentage of ash, approximately 2 per cent, is two or three times as high as that of most of our foods which yield an alkaline ash. Most fresh fruits and many vegetables have less than 1 per cent of ash. Other dried fruits, such as prunes and raisins, have a percentage of ash comparable to that of dates, but it must be pointed out that, in their manner of use

in the diet, dates are more in the class of fresh fruits than in that of dried fruits.

The outstanding characteristic of the ash is the large proportion of potash. Calcium, in which the greatest deficiency in the mineral nutrients of common food occurs, is also present in considerable amount. Phosphorus, likewise sometimes deficient in common foods, is present to the extent of 7 to 10 per cent of P_2O_5 .

TABLE II. MINERAL COMPOSITION OF EDIBLE PORTION OF DATES

	HALLOWI %	SAYER %
Total ash, moisture-free basis	2.02	1.94
Alkalinity of ash ^a	16.7	15.9
Composition of ash:		
K ₂ O	42.7	40.8
Na ₂ O	2.47	2.65
CaO	4.51	6.96
MgO	5.86	6.77
P ₂ O ₅	9.50	7.47
Fe ₂ O ₃	0.26	0.23
Al ₂ O ₃	0.48
Cl	0.015	0.014
SO ₂	13.33	16.64
MnO	6.44	7.62
SiO ₂	0.21	0.30
	7.01	7.24

^a Cc. of *N* HCl required to neutralize the ash from 100 grams of moisture-free edible portion.

The alkalinity of the ash is high because of the large proportion of potash. Ash from 100 grams of edible portion is equivalent to from 13.6 to 14.7 cc. of normal alkali. The following data, taken from Sherman (3), give a basis for comparison: spinach, 27.0; raisins, 23.7; dried beans, 18.0; lettuce, 7.4; potatoes, 7; tomatoes, 5.6; oranges 5.6; lemons, 5.5; apples, 3.7.

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Rapid Centrifugal Method for Pectic Acid Determination

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IN THE course of extended studies on the heat extraction of fruit juices for jelly manufacture (5), the writers gaged the efficiency of extraction by a determination of the pectin (or pectic acid) in both juices and marc. After comparing various chemical precipitation or titration methods, including those of Carré and Haynes (3), Ahmann and Hooker (1), and Wichtmann (2), the latter was found to be the most direct and yielded reasonably satisfactory results. Briefly the method consists of a double precipitation of pectic substances with ethyl alcohol, filtration, and subjecting the aqueous pectin solution to a mild alkaline hydrolysis under controlled conditions to form pectic acid. The latter is then precipitated by addition of hydrochloric acid, filtered, and washed free from the acid and finally dried, weighed, ignited, and reweighed. The technic is extremely time-consuming and

only moderately accurate. Pectin itself is difficult to estimate. The only reasonably satisfactory procedure is precipitation with alcohol as tentatively recommended by the A. O. A. C. (2). Pectic acid may be roughly computed to pectin or vice versa, though various fruits have different ratios. In the Baldwin apple, the pectic acid-pectin is approximately 1.0 to 1.7, and for liquid apple pectin, 1.0 to 2.0. Pectin itself is not a simple substance, but is rather a complex of several closely allied carbohydrate derivatives having galacturonic acid as an essential constituent (7, 9). However, alcohol precipitation yields not only pectins, but gums, proteins, etc., which are insoluble in alcohol. Notwithstanding these facts, this crude technic is the basis of nearly all quantitative work on the pectic substances of plants.

Experiments were conducted on a centrifugal method for determining pectin (alcohol precipitate). Using 15-ml. tapered, graduated centrifuge tubes, much time was spent in attempting to throw down alcohol precipitate in an even, compact layer that could be measured. All efforts were unsuccessful. The pectin formed bulky gelatinous precipitates of varying physical properties and densities and could not be centrifuged with success.

After much preliminary work, the method for pectic acid as here described was worked out.

RAPID PROXIMATE METHOD FOR PECTIC ACID

Depending on the concentration, measure at room temperature 5 or 10 ml. of fruit juice free from sediment, or other filtered pectinous solution, into a 15-ml. tapered, graduated glass centrifuge tube. If 5 ml. of juice are taken, dilute to the 10-ml. mark with water. Add 1 ml. of 10 per cent sodium hydroxide, mix, and let stand for 15 minutes. The alkali hydrolyzes the pectin to pectic acid. Then add 2 ml. of 10 per cent hydrochloric acid solution to precipitate the pectic acid and mix thoroughly. Place the tubes (usually twelve at a time) in a wire basket immersed in a water bath near the boiling point, and allow to flocculate for 8 to 15 minutes, or until flocculation is complete. Stir with a small glass rod to remove air bubbles and to prevent floating, and thus hasten the formation of the uniform, flaky precipitate. Cool to below 25° C., centrifuge at 2400 to 2500 r. p. m. for 15 minutes on a 14-inch head, and immediately read the volume of precipitate. Make the reading by turning the tube upside down at eye level.

If fruit or pulp is used, prepare the sample by boiling 100 grams with 200 ml. of water for 1 hour, replacing at intervals the water lost by evaporation. After transferring to a 500-ml. volumetric flask and cooling, adjust the volume to exactly 500 ml. and filter through filter paper. Aliquots of this solution may be used for samples. If too dilute, the solution may be concentrated to a definite volume by evaporation.

STANDARDIZATION OF TECHNIC

Such variables as quantities of sample, alkali and acid, speed of pectin hydrolysis, speed and optimum temperature of flocculation and centrifuging were studied experimentally.

Enough sample should be taken so that from 0.7 to 1.5 ml. of centrifuged precipitate are obtained. When more pectic acid than this was present, difficulty was experienced during the precipitation with hydrochloric acid and subsequent flocculation because of the bulk of the precipitate. Very small amounts of precipitates always gave high results and did not pack down well during centrifuging. Between 20° and 25° C. no temperature effects were observed.

Fruit juices are sufficiently similar in acidity that the hydrolysis of the pectin is carried out at a fairly definite hydroxide-ion concentration. An excess of alkali broke down the pectin too quickly and gave a dark brown liquid from which the hydrochloric acid incompletely precipitated the pectic acid and left it in poor physical condition. The time required for hydrolysis as shown by quantitative determination of pectic acid was variable for the several pectin solutions

A new, simple, rapid, proximate method for the determination of total pectic substances as pectic acid in fruit juices, extracts, or pectin solutions is described. The filtered sample, in a 15-ml. tapered, graduated centrifuge tube, is hydrolyzed under controlled conditions by alkali, and the resulting pectic acid gel is precipitated by hydrochloric acid, flocculated in a water bath, cooled, and centrifuged. The volume of precipitate is correlated with results obtained by the usual long gravimetric method.

The method is particularly adapted to the routine examination of a large number of samples of pectin solutions of similar composition. In a series of fifty-five trials with six products, the per cent deviation ranged from 2.9 to 12.6. The results are accurate to about 5.5 per cent.



tried. However, since the reaction was always complete in 15 minutes, this period was chosen. The hydrolysis of pectin is accompanied by a gradual demethoxylation, and according to Mehlitz (7) and others, as the pectin is hydrolyzed, the eight methoxyl groups are successively lost, one by one. The number of methoxyl groups present in the pectin molecule at any given time may possibly be correlated with the jelly strength of the pectin gel, as shown by Lüers and Lochmüller (6) and Sucharipa (10). However, Myers and Baker (8) were unable to verify these results.

In this test complete flocculation of the pectic acid by heat is necessary.

A large number of tests gave promising results when the cold unflocculated gel was centrifuged. At times excellent checks were obtained, but the results were too variable to be of great value. Since a larger volume of precipitate is secured by not flocculating the gel, more accurate readings should follow. After many trials it was decided that the more uniform readings of the centrifuged flocculated precipitate were preferable to the greater volume of the centrifuged gel. It may be possible to manipulate this pectic acid gel so that it can be satisfactorily centrifuged.

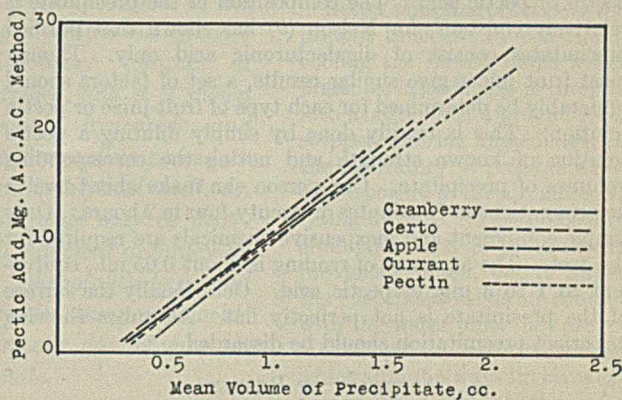


FIGURE 1. RELATION OF VOLUME OF CENTRIFUGAL PRECIPITATE TO PECTIC ACID

The flocculation time varies according to the kind of pectin and the quantity of pectic acid gel in the tubes. Small quantities lose their air bubbles and settle to the bottom in 5 or 6 minutes, whereas dense gels containing much entrapped air require 12 or 15 minutes with occasional stirring with a small glass rod.

Too low results are obtained unless the hot flocculated tubes are cooled before centrifuging. It has been customary to cool to below 25° C.

Various speeds were used on the centrifuge, but optimal results were obtained at 2400 to 2600 r. p. m. in 15 minutes. Results at 1500 or 2000 r. p. m. were always somewhat higher than at 2500. Though 10 minutes in the centrifuge were usually sufficient to give uniform readings, slightly better checks were obtained in 15 minutes, hence this period was adopted. Though a still longer period in the centrifuge gave slightly lower readings, they were no more uniform than at 15 minutes.

Readings should be made within a few minutes after removing the tubes from the centrifuge. There was a tendency for the volume to increase gradually on standing. The best method of taking readings was by holding a finger over the open end of the tube and inverting at eye level. It is essential that tubes be cleaned with chromic acid or other good cleaning solution once a day.

Readings may vary from 0 to 2.0 ml., but best results are obtained at from 0.7 to 1.5 ml. With a little experience one can so regulate the concentration of the pectin solution that the proper amount of precipitate is obtained. Duplicate, or better, triplicate tubes are made and the results averaged.

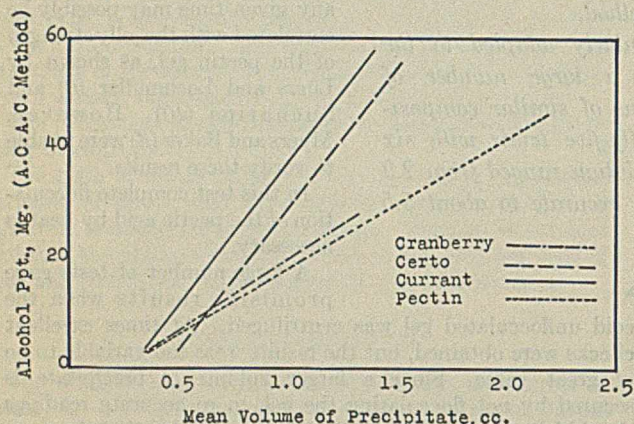


FIGURE 2. RELATION OF VOLUME OF CENTRIFUGAL PRECIPITATE TO ALCOHOL PRECIPITATE (PECTIN)

Within the limits mentioned above, the volume of pectic acid may be correlated with the chemical A. O. A. C. values for pectin or pectic acid. The composition of the precipitate is relatively constant, for Nelson (9) has shown that purified precipitates consist of digalacturonic acid only. Though most fruit juices give similar results, a set of factors should preferably be determined for each type of fruit juice or pectin solution. This is readily done by simply diluting a pectin solution of known strength and noting the corresponding volumes of precipitate. One person can make about twelve determinations in 70 minutes or twenty-four in 2 hours. Only simple equipment and inexpensive chemicals are required for the test. The accuracy of reading is about 0.05 ml., equivalent to 1 to 3 mg. of pectic acid. Occasionally the surface of the precipitate is not perfectly flat. All tubes showing imperfect precipitation should be discarded.

ACCURACY OF RESULTS

Several citrus and apple pectin solutions as well as heat-extracted fruit juices were used so as to have representative types of product. Detailed data were obtained on six different types of solutions and statistically treated. For the sake of brevity only two representative tables are here reproduced, Tables I and II.

TABLE I. ACCURACY OF RAPID CENTRIFUGAL METHOD AS APPLIED TO CITRUS PECTIN SOLUTIONS (A. O. A. C. method used)

No. OF DETNS.	VOL. OF JUICE IN SAMPLE	MEAN VOL. OF PPT.	P. E. ² MEAN	AV. DEVIATION	PECTIN ACID	PECTIN. (ALC. PPT.)	
	ML.	ML.	ML.	%	Mg.	Mg.	
12	0.5	0.48	0.0058	0.025	5.2	1.81	2.80
12	1.0	0.70	0.0021	0.025	2.9	3.63	5.60
12	1.5	0.95	0.0072	0.032	3.4	5.44	8.40
12	2.0	1.11	0.0086	0.130	11.7	7.26	11.21
12	2.5	1.31	0.0011	0.040	3.0	9.07	14.00
12	3.0	1.46	0.0095	0.0510	3.5	10.89	16.81
12	3.5	1.66	0.0370	0.160	9.7	12.70	17.60
12	4.0	1.82	0.051	0.230	12.6	14.52	22.42
12	6.0	2.25	0.041	0.180	8.0	21.78	33.60
11	8.0	2.85	0.074	0.310	10.9	29.10	44.80

Av. 7.1

² P. E. = probable error.

TABLE II. ACCURACY OF RAPID CENTRIFUGAL METHOD AS APPLIED TO HEAT-EXTRACTED CURRANT JUICE

No. OF DETNS.	VOL. OF JUICE IN SAMPLE	MEAN VOL. OF PPT.	P. E. MEAN	AV. DEVIATION	PECTIC ACID (ALC. PPT.)	PECTIN (ALC. PPT.)	
	ML.	ML.	ML.	ML. %	Mg.	Mg.	
16	1.0	0.31	0.0047	0.02	6.4	1.48	5.03
16	2.0	0.45	0.0045	0.02	4.4	2.96	10.10
16	3.0	0.60	0.0055	0.024	4.0	4.44	15.10
20	4.0	0.67	0.006	0.035	5.1	5.92	20.10
16	5.0	0.74	0.0066	0.034	4.6	7.40	25.20
16	6.0	0.86	0.0123	0.040	4.7	8.8	30.2
16	7.0	0.92	0.0221	0.042	4.3	10.36	35.2
16	8.0	1.063	0.0333	0.080	7.6	11.84	40.2
4	9.0	1.130	0.0442	0.110	9.7	13.32	45.3
16	10.0	1.22	0.0976	0.044	3.6	14.80	50.3

Av. 5.4

This method is shown to be reasonably reliable when used on a single type of product. For example, with extracted apple juice, apple pectin, citrus pectin, or pectinous juices of small fruits, the pectic acid content can be closely estimated. The per cent deviation among fifty-five sets of readings varied from 2.9 to 12.6 with mean percentage deviations of from 3.4 to 7.1 in the several products tested. The grand average per cent deviation is 5.5. On the basis of a maximum pectin content in fruits of 2 per cent, the percentage error in using the method will normally be less than 0.1 per cent of pectic acid.

In order to test the personal equation in the method, four independent technicians made tests on a commercial apple pectin extract. The results were mean volumes of precipitate of 1.00 and 1.03, 1.09 and 1.04, 1.07 and 1.01, and 1.06 and 1.015, corresponding to 12.3, 13.4, 13.16, and 13.02 mg. of pectic acid (A. O. A. C. method), respectively. These data indicate that different operators can use the test with a fair degree of accuracy.

Figure 1 shows the relationship between volume of precipitate and weight of pectic acid, Figure 2 the relation of alcohol precipitate to volume of centrifuged pectic acid. By means of similar graphs the pectin content of fruit juices or pectin extracts may be read directly in terms of volume of centrifuged precipitate. In citrus pectin, for example, the ratio of pectic acid to alcohol precipitate was 0.646 to 1, and in heat-extracted currant juice 0.29 to 1.

APPLICATION OF METHOD

The principal application of the rapid centrifugal method for pectic acid is in routine work where large numbers of samples of pectins or pectinous solutions have to be examined in a short time. The results are accurate enough for ordinary control or even routine research work. A few chemical determinations by the A. O. A. C. method should be made from time to time to serve as controls, as it is by this method that the volume of precipitate is translated into terms of weight or per cent of pectin or pectic acids.

Though there may be no definite correlation between volume of precipitate (pectic acid or pectin) and jellifying power of the juice, these determinations are considered to give an approximation of the value of a fruit juice for jelly manufacture, or of the quantity of pectin present in a pectin preparation. Myers and Baker (8) found that the jellifying power of pure pectins was not correlated with their content of pectic acid.

This paper does not seek to establish a definite relationship between volume of pectic acid precipitate, as obtained by this procedure, and jellifying power. Factors such as fruit maturity and extraction methods would probably cause variations to occur. At best, the only really practical method of determining jelly value of pectinous solutions is actually to prepare a series of experimental jellies from an aliquot.

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Determination of Hydroxide and Carbonate in Boiler Waters

I. Methods

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THE determination of the composition of a boiler water involves two fundamental operations, the removal of a representative sample from the boiler, and the accurate analysis of this sample. In discussing the removal of samples from a boiler, the writers have not made a complete survey of current practice but have indicated the conditions which should be fulfilled and have shown a practical sampling system which meets these conditions. In outlining the analytical methods which have been or might be applied to the determination of carbonate, hydroxide, and sulfate in boiler waters, references to important articles have been given but no attempt has been made to include the countless papers in which methods have been endlessly modified or rediscovered.

SAMPLING OF BOILER WATERS

It is still the practice in some plants to collect a sample from a boiler by draining water from a blow-off line or water-column connection into an open vessel. This sample is then cooled, frequently in contact with the air, filtered after the lapse of more or less time, and then analyzed. Such a procedure is obviously worthless for purposes of exact control, even when carried out rapidly. In the first place, the hot solution obtained may have a composition differing widely from that of the boiler water at the time of sampling. Even if it represents the boiler water at the instant of removal, it soon will not, however. During cooling its composition will change owing to re-solution of suspended particles of calcium carbonate, calcium sulfate, or other substances having inverted solubility curves. Moreover, if it is left in contact with the air it will absorb carbon dioxide at a rapid rate, so that a

Titration methods commonly used for the determination of carbonate in boiler waters yield inaccurate values due to uncertainty in end points and error in interpretation. The various methods available for determining carbonate are reviewed. The development and testing of a simple apparatus which gives accurate and consistent results for total carbon dioxide even at very low concentrations is described. Plant tests using a simple but effective method of filtering boiler-water samples at boiler temperature are described, and it is shown that large errors in carbonate, hydroxide, and sulfate may result from poor sampling procedure and the use of inadequate analytical methods.

It is concluded that hydroxide may be determined in boiler water with sufficient accuracy by either the titration with phenolphthalein and methyl orange or the Winkler barium chloride method, but that these methods do not give an accurate value for carbonate.

boiler water which actually contains little carbonate and considerable hydroxide may be reported as showing low hydroxide and high carbonate, or even a considerable concentration of bicarbonate. Such analytical data, when used for control purposes, are dangerous as well as ridiculous.

Better sampling practice at the present time usually consists of cooling the sample under boiler pressure, introducing it directly into a bottle with a ground-glass stopper, filtering immediately in the laboratory, if possible without exposure to the air, and analyzing at once. This procedure eliminates most of the defects previously noted, but it leaves the suspended solids in contact with the water until they are removed by a laboratory filtration which almost always involves exposure of the sample to the air for

several minutes. That even brief exposure may result in high values for carbonate is indicated by Ellms and Beneker (9) and Johnston (13), and proved by the results reported in the third part of the present paper.

The ideal sampling procedure would involve the continuous removal of a small amount of water from the boiler, suspended solids being separated from the sample by means of a filter located within the boiler. The rate of flow and resistance of the filter should be such that no flashing of solution into vapor could take place because of decrease in pressure on passing through the filter. The hot solution free from suspended solids should then pass through a cooling coil maintained under boiler pressure by a throttling valve on the cold discharge side. The continuous stream of cold, filtered boiler water should be introduced at the bottom of a glass-stoppered sampling bottle from which it is allowed to overflow for a few minutes. On removal from the sampling line the bottle should be stoppered at once. Although it is desirable to analyze the sample immediately because of the action of alkaline water upon glass, if bottles or glass-stoppered flasks

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of resistant glass are used, the sample may probably be kept for a considerable time without serious change in composition.

An internal filter combined with external cooling under pressure was first used in connection with boiler waters by Hall, Robb, and Coleman (13), and later by Partridge and White (33), in determining the solubility of calcium sulfate at boiler temperatures; but it is believed that this type of sampling system has never been applied to an operating boiler, largely because of the difficulty of finding a filter medium which would stand up satisfactorily within a boiler, and the difficulty of introducing an internal filter without violating the provisions of the boiler code.

In the third part of this paper there is described a sampling system of rather simple construction which fulfils all the requirements previously noted, although the filter is located just outside the boiler rather than within the boiler drum. This system has demonstrated its practical value in plant service.

SURVEY OF ANALYTICAL METHODS

Accurate knowledge of the carbonate, hydroxide, and sulfate concentrations within a boiler is necessary in any plant where the sulfate-carbonate ratio is controlled to prevent the deposition of sulfate scale,³ and where the sodium sulfate-alkalinity ratio is controlled in an effort to obviate "caustic embrittlement." The routine control methods used in the determination of the stoichiometric concentrations of these ions in boiler water have been inherited by the boiler operator from the investigator interested in the sanitary examination of water supplies. Like many legacies, these methods are rather out of place in their new surroundings, particularly that for the determination of carbonate and hydroxide discussed under the heading of "alkalinity" in the A. P. H. A. Manual (1).

This method, which is the familiar titration with phenolphthalein and methyl orange, and the barium chloride method of C. Winkler⁴ are the only ones which have been used extensively in boiler-water control. Examination of the literature shows a number of other methods which have been, or might be, applied to the determination of carbonate and hydroxide in solutions. A number of these are briefly discussed in the following sections. Only the more important papers dealing with the various methods are noted, for a complete list of the modifications and rediscoveries would contain many hundred items.

The various analytical methods for carbonate may be classified in two main groups, one including methods based on titration of the original sample, the other including methods involving an initial evolution of the carbon dioxide content of the sample.

TITRATION OF ORIGINAL SAMPLE. The methods available for the determination of carbonate and hydroxide in boiler waters by titration of the original sample depend either upon the color change of indicators or upon changes in electrical potential as measuring devices. Any method involving titration of the original sample with the aid of color indicators is subject to the effect of neutral salts upon these indicators, to uncertainty in end points, and to error in interpretation when phosphates, aluminates, silicates, or salts of weak organic acids are present. The large effect of neutral salts upon phenolphthalein is shown by the data of Rosenstein (38) and of Kolthoff (20). Methyl orange, on the other hand, is nearly free from "salt error" (20, 21). On the score of definition of end points in the titration of carbonate-hydroxide solutions,

phenolphthalein again shows less desirable properties than methyl orange. The "sliding end point" of phenolphthalein in such solutions has been noted by Thomson (44), Küster (23), Hildebrand (16), Brubaker (3), and Truog (47). While the methyl orange end point is frequently considered to be uncertain, good precision may be attained by the use of a comparison standard containing the same concentration of indicator and saturated with carbon dioxide, as suggested by Küster in his thorough study (23). The theoretical limit of accuracy in determining the halfway point in the titration of carbonic acid has been estimated by Noyes (32), Tizard and Boeree (45), and Bjerrum (2) as greater than 1 per cent. An error of several per cent would probably be present in most routine analyses of boiler waters. The utmost care in titration technic would be of no avail, however, if part of the effect attributed to carbonate by the ordinary method of interpretation were actually due to the presence in the boiler water of ions of acids with dissociation constants in the same range as those of carbonic acid. The use of indicators other than phenolphthalein and methyl orange obviously offers little chance of improvement in accuracy.

As far back as 1897 Küster concluded that the titration with phenolphthalein and methyl orange was not an accurate method for determining carbonate in carbonate-hydroxide solutions. After a painstaking investigation he recommended the Winkler barium chloride method for the determination of hydroxide, and the titration with methyl orange for the determination of total alkali. In searching for an accurate method for the control of boiler-water conditioning with soda ash, Hall (12) discarded the phenolphthalein-methyl orange titration because it gave high values for carbonate which he attributed to the presence in the boiler waters of salts of weak organic acids. He adapted the Winkler barium chloride method by using phenolphthalein as indicator in the titration of duplicate samples, to one of which barium chloride was added to precipitate carbonate. Experiments by McKinney (15, 30) question the accuracy of this method for carbonate, and Larson (24) has recently announced that it yields unreliable carbonate values in the presence of sulfate. Poethke and Manicke (36) in their very complete investigation of the Winkler barium chloride method found that the phenolphthalein used as indicator was very readily removed from solution by adsorption on the precipitate of barium carbonate. When the method is applied to a water containing sulfate, it is possible that the barium sulfate precipitated with the barium carbonate may remove the indicator from solution so rapidly as to prevent the satisfactory location of the titration end point. The error introduced by the use of the Winkler method on solutions containing sulfate has been independently observed by the present writers and is discussed in the second part of this paper.

The excess-acid method was apparently first used with phenolphthalein by Warder (53). Its application in connection with water softening is mentioned by Handy (14), and Hall (11) compared it with the phenolphthalein-methyl orange titration and modified Winkler method for the determination of carbonate in boiler waters. Hall's data show that the values obtained with the excess-acid method were quite consistently somewhat lower than those from the other titrations. In the light of present knowledge, this may indicate that the excess-acid method yields more accurate results for carbonate in boiler waters than either the phenolphthalein-methyl orange titration or the modified Winkler method. Further investigation seems justified.

Electrometric titration has not, to the writers' knowledge, been applied to actual boiler-water analysis, although Hildebrand (16), Greenfield and Buswell (10), and Davis, Oakes, and Salisbury (8) obtained satisfactory breaks in their titration curves for sodium carbonate solutions. Cox (7), using a

³ Where phosphate is used as a conditioning chemical, the PO_4 concentration must similarly be known.

⁴ The writers have been unable to procure a copy of Winkler's "Mass-analyse," in which this method was first described. For discussion of the method, see Küster (23).

differential method, located the end points more definitely. Zhukov and Gortikov (57), also using the differential method, found that small amounts of carbonate showed up clearly in the titration of sodium hydroxide, so that this method may have some promise for use on boiler waters not containing phosphate, aluminate, silicate, or similar ions in amounts sufficient to prevent interpretation of the titration curve. The potentiometric method has also been applied to carbonate-hydroxide mixtures by Little and Durand (28), whereas Kolthoff (22) found the conductimetric method usable within limits.

The method recently suggested by McKinney (30) for the determination of carbonate by titration between definite pH values and the application of dissociation data is subject to the errors of any other titration method if the pH reference levels are determined colorimetrically. More accurate measurement of pH by the electrometric method in the control of boiler-water conditions is quite possible, but to date this method has not been applied outside of a few special investigations.

McKinney's proposal to calculate hydroxide concentrations from pH measurements is perfectly logical, but since the pH value of most boiler waters is close to or above 11, and since colorimetric methods employed in a routine manner will frequently not yield values accurate to within 0.2 unit, the hydroxide values calculated from such measurements will be only approximate. Electrometric measurement of pH here again offers increased accuracy.

EVOLUTION OF CARBON DIOXIDE FROM SAMPLE. The total carbon dioxide content of a solution may be determined in a variety of ways, all of which depend upon the initial evolution of the carbon dioxide from the original sample. The various methods utilize measurement of gas pressure or volume, the freezing-out of solid carbon dioxide, and absorption in various solid or liquid media. Many of these methods have been developed in fields rather distant from boiler-water chemistry. Their possible application to the latter depends upon how simply and how accurately they may be used for the determination of the small amounts of carbon dioxide present in boiler waters.

The absorption of carbon dioxide in potassium or sodium hydroxide is old enough to pass for a tradition. Petterson and Palmquist (35) adapted this process to the determination of the small carbon dioxide content of air by measuring the volume of a sample before and after absorption of carbon dioxide. L. W. Winkler (54) translated the gas-volumetric method to the realm of solutions, Van Slyke (48) added the use of vacuum to remove the carbon dioxide from the solution without heating, and McClendon (29) extended the use of Van Slyke's apparatus to the determination of the total carbon dioxide in sea water. Further applications of the general method to solutions were made by Shaw (41) and Hall (11), the latter being specifically interested in boiler waters. Van Slyke and Neill (49) also developed a manometric method to measure the carbon dioxide evolved from a sample.

Determination of carbon dioxide by freezing it out from a gas mixture has been used by Theis in solid-gas equilibrium studies (43). Yensen (56) also used this method with subsequent expansion of the carbon dioxide into a known volume whose pressure was measured.

The determination of evolved carbon dioxide by absorption offers an embarrassing variety of media and methods. The use of solid absorbents in connection with the determination of carbon in steel has become so well standardized that it need not be discussed. The problem here, as in the use of potassium hydroxide for absorption in weighing bottles, is to remove all of the carbon dioxide from the gas stream without gain or loss of water in the absorption unit which is weighed.

L. W. Winkler (55) avoided heating his water samples by using hydrogen generated in them by the action of acid on zinc to sweep the carbon dioxide into the absorption bulb. Waggaman (51) has described an arrangement which might prove applicable to boiler-water analysis. Absorption methods involving determination of carbon dioxide by titration seem, however, to be more generally applicable to boiler-water control than gravimetric methods.

When potassium or sodium hydroxide is used as an absorbent, the subsequent titration of the carbonate-hydroxide mixture will be more accurate if the barium chloride method of C. Winkler is used to determine residual hydroxide than if the titration is made with phenolphthalein and methyl orange, owing to the uncertainty in the phenolphthalein end point in the latter case.

The advantages of replacing potassium or sodium with calcium hydroxide, or better still, barium hydroxide, have been periodically rediscovered for the past century, if it is true that Dalton originated the method, as claimed by Letts and Blake (26). The latter investigators made a comprehensive survey of the method, which is usually associated with the name of Pettenkofer (34). They concluded that the barium carbonate precipitate produced by absorption of carbon dioxide should not be removed by filtration, but that the residual barium hydroxide should be titrated in the presence of the precipitate with phenolphthalein as an indicator. Nearly all of the possible variations of the methods have been tried. J. Walker (52), Nishi (31), and Johnston and A. C. Walker (19) have preferred to filter out the barium carbonate precipitate before titrating the excess barium hydroxide. J. R. Cain (4) and Schollenberger (39), on the other hand, recovered the barium carbonate, the former titrating it with methyl orange as indicator, the latter weighing it. In general, however, titration of the residual barium hydroxide without removal of the barium carbonate has been found satisfactory (26, 27, 47). When acids other than carbon dioxide may be absorbed also, it is possible to titrate both the residual barium hydroxide and the precipitated barium carbonate. An entirely different method of measurement was used by Itano (17), who determined the amount of carbon dioxide absorbed by the decrease in the conductivity of the barium hydroxide solution. Spohr and McGee (42) and Raymond and Winegarten (37) have also adopted this method. Lindner (27) has pointed out possible sources of error in the barium hydroxide absorption, whereas Schollenberger (40) has stated that thymolphthalein yields a sharper end point than phenolphthalein in the titration of the excess adsorbent.

Many devices have been used to insure complete absorption of carbon dioxide in the barium hydroxide solutions used. Vesterberg (50) found that a 10-bulb tube was satisfactory. Truog (47) devised a simple and very ingenious scrubbing tower. T. L. B. Cain (5) added gelatin to his barium hydroxide solution to increase the time of retention of gas bubbles at its surface. It was left for Constantino (6) to make the important improvement of circulating a small volume of gas through a closed system containing two flasks, in one of which the carbon dioxide was evolved from the sample, and in the other it was absorbed in barium hydroxide. Lescoeur and Manjean (25) subsequently used the same idea.

The accuracy attainable in the measurement of small quantities of carbon dioxide by absorption in barium hydroxide and titration of the excess absorbent has attracted many investigators in widely different fields of research. In searching for an accurate means of determining carbonate concentrations in boiler waters, the writers saw more promise in this method than in any of the others noted. This led to the development of two types of apparatus which are described in the second part of this paper.

II. Development and Testing of Apparatus for Carbonate Determination by Evolution and Absorption in Barium Hydroxide

TWO pieces of apparatus were designed by the writers for the determination of carbonate in boiler waters. The first of these was used in the laboratory in connection with work on an experimental boiler, the results of which will be reported in another paper. The second apparatus, which was both simpler and more accurate, was subsequently developed for the plant-control tests described in the third part of the present paper. The fundamental idea was the same in both cases. The total carbon dioxide content of a water sample was liberated by addition of excess acid and heating, and this carbon dioxide was carried by an air stream into an excess of standard barium hydroxide, precipitating barium carbonate. The residual barium hydroxide was then titrated with standard acid.

The successful application of this method to the determination of carbonate in solution depends upon the following factors: (1) complete removal of all carbon dioxide from the sample; (2) complete absorption of liberated carbon dioxide in barium hydroxide; (3) complete precipitation of barium carbonate equivalent to carbon dioxide liberated and absorbed; (4) titration of residual barium hydroxide to a definite

reproducible end point; and (5) freedom from contamination by carbon dioxide of the atmosphere. The ways in which these conditions were met will be discussed in connection with the description of each piece of apparatus. In general, the second condition is the one least likely to be satisfied by ordinary apparatus. Since it is necessary to sweep the carbon dioxide out of the original sample by means of an air stream initially free from carbon dioxide, a considerable volume of gas must be passed through whatever absorbing unit is used. As a bubble of gas containing carbon dioxide on passing through barium hydroxide immediately forms a film of barium carbonate at the gas-liquid interface, it is highly improbable that complete absorption can be attained except by prolonged contact or intimate mixing.

Since the absorption method determines only the total carbon dioxide in the sample, it must be combined with one of the ordinary titration methods if a value for hydroxide is also desired. In designing the apparatus for the absorption method, provision was therefore made for carrying out either the standard titration with phenolphthalein and methyl orange, or the Winkler barium chloride titration on the sample before determining the total carbon dioxide.

FIRST ABSORPTION APPARATUS

The method of operation of the first absorption apparatus, shown in Figure 1, is as follows: Air is first pumped through the apparatus for 10 minutes by the aspirator. Towers A and B, which are filled respectively with soda lime and barium hydroxide, free the entering air from carbon dioxide so that the pumping operation removes all of this gas from the system. Flask D, which is used to contain the sample, is quickly

removed and stoppered. The measured sample is then introduced into this flask and it is replaced on the apparatus as quickly as possible to prevent contamination by atmospheric carbon dioxide. The sample is then titrated in this flask with standard 0.05 N or 0.1 N hydrochloric acid to the phenolphthalein and methyl orange end points, or if the Winkler barium chloride method is being used, to the phenolphthalein end point alone. After this titration, excess hydrochloric acid equivalent to 2 cc. of normal acid is added to the sample through tube M, and air is slowly pulled through the sample and through flask E and tower K, each of which contains part of a measured amount of standard barium hydroxide. At the same time the sample is heated to boiling by the

heater C. The air sweeps the carbon dioxide from the heated acid solution into the barium hydroxide where it is removed as a precipitate of barium carbonate. The barium hydroxide in K is then drained into E, and K is washed up and drained down repeatedly with carbon dioxide-free water introduced in funnel L. Phenolphthalein is added with the last portion of wash water. The excess hydroxide in E is then titrated with standard acid from

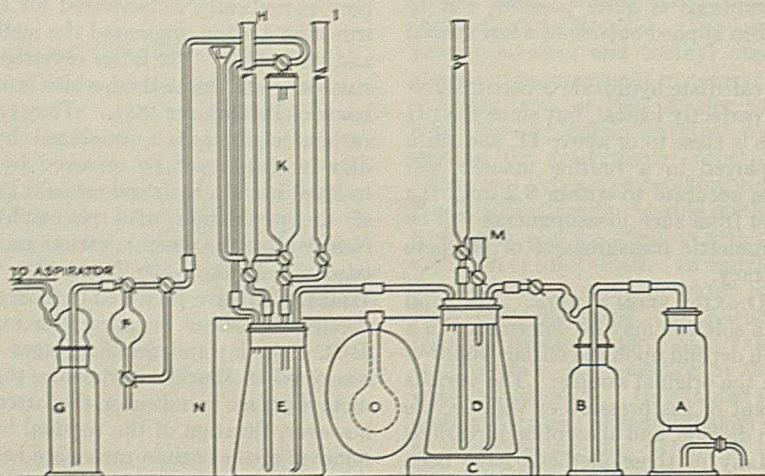


FIGURE 1. ARRANGEMENT OF FIRST APPARATUS

buret H to the disappearance of the last trace of color. The difference between this end point and the acid equivalent of the hydroxide used in the tower and flask gives the acid equal to the total carbon dioxide in the sample.

The bulb F at the end of the absorption system is a sight bulb which is filled with a saturated solution of barium hydroxide. During the absorption of the carbon dioxide from the sample, the gas leaving the apparatus is passed through this bulb. If for any reason some of the carbon dioxide is not removed in the absorption system, the saturated barium hydroxide in the bulb becomes cloudy, indicating that some of the gas is escaping and that the results of the analysis will not be correct. G is a guard bottle containing barium hydroxide. N is a box painted white on the inside and equipped with a daylight bulb and a reflector, O. Flasks D and E are contained in this box so that all titrations are carried out with the same constant illumination. I is a buret from which the barium hydroxide is measured out into E and K. The authors customarily use 50 cc. of approximately 0.02 N barium hydroxide, about 30 cc. being run into K and the remainder into E. The excess of barium hydroxide remaining after absorption was titrated with 0.02 N hydrochloric acid. The barium hydroxide was initially saturated with respect to barium carbonate.

In this system complete removal of carbon dioxide from the acidified and heated sample could be insured by passing the air stream through it for a sufficiently long time. A period of 15 minutes was found to be ample for solutions containing up to 90 parts per million carbonate. Practically complete absorption of the liberated carbon dioxide was insured by passing the gas stream first into barium hydroxide in E and

then through *K*, which was 30 cm. high, 3 cm. in diameter, and was filled with 3-mm. glass beads. The rate of flow of air was about 5 bubbles per second from the tip in *E*. By carrying out the titration of the excess barium hydroxide with constant illumination, closely reproducible results were obtained. Blank tests indicated that all carbon dioxide was scrubbed from the entering air by passing through *A* and *B*. Further blank tests showed that hydrochloric acid could be used for acidifying the sample without danger of carrying over acid in the gas stream to the barium hydroxide.

The accuracy of the apparatus was tested and the method was compared with both the standard phenolphthalein-methyl orange and the modified Winkler barium chloride titrations, using samples prepared from standard solutions of pure sodium carbonate and pure sodium hydroxide. The standard carbonate solution was prepared by heating c. p. sodium bicarbonate in a jacketed crucible at 270° to 300° C. for 30 minutes, weighing out a given amount of the sodium carbonate formed, and diluting to the desired volume with distilled water. The sodium hydroxide solution was prepared by adding c. p. sodium metal to water protected from the atmosphere by a layer of ether. The ether was then evaporated and the concentration of the hydroxide determined by titration with hydrochloric acid. This gave a sodium hydroxide solution which was carbonate-free. Both standard solutions were kept in paraffined bottles. The necessary volumes of the standard solutions were added to distilled water to make up 200-cc. samples of the desired concentrations. The distilled water used in making up these samples contained some carbon dioxide which was determined by the absorption method to be equivalent to 6 parts per million carbonate. This constant carbonate concentration in the distilled water is included in the known concentrations shown in the subsequent tables.

TITRATIONS WITH PHENOLPHTHALEIN AND METHYLORANGE. The values obtained with a series of hydroxide-carbonate samples titrated by the standard method using phenolphthalein and methyl orange are shown in Table I.

TABLE I. TESTS OF STANDARD TITRATION WITH PHENOLPHTHALEIN AND METHYLORANGE ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE No.	HYDROXIDE		CARBONATE	
	Known P. p. m.	Found P. p. m.	Known P. p. m.	Found P. p. m.
1	55	47	6.0	24.7
2	55	45	6.0	29.7
3	81	77	6.0	9.1
4	81	66	26.1	31.3
5	81	78	46.1	47.9
6	81	77	86.2	89.0
7	191	188	26.1	31.6
8	191	187	46.1	53.9
9	191	189	46.1	53.9
10	285	277	6.0	16.5
11 ^a	285	277	6.0	19.0
12 ^a	285	276	26.1	34.9
13 ^a	285	277	46.1	57.0
14	285	284	86.2	85.5
15 ^a	407	411	6.0	0.0
16	407	403	6.0	11.1
17 ^a	407	403	6.0	6.4
18 ^a	407	398	26.1	34.8
19 ^a	407	400	46.1	47.6
20 ^a	407	395	86.2	101.2

^a Calcium sulfate added in solution.

The titrations were carried out in flask *D* of the apparatus shown in Figure 1 under conditions superior to those usually surrounding control titrations of boiler waters. Loss of carbon dioxide was obviated by introducing the acid slowly near the bottom of the flask which was agitated only by a gentle swirling motion. The values calculated for carbonate by the customary method of interpretation (1) are, however, consistently high and rather irregular, particularly for the lower concentrations. As a result of the arbitrary method of calculation, high values for carbonate lead to slightly low values for hydroxide.

The titrations shown in the table were made on distilled-water solutions containing no impurities. In the analysis of boiler waters it is doubtful if the relative accuracy shown here could be expected, since salts of slightly dissociated acids other than carbonic acid may be present, the neutral salt content is generally much higher, and the solutions are in the main more or less colored.

TITRATIONS BY MODIFIED WINKLER BARIUM CHLORIDE METHOD. The results of titrations by the modified Winkler barium chloride method on a series of samples of known concentration are shown in Table II.

TABLE II. TESTS OF BARIUM CHLORIDE TITRATION ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE No.	PROCEDURE IN TITRATION	HYDROXIDE		CARBONATE	
		Known P. p. m.	Found P. p. m.	Known P. p. m.	Found P. p. m.
1	(1)	81	86	26.1	0.0
2	(1)	81	90	46.1	3.3
3	(1)	81	101	86.2	5.0
4	(1)	191	194	26.1	9.5
5	(2)	191	188	26.1	31.6
6 ^a	(2)	191	188	26.1	34.8
7	(3)	191	190	26.1	26.9
8	(4)	191	186	26.1	41.2
9 ^a	(4)	191	182	26.1	53.9
10 ^a	(3)	191	186	26.1	41.2
11	(2)	191	189	46.1	49.1
12	(5)	191	189	46.1	49.1
13	(6)	191	192	46.1	39.6
14	(1)	191	193	46.1	36.4
15	(1)	191	196	46.1	23.8
16 ^a	(2)	191	187	46.1	55.5
17 ^a	(3)	191	186	46.1	61.7
18 ^a	(4)	191	183	46.1	71.4
19	(3)	191	190	46.1	46.0
20	(1)	285	290	26.1	0.0
21 ^a	(1)	285	292	46.1	6.3
22	(1)	285	308	86.2	0.0

- (1) 10 cc. of 0.2 *N* BaCl₂ added, sample titrated immediately.
- (2) 10 cc. of 0.2 *N* BaCl₂ added, sample boiled, titrated hot.
- (3) 10 cc. of 2 *N* BaCl₂ added, sample titrated immediately.
- (4) 10 cc. of 2 *N* BaCl₂ added, sample boiled, titrated hot.
- (5) 10 cc. of 0.2 *N* BaCl₂ added, sample boiled, titrated cold.
- (6) 10 cc. of 0.2 *N* BaCl₂ added, sample let stand 1 hour, then titrated.

^a Solution of calcium sulfate used to make sulfate concentration of sample about 700 parts per million.

These samples were treated in a variety of ways as indicated by the number in the column headed "Procedure in Titration." In the case of the first method, in which 10 cc. of 0.2 *N* barium chloride were added and the sample titrated immediately, it is seen that the values for carbonate are consistently far too low. This is undoubtedly due to the fact that not enough excess of barium chloride was added to produce rapid and complete precipitation. In fact, even in some of the samples containing fairly high carbonate concentrations, no precipitate could be seen on the addition of the barium chloride. These tests were all made at room temperature.

In the case of the second method of treatment, where 10 cc. of 0.2 *N* barium chloride were added and the samples boiled for a few seconds and then titrated hot, the values are seen to be much closer to the known concentrations than in the previous case. Here, however, they are in general high, particularly for those samples which contained calcium sulfate. The amount of barium chloride added to numbers 6 and 16 was not more than enough to precipitate the sulfate, leaving none for the carbonate. This would mean that the carbonate in the solution would be titrated in almost exactly the same manner as in the sample to which no barium chloride has been added. As a result, the calculations for these samples should have shown almost no carbonate rather than values higher than the known concentrations. The conclusion that the sulfate seriously interferes with the titration is inescapable.

The third method, that in which 10 cc. of 2 *N* barium chloride were added and the sample immediately titrated, gave accurate results on numbers 7 and 19. When calcium sulfate

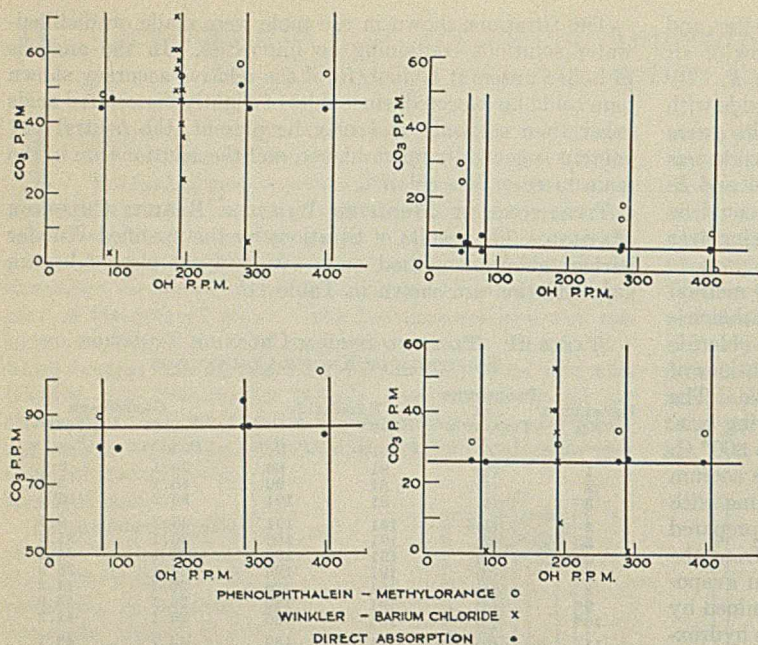


FIGURE 2. COMPARISON OF RESULTS OBTAINED BY VARIOUS ANALYTICAL METHODS ON HYDROXIDE-CARBONATE SOLUTIONS OF KNOWN COMPOSITION

was introduced into the samples as in numbers 10 and 17 the results were again too high.

The fourth method, in which 10 cc. of 2 *N* barium chloride were added and the sample boiled for a few seconds and titrated hot, gave high results. The presence of calcium sulfate increased the error.

Two other methods of treating the samples were tried as indicated in Table II. Since they were rather inconvenient and demanded considerable time, and furthermore because they did not seem to offer any greater accuracy than some of the other methods, they were not investigated further.

TABLE III. TESTS OF DIRECT ABSORPTION METHOD ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE No.	Known P. p. m.	Found P. p. m.
1	6.0	5.7
2	6.0	5.7
3	6.0	4.5
4	6.0	6.4
5	6.0	7.1
6	6.0	4.4
7	6.0	9.6
8	6.0	5.8
9 ^a	6.0	6.5
10	6.0	6.8
11 ^a	26.1	26.7
12	26.1	25.2
13 ^a	26.1	25.6
14	26.1	27.7
15 ^a	26.1	25.6
16	46.1	43.8
17	46.1	47.5
18 ^a	46.1	51.0
19 ^a	46.1	43.8
20 ^a	46.1	43.9
21	86.2	80.0
22	86.2	80.0
23	86.2	93.6
24	86.2	86.3
25 ^a	86.2	83.5

^a Calcium sulfate added to the sample in solution.

In general the barium chloride titration will yield the best results when an appreciable excess of the chloride is used. Letting the sample stand or heating it before titration does not increase the accuracy. When a considerable amount of sulfate is present in the solution, the barium chloride titration gives high values for carbonate and, consequently, slightly low values for hydroxide.

DIRECT ABSORPTION METHOD FOR CARBONATE.

The results of the direct absorption method for the determination of carbonate are shown in Table III. These results are very close throughout the entire range of concentrations investigated, the method is accurate at low carbonate concentrations, and the presence of calcium sulfate introduces no error. It is to be expected that the presence of most impurities would have little effect when it is remembered that the actual titration for the carbonate is conducted in a distilled-water solution containing only barium hydroxide and suspended barium carbonate resulting from the absorption of carbon dioxide evolved from the original sample.

The results of all of the determinations by the various methods are shown graphically in Figure 2. The heavy horizontal lines indicate the known carbonate concentration of the samples, and the heavy vertical lines, the known hydroxide for the samples plotted close to them.

Although the results shown in Tables I to III and Figure 2 by no means represent a complete study of the three methods tested, they do show that even with uncontaminated solutions under the optimum conditions of experimentation neither the

standard titration with phenolphthalein and methyl orange nor the modified Winkler barium chloride method is consistently satisfactory for the estimation of small concentrations of carbonate in the presence of hydroxide up to 400 parts per million hydroxide. With actual boiler waters under ordinary routine analytical conditions, the results may be expected to be much less exact. Even when working with relatively uncontaminated⁵ water in an experimental boiler, the writers found tremendous discrepancies between the carbonate concentrations indicated by the ordinary interpretation of the phenolphthalein-methyl orange titration and those found by the direct absorption method. Table IV presents a comparison of values for carbonate obtained by the two methods for four successive samples of water taken at intervals of one day from an experimental boiler during a scale-formation test.

TABLE IV. CARBONATE DETERMINATIONS BY TWO METHODS ON WATER FROM AN EXPERIMENTAL BOILER

Hydroxide P. p. m.	PHENOLPHTHALEIN-METHYL ORANGE TITRATION		DIRECT ABSORPTION Carbonate P. p. m.
	Carbonate P. p. m.	Carbonate P. p. m.	
102	88	12	
109	64	11	
108	71	10	
111	60	11	

In contrast to the uncertain results obtained with the customary titration methods, the absorption method for total carbon dioxide shows consistent results, particularly in the case of the lower concentrations of carbonate, and it may be expected to serve as satisfactorily for actual boiler waters as for pure solutions. The only source of possible misinterpretation of the results would be the presence in the boiler water of sulfides, sulfites, or some organic salts which might yield a volatile acid in the direct absorption determination.

As carried out in the apparatus of Figure 1, the chief disadvantages of the absorption method are the complicated apparatus and the time required, which is approximately 1 hour for each sample.

⁵ This water contained a small concentration of aluminate resulting from the attack of the alkaline solution on an alundum filter used within the boiler at the time.

IMPROVED ABSORPTION APPARATUS

The disadvantages of the absorption method just described arose from the complicated apparatus used. An effort at simplification resulted in the development of an improved apparatus which requires a relatively short time for an analysis of total carbon dioxide and which may be operated satisfactorily by a person not familiar with the chemistry of the process or skilled in the manipulation of apparatus.

The essential difference between the original and the simplified absorption apparatus is the manner in which the carbon dioxide is absorbed. In the simplified equipment the sample flask and the absorption flask form a closed system in which the air containing carbon dioxide is circulated continuously by a small pump until absorption is complete, thus eliminating the need for a scrubbing tower on the absorption flask. Absorption is hastened by the use of a device to produce many small bubbles in the absorption flask, although this is not essential to the satisfactory operation of the apparatus.

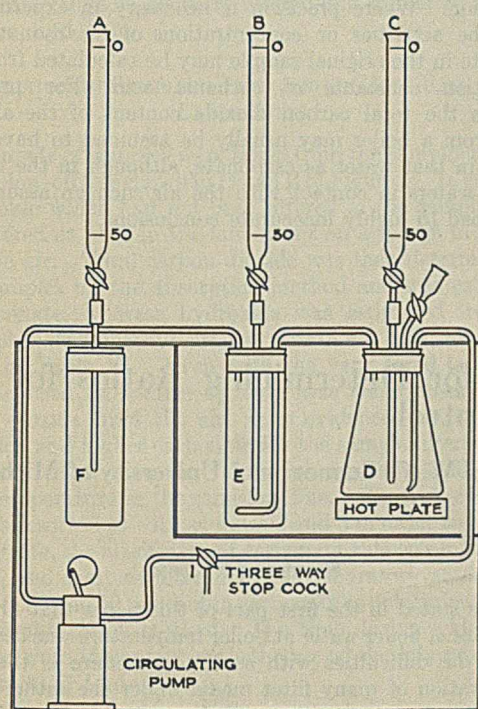


FIGURE 3. IMPROVED APPARATUS

The apparatus consists of a box equipped with daylight bulbs and a ground-glass panel for even illumination. Inside the box are fastened three stoppers connected to the burets and air-circulating system as shown in Figure 3. The evolution flask *D* containing the sample is attached to the right-hand stopper and is supported in place by a small hot-plate which is swung up beneath it. The absorption tube *F* is filled with 0.03 *N* barium hydroxide from the buret on the left-hand stopper, and is then attached as at *E* to the middle stopper for the absorption and subsequent titration.

The air outlet from the absorption tube *E* is connected directly to the suction side of a small air pump. The delivery side of the pump is connected back to the sample flask *D*, as shown. The air line from the pump to this flask is provided with a three-way stopcock with one connection open to the atmosphere to make it possible to vent air from the system before and after an absorption in order to relieve pressure differences. The bubbling device shown inside the absorption tube is a perforated platinum disk sealed in glass.⁶ The

⁶ Supplied by the Fisher Scientific Company.

purpose of this disk is to break up the gas stream into fine bubbles so that the carbon dioxide may be rapidly absorbed by the barium hydroxide. A small air condenser, not shown in Figure 3, is placed between *D* and *E* to prevent condensate from *D* from collecting back of the disk on the bubbling device and stopping the air flow. The circulating pump, which may be driven by any convenient means, consists of two sliding sleeves sealed with mercury to prevent the possibility of any air escaping.

The supply bottles for acid and barium hydroxide are mounted on a shelf formed by the projecting base of the box, and are connected to the burets, *A*, *B*, and *C*, by glass tubes. Rubber bulbs are also connected to the supply bottles to allow rapid filling of the burets by air pressure. Excess acid above the zero mark of the buret is automatically siphoned back into the supply bottle on release of pressure.

The operation of this apparatus is extremely simple. The measured sample is placed in flask *D*, phenolphthalein is added, the flask is placed on the apparatus, and the heater lifted into position as shown. The absorption tube is filled with 0.03 *N* barium hydroxide from buret *A* as at *F*, and is then put in position at *E*. The sample in *D* is titrated to the phenolphthalein end point with 0.1 *N* hydrochloric acid. Methyl orange is then added to the sample through the small tube shown at the top of *D*, and the sample is titrated to this second end point. Titration with either phenolphthalein or methyl orange is necessary to give a value for hydroxide; by using both indicators a comparison value for the carbonate may be calculated if desired. Excess hydrochloric acid equivalent to 2 cc. of normal acid is then added to the sample, and it is heated just to the boiling point. The carbon dioxide evolved from the sample is swept by the circulating air into the barium hydroxide where it is precipitated as barium carbonate. During a 10-minute absorption period, the gas is passed through the hydroxide about 15 times, insuring practically complete absorption. The excess hydroxide in *E* is then titrated, the phenolphthalein used as indicator being contained in the 0.03 *N* acid added. From the acid equivalent of the hydroxide originally introduced into tube *E* and the amount of acid used for the final titration, the amount of carbon dioxide evolved from the sample is calculated. In alkaline solutions whose pH is in the range above 11, the total carbon dioxide as determined by the absorption method may be assumed to be equivalent to the carbonate concentration of the solution. For less alkaline solutions, the concentrations of carbonate and bicarbonate may be calculated conveniently from the total carbon dioxide and pH by the method outlined by McKinney (30).

TABLE V. RESULTS OF ANALYSIS OF SOLUTIONS OF KNOWN CARBONATE CONCENTRATION BY MEANS OF IMPROVED ABSORPTION APPARATUS

Known P. p. m.	CARBONATE	
	Found P. p. m.	
8.8	8.6	8.8
22	21.6	22.0
44	42.0	42.5
87	83	82

Eight samples of known concentration prepared from pure standard sodium carbonate solution were analyzed in the manner described. The results, as shown in Table V, were very consistent and considerably more accurate than were the results obtained on the more complicated apparatus shown in Figure 1.

The standard sodium carbonate solution used in this series was made up with double-distilled water which had been

boiled for 20 minutes and cooled in a flask protected from carbon dioxide by ascarite. The water used in diluting given volumes of the standard carbonate solution to the standard volume of 200 cc. was also prepared from double-distilled water boiled and cooled in the same manner. Blank runs in the absorption apparatus on samples of water prepared in this manner showed it was free of carbon dioxide. These precautions were taken to obviate the necessity of adding a carbonate correction for the distilled water used in making up the standard solution. It was also desired to determine whether, at low concentrations of carbonate, all of the carbonate was evolved from the solution. The extremely good checks obtained at the low concentrations indicated that all the carbonate was evolved.

It is interesting to note that the barium hydroxide used in this simplified apparatus may be standardized in such a manner as to correct for the carbon dioxide in the system at the start of a determination. This is done by filling the absorption tube with the volume of barium hydroxide it is desired to use, then putting distilled water, carefully freed of all carbon dioxide and equal in volume to the samples to be analyzed, in the evolution flask, circulating the air through the system for 10 minutes, and titrating the barium hydroxide with the standard acid. The acid equivalent of the hydroxide thus obtained is a value corrected for any carbon dioxide initially present in the system. This procedure was followed in the analysis of the solutions shown in Table V, and also in

the analysis of the boiler-water samples referred to in the third part of this paper.

Tests were also run with varying periods of boiling the sample and with varying amounts of excess acid up to 4 cc. of normal hydrochloric acid added to a 200-cc. sample to determine whether any acid might be carried over into the barium hydroxide. In no case could any effect be measured.

The results obtained in the direct absorption determination are probably more accurate than those given by any standard titration method, especially when applied to impure waters. The improved apparatus is not complicated, and may be satisfactorily operated by an inexperienced person. Although approximately 20 minutes are required for one complete determination, in many cases it would seem better for control purposes to have a single accurate analysis than any number which cannot be relied upon.

It should be remembered that the absorption apparatus yields a value only for the total carbon dioxide present in a sample of water, regardless of the form in which it may exist in solution. Where precision is necessary in experimental work, the activities or concentrations of bicarbonate and carbonate in the original sample may be calculated from the dissociation constants of carbonic acid. For practical purposes the total carbon dioxide content of the alkaline water from a boiler may usually be assumed to have been present in that water as carbonate, although in the case of natural waters in contact with the air such an assumption would lead to highly inaccurate conclusions.

♦♦♦♦

III. Plant Tests of Various Methods for Determining Ratios for Boiler-Water Control

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SUBSEQUENT to the development and laboratory testing of the simplified absorption apparatus for the determination of total carbon dioxide, a series of boiler-water tests was carried out on one of the 125-pound W-type Stirling boilers in the Congress Street Heating Plant of the Detroit Edison Company. The make-up of this plant is nearly 70 per cent, the remaining 30 per cent being condensate returned from the customers' heating systems. Detroit city water is used for make-up and the total boiler input is passed through a feed-water heater and live-steam purifier, where part of the carbon dioxide content is removed with a corresponding precipitation of some calcium carbonate. Soda ash is added continuously by a proportioning device to the water as it goes to the heater. As a result of the rapid hydrolysis of carbonate in the boiler water, the latter contains a low concentration of carbonate and a relatively large concentration of hydroxide.

The tests had three objectives: the comparison of results obtained by filtration in the sampling line at boiler temperature with those obtained by filtration of the cooled sample in the laboratory; the comparison of the values for carbonate, hydroxide, and sulfate obtained by various methods, and of the values for the sulfate-carbonate and sodium sulfate-alkalinity ratios resulting from the use of these different methods; and the comparison of boiler-water concentrations in the upper and lower drums of a boiler steaming at normal rating.

SAMPLING SYSTEM

It was stated in the first part of this paper that filtration of samples of boiler water at boiler temperature was desirable. One of the difficulties with such a procedure is the rapid disintegration of many filter media under the rather severe conditions of contact with an alkaline solution at an elevated temperature. Filters of cloth supported on wire disappeared completely during runs with an experimental boiler, whereas aluminum tubes disintegrated in a period of several days. A small filter consisting of fine-mesh copper screen wrapped in several layers on a perforated pipe finally solved the problem of filtration in the experimental boiler, the suspended particles in the boiler water being trapped between the layers, thus forming their own filter medium. Such a system is fundamentally correct as long as the character of the solid phases in the boiler does not vary.

Since it did not seem feasible to insert a filter within the boiler at the Congress Street plant, the copper-screen type of filter was adapted, as shown in Figure 4, for insertion in the sampling line between the boiler and the cooling coil. The operation of this filter proved as satisfactory as the construction was simple. If necessary, this type of filter might readily be arranged for cleaning by back-washing.

It is believed that the fourteen layers of copper screen specified in Figure 4 will be sufficient for satisfactory filtration of any boiler water. At the Congress Street plant a filter with but six layers gave excellent results on water from the center drum, but did not completely clarify water from the

⁷ Detroit Edison Fellow in Chemical Engineering, 1930-31.

blow-off line. Another filter with twelve layers of copper screen proved satisfactory for the latter service.

The general arrangement of the sampling system relative to the boiler is shown in Detail A of Figure 5. One sampling line was taken from the water column and another from the blow-off connection on one of the mud drums. Each led to a separate copper-screen filter and cooling coil, with throttling valves on the cold discharge side of the latter. Boiler water was removed continuously through each sampling line at the rate of approximately 1 liter per minute, and was introduced at the bottom of a sampling bottle from which it overflowed into a drain trough.

An additional sampling line containing a cooling coil but no filter was connected to the blow-off line from the mud drum, as shown in Detail B of Figure 5, so that the results obtained by filtration respectively in the sampling line and in the laboratory might be compared. The complete sampling system thus made it possible to compare filtered samples obtained simultaneously from the steam drum and the mud drum, and at the same time to compare filtered and unfiltered samples from the mud drum.

FILTRATION IN SAMPLING LINE AND OF COLD SAMPLE IN LABORATORY

Three sets of samples were taken from the sampling system on the blow-off line shown in Detail B of Figure 5. In each case the sample which had not been filtered in the sampling line was filtered at once in the laboratory on a funnel in contact with the air. Total carbon dioxide was then determined on both samples by the absorption method and was calculated as carbonate, whereas hydroxide was estimated from the phenolphthalein-methyl orange titration. The results are shown in Table VI. Even with the very rapid laboratory filtration used on sample 1, there was some absorption of carbon dioxide from the air, as is evidenced by the lower hydroxide and higher carbonate for the sample filtered in the laboratory relative to the values for the sample filtered at boiler temperature in the sampling line. When slower filtration was resorted to with samples 2 and 3 in order to obtain a clear filtrate, the absorption of carbon dioxide was much more definite, the samples filtered in the laboratory showing increases of 80 and 50 per cent in carbonate as determined by the accurate absorption method. The time during which these solutions were in contact with the air of the laboratory was not more than 4 minutes.

TABLE VI. EFFECT OF FILTRATION IN LABORATORY UPON COMPOSITION OF ALKALINE BOILER WATER

SAMPLE	METHOD OF FILTRATION IN LABORATORY	SAMPLE FILTERED IN LABORATORY		SAMPLE FILTERED IN SAMPLING LINE	
		Hydroxide <i>P. p. m.</i>	Carbonate <i>P. p. m.</i>	Hydroxide <i>P. p. m.</i>	Carbonate <i>P. p. m.</i>
1	Very rapid filtration through coarse filter paper. Filtrate not clear	291	17.5	305	15
2	Filtration at maximum rate for clear sample	254	27	305	15
3	Filtration at maximum rate for clear sample	262	19	266	13

The rapid absorption of carbon dioxide by these samples of boiler water emphasizes the warning of Johnston (18) that even brief exposure to the atmosphere will lead to erroneous results. The authors believe that little attention has been paid to this point by operators responsible for boiler-water control, and that the majority of values reported for carbonate in boiler waters are high by from 50 to several hundred per cent as a result of this one factor, in addition to errors introduced by the inaccurate standard methods of titration.

No attempt was made in the present tests to determine the

possible increase in calcium in boiler-water samples as a result of filtration in the laboratory. Any error in this respect would be important only from the standpoint of fundamental research on equilibria in boiler waters and would not be significant to the operator responsible for control.

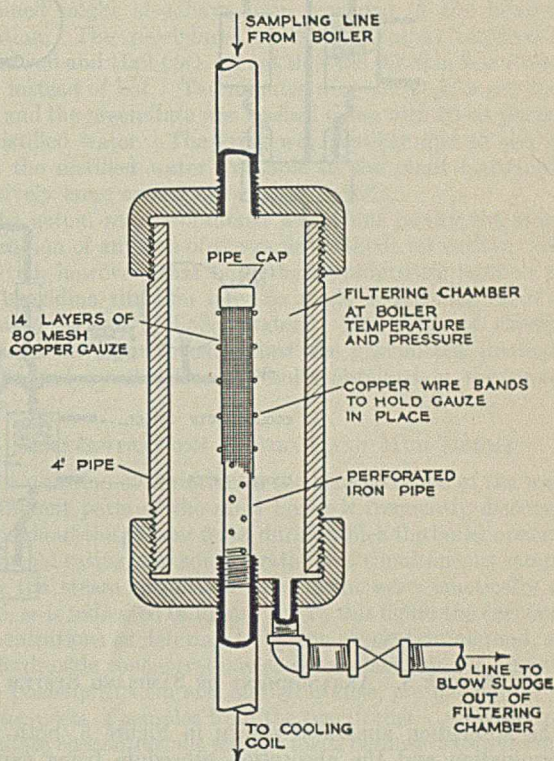


FIGURE 4. COPPER-SCREEN FILTER FOR FILTRATION OF BOILER-WATER SAMPLES AT BOILER TEMPERATURE

The tests reported establish the definite necessity for the utmost care in the handling of boiler-water samples, where carbonate concentrations must be known accurately for purposes of control. It cannot be emphasized too strongly that filtration at boiler temperature, either within the boiler or in the sampling line close to the boiler, removes one important source of error.

COMPARISON OF VALUES OBTAINED ON BOILER WATER BY DIFFERENT METHODS

Fourteen sets of boiler-water samples were taken during 3 successive days for a comparison of various methods of determining carbonate, hydroxide, and sulfate. The actual times at which samples were removed are shown in Table VII. Samples were taken simultaneously from the two lines shown in Detail A of Figure 5, all being filtered through copper-screen filters at boiler temperature before passing through the cooling coils. The pH of each sample as determined by colorimetric comparison with solution standards is given in Table VII. All samples were analyzed immediately upon removal.

CARBONATE. Values for carbonate were determined by four different methods: (1) the direct absorption method, using the simplified apparatus described in the second part of this paper; (2) the modified Winkler barium chloride titration; (3) the standard titration with phenolphthalein and methyl orange; and (4) the abridged equilibrium calculations of McKinney (30), based on the amount of acid required to titrate the sample between pH values of 8.5 and 5.0. The titration with phenolphthalein and methyl orange was made in flask *D*

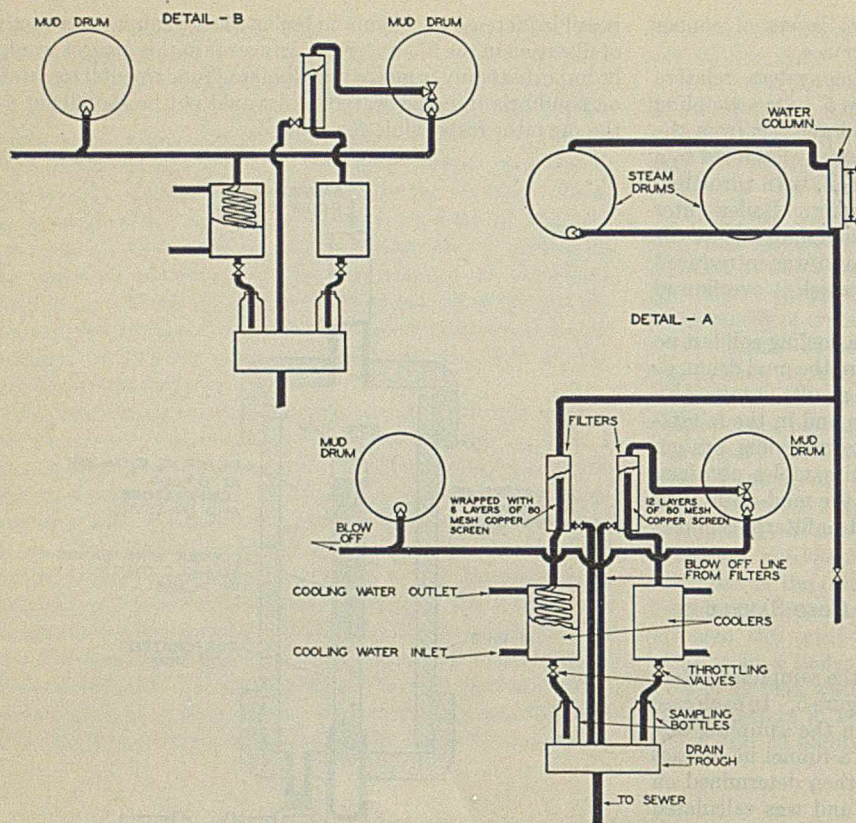


FIGURE 5. ARRANGEMENT OF SAMPLING SYSTEM FOR PLANT TESTS

of the absorption apparatus shown in Figure 3, both this determination and the absorption procedure being carried out by one of the writers. The barium chloride titration, which has been used as the control method in the Congress Street plant, was made by the regular plant operator who was not a chemist. The titration necessary for McKinney's method was made by a chemist familiar with the use of color indicators.

TABLE VII. LOG OF BOILER-WATER SAMPLES

SAMPLE	DATE	HOUR	pH ^a IN STEAM DRUM	pH ^a IN MUD DRUM
1	4-14-31	1:30 P. M.
2		2:45
3		4:00
4	4-15-31	10:00 A. M.	11.8	11.8
5		11:00	11.8	11.8
6		12:30 P. M.	11.8	11.8
7		1:30	11.8	11.8
8		2:45	11.8	11.8
9	4:00	11.8	11.8	
10	4-16-31	9:30 A. M.	11.9	11.9
11		11:00	12.0	12.0
12		12:30 P. M.	12.0	12.0
13		1:30	11.9	11.9
14		2:30	11.9	11.9

^a Determined colorimetrically by comparison with La Motte solution standards.

The values for carbonate calculated from the results of the four methods of analysis are shown in Figure 6. The writers place great reliance on the accuracy of the values obtained by the absorption method which vary above and below an average value of 10 parts per million. The values indicated by all three of the other methods are high, deviating with no apparent consistency by amounts ranging from a few per cent up to 300 per cent. The results from the barium chloride titration are only slightly better than those from the titration with phenolphthalein and methyl orange. McKinney's method is subject to the same difficulties encountered with

the other titration methods when the end points at pH 8.5 and 5.0 are determined colorimetrically.

If it is granted that the accuracy of the absorption method is established by the tests on solutions of known composition reported in the second part of this paper, it is evident that none of the other methods for carbonate investigated during the plant tests was sufficiently precise for the purpose of boiler-water control.

HYDROXIDE. Values for hydroxide were calculated for the fourteen sets of samples in three ways: (1) from the phenolphthalein-methyl orange titrations; (2) from the barium chloride titrations; and (3) from the pH of the original sample using the conveniently tabulated values of McKinney (30) for the activity of hydroxyl ion at different pH values. The activity coefficients necessary to convert the activities into concentrations were estimated as 0.89 for the samples through number 9 and as 0.85 for the subsequent samples.⁸

The values for hydroxide obtained by the three methods of calculation are shown in Figure 6. It is seen that the two titration methods agree fairly well, the barium chloride method yielding values consistently somewhat lower

than those indicated by the titration with phenolphthalein and methyl orange. The hydroxide concentrations calculated from pH measurements fall still lower, with considerable deviation in the case of a few samples. Since the three concentration levels on the curve for this method in Figure 6 represent pH values of 11.8, 11.9, and 12.0, respectively, it is obvious that a slight uncertainty or error of judgment in placing the pH of samples 10, 13, and 14 at 11.9 instead of 12.0 might have been responsible for the larger deviations in the case of these samples. An error of 0.1 in the estimation of pH by comparison with colorimetric standards at intervals of 0.2 is quite possible.

Although the method of calculating hydroxide concentrations from pH proposed by McKinney for boiler-water control is theoretically sound, its rigorous application necessitates a complete analysis of the water and a determination of pH by some more accurate means than is afforded by ordinary colorimetric methods. If, as in the case of the present tests, the composition of the water is estimated from incomplete data and pH is determined colorimetrically, the values may vary in rather large jumps which will increase in size as the hydroxide concentration, and hence the pH increase. On the other hand, it was shown in the second part of this paper that both the phenolphthalein-methyl orange and the barium chloride titrations yielded satisfactory results for hydroxide with solutions of known composition. The general agreement between the two methods during the plant tests would indicate that either might be used for control purposes

⁸ Although a complete analysis of the boiler water was not made during the present tests, it was possible to estimate ΣCr^2 rather closely from the determined values for carbonate, hydroxide, and sulfate by assuming concentrations of sodium, chlorine, calcium, and magnesium in line with those shown in previous complete analyses of the water. Since the feed-water is quite constant in composition, the error in determining ΣCr^2 in this manner is probably less than that in the colorimetric determination of pH or the application of the Debye-Hückel equation to the calculation of the activity coefficient.

with boiler waters in which the alkalinity is due only to hydroxide and carbonate. Where phosphate or aluminate are also present, interpretation of the ordinary titrations becomes difficult if not impossible.

SULFATE. Concentrations of sulfate were determined on all fourteen sets of samples by three methods: (1) the Hagan gage (12) ordinarily used for control of the sulfate-carbonate ratio in boiler waters; (2) the old-style Parr sulfur-photometer; and (3) the benzidine titration method. In addition, sulfate was determined gravimetrically as barium sulfate on samples 10 to 14, inclusive. The results are presented in Figure 6.

The sulfate values indicated by the Hagan gage are obviously high throughout the tests relative to those obtained by the use of the sulfur-photometer and the benzidine titration. Although the last two methods are generally in fair agreement, the concentrations which they yielded were high relative to the gravimetric determinations run on samples 10 to 14.

The gravimetric method has usually been considered the most accurate means of determining sulfate concentrations. In the present case there is no reason to doubt the accuracy of the values obtained by this method, so that the burden of error must be shared to varying degrees by the other three methods. The Hagan gage is, of course, intended only for approximate estimate, although the general trend of the lines for sulfate in Figure 6 indicates that it might have given fairly consistent results if accurate calibration had been possible on the boiler water itself. The instrument was found to give correct results with sodium sulfate solutions, but the presence of other substances in the boiler water evidently affected the character of the barium sulfate suspension.

The lack of agreement between the values indicated by the Parr sulfur-photometer and the gravimetric determinations is surprising, as in previous work with an experimental boiler the turbidimetric method had generally checked very creditably the values obtained by precipitation as barium sulfate. The discrepancies in the plant results may have been due to the fact that the photometer was used in a lighted room, whereas in the laboratory it had been calibrated and used in the dark. It is also probable that an error was introduced by a different degree of dispersion of the barium sulfate precipitate in the boiler-water sample from that obtained in the pure

sodium sulfate solution used for calibration. In the tests the voltage across the lamp bulb of the photometer was maintained constant at the value previously used in the laboratory, so that no error due to variation in the intensity of the light source should have been experienced.

Better agreement with the gravimetric method than that obtained might also have been expected of the benzidine titration. The procedure followed was that outlined by Treadwell and Hall (46), except that the solution was titrated cold instead of hot. Ten minutes were allowed for precipitation and the precipitate was washed twice with 20-cc. portions of distilled water. The error was possibly due to the fact that the distilled water available in the plant contained a relatively large amount of carbon dioxide.

The actual results obtained would not justify the recommendation of any one of the rapid methods for sulfate. It is believed, however, that both the turbidimetric method and the benzidine titration may be made sufficiently exact for accurate control of boiler waters. The value of checking routine control methods against the gravimetric method is emphasized by the diverse results obtained in the present tests.

CONCENTRATIONS IN STEAM AND MUD DRUMS

The question of variation in the concentration of the water in different parts of the same boiler is frequently discussed. Throughout the present tests, during which the boiler operated at normal rating, the concentrations of simultaneous samples from the steam drum and mud drum were practically the same, as is indicated in Figure 7. In this figure the carbonate concentrations as determined by the absorption method, and the hydroxide concentrations as determined by the titration with phenolphthalein and methyl orange, are plotted for the fourteen sets of samples from the two drums. A similar plot of sulfate concentrations was not made because determinations by the accurate gravimetric method were available for but five sets of samples. The general agreement between values for the two drums by either the sulfur-photometer or the benzidine titration was, however, very good. Although some difference in concentration between the steam drums and the mud drums of a boiler may exist at high ratings because of rapid vaporization coupled with imperfect circulation, the

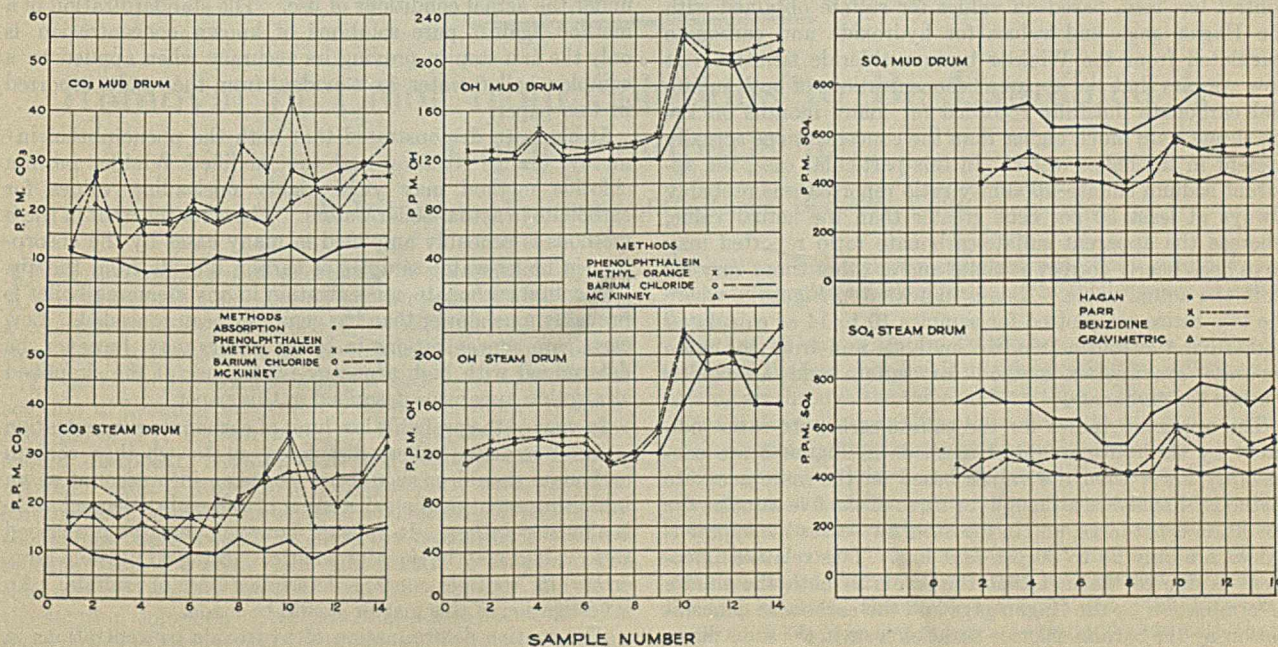


FIGURE 6. CONCENTRATIONS OF CARBONATE, HYDROXIDE, AND SULFATE IN BOILER WATER AS DETERMINED BY VARIOUS METHODS

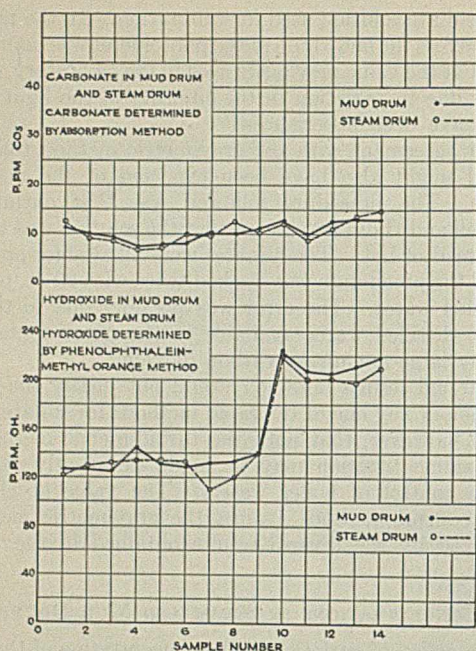


FIGURE 7. COMPARISON OF VALUES FOR CARBONATE AND HYDROXIDE IN SIMULTANEOUS SAMPLES FROM MUD DRUM AND STEAM DRUM

writers believe that such differences are smaller than they are usually conceived to be.

BOILER-CONTROL RATIOS

The rather wide variation in the results for carbonate and sulfate obtained by different analytical methods during the plant tests is significant, since it indicates that the maintenance of certain definite limits for the sulfate-carbonate ratio for scale prevention or the sodium sulfate-alkalinity ratio for inhibition of "caustic embrittlement" must have given a fictitious air of exact control in many cases where the true values were unknown and differed widely from the apparent ones. For example, at the Congress Street plant, the routine control has been based on values for sulfate obtained with the Hagan gage and values for hydroxide and carbonate calculated from the Winkler barium chloride titration. It now appears that the apparent concentrations of both sulfate and carbonate dutifully recorded for many months on the log sheets were much higher than the concentrations actually present in the boiler water. In this particular case, the apparent sodium sulfate-alkalinity ratio reported was probably always at least 50 per cent greater than the actual value, whereas the apparent sulfate-carbonate ratio reported may have been nearly correct at times and at other times very far from the actual value. This is indicated in Figure 8, where the two ratios are plotted for samples 10 to 14 as calculated both from the routine control methods and from the more accurate gravimetric method for sulfate and absorption method for carbonate.

The apparent values for the sulfate-carbonate ratio indicated by the routine control methods in Figure 8 are consistently lower than the values based on the more accurate methods of analysis, although for three of the five samples the deviation is not large, and in the other two cases the apparent values are only 25 to 30 per cent low. This relative agreement is due to the fact that the errors in both the sulfate determination by the Hagan gage and the carbonate determination by the barium chloride titration were in the same direction.

In the case of the sodium sulfate-alkalinity ratio, a large consistent error in the apparent value resulted from the high values for sulfate obtained by the routine control method. The actual values of this ratio as determined by the more accurate methods of analysis run consistently slightly under a value of 1, whereas the apparent values range from 50 to 90 per cent higher. Such a deviation might under some conditions represent the difference between safety and danger.

The inaccuracies in control methods at the Congress Street plant which were discovered as a result of the tests just reported are probably present in many other plants which pride themselves upon the exact chemical control maintained on their boiler-water conditions. The function of this paper will have been fulfilled if it stimulates other critical investigations leading to the general adoption of more accurate control methods.

CONCLUSIONS

Although the writers have no wish to discredit with one sweeping statement all of the boiler-water control analyses painstakingly recorded in hundreds of notebooks, it seems evident that any data of this type should not be accepted too seriously until the accuracy of the methods employed has been established under the actual conditions of use. The standardization of a method against pure solutions of known concentration is only the first step in proving its accuracy when applied to a complex boiler water, as is evident from the results reported in this paper.

It has been demonstrated that both the phenolphthalein-methyl orange titration and the modified Winkler barium chloride method may yield highly misleading values for carbonate in actual boiler waters. The error inherent in these methods is probably amplified in many cases by the absorption in boiler-water samples of carbon dioxide from the air. The actual carbonate concentration in any steaming boiler is probably much lower than has generally been conceded. Low carbonate concentrations in boiler waters may, however, be determined with high accuracy by the use of the simplified absorption apparatus described in this paper.

In view of the probable low limit of carbonate concentration in an operating boiler, discussion as to whether sodium carbonate should or should not be taken into account as an inhibiting agent in the calculation of the embrittlement ratio is almost pointless. It appears, however, that the prescribed ratio values may be equally pointless, owing to possible large errors in routine control determinations of sulfate. An investigation of this matter should be made.

The routine determination of hydroxide concentrations in boiler waters is probably subject to less error than the deter-

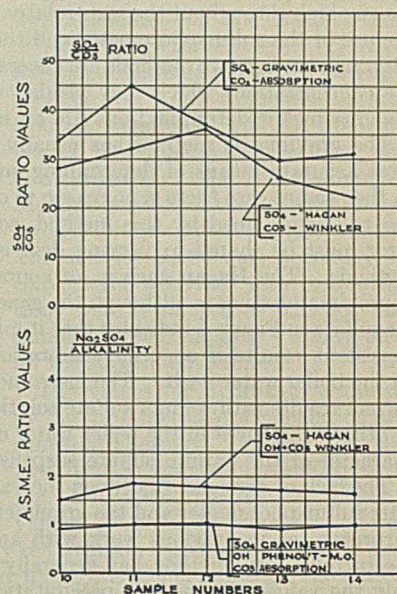


FIGURE 8. COMPARISON OF VALUES OBTAINED BY VARIOUS METHODS FOR SULFATE-CARBONATE SCALE-PREVENTION RATIO AND FOR SODIUM SULFATE-ALKALINITY RATIO FOR INHIBITION OF EMBRITTEMENT

minations of either carbonate or sulfate since, when limited to its purpose of measuring the hydroxide concentration, the original Winkler barium chloride method yields satisfactory results. The value for hydroxide indicated by the phenolphthalein-methyl orange titration should also generally not be far in error unless unusual amounts of phosphate, aluminate, silicate, or similar ions of slightly dissociated acids are present.

ACKNOWLEDGMENT

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Removal of Color from Solutions to Be Examined by Color Comparisons

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FOR determination of phosphate in soil extracts by the molybdenum blue method and for some other purposes a colorless solution is desired. The color may be removed from most such solutions by the following simple procedure.

To 50 cc. of the colored solution add 5 cc. of saturated solution of bromine water and 5 drops, or enough to make alkaline, of 5 N sodium hydroxide. Mix, the brown color should disappear, showing that the solution has become alkaline. Add 5 drops of 5 N hydrochloric acid, or other suitable acid, to make the solution acid again. Free bromine should now be apparent; if not, the treatment should be repeated from the first. Now add a little (5 cc. of a 5 per cent solution) sodium sulfite to reduce the bromine and leave the solution colorless. The bleaching action seems to take place mostly at the moment the bromine is liberated by adding acid to the sodium hypobromite first formed. In the alkaline

state, the color is slowly removed but, when acidified, the solution becomes colorless instantly in the presence of sulfur dioxide.

If there is any objection to the use of sodium sulfite for removing the free bromine, it may be expelled by boiling or by passing air through the solution for a time. Excess of sodium sulfite is not objectionable in the solution in which phosphate is to be estimated by the molybdenum blue method.

The procedure described removes the color from soil extracts, plant extracts, dye solutions, indicator solutions, etc. If the solution is strongly colored, it may be necessary to use more than 5 cc. of bromine water. Of course, the bromine water and the sodium hydroxide may be combined and used as a single solution, although it appears that the bleaching power of the sodium hypobromite is gradually lost with time.

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Rapid Determination of Zinc and Other Impurities in Cadmium

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THE usual methods for the determination of impurities in cadmium depend upon the preliminary separation of the cadmium as sulfide and the subsequent estimation of the other elements sought. This procedure is not entirely satisfactory when the metal is relatively pure. Since the pH ranges through which cadmium, lead, and zinc may be precipitated as sulfides are quite close together, it is difficult to separate them when the cadmium is preponderant. It is then necessary to pass large samples through a laborious series of filtrations and evaporations in order to separate the impurities. Consequently, the analysis is tedious and expensive. In view of this, a rapid, routine method of analysis would be very acceptable.

Numerous methods have been published for the determination, with a minimum of separations, of impurities in most of the common metals. Some of these methods, it was believed, could be adapted to the estimation of lead, copper, zinc, iron, arsenic, and sulfur in cadmium metal. These procedures were studied to determine what modifications, if any, were necessary in order to secure concordant results in the presence of large amounts of cadmium.

Well-known methods for lead, copper, iron, arsenic, and sulfur were found to be easily applied to this determination. The estimation of zinc, however, offered more difficulties.

A survey of the literature dealing with the detection and estimation of small quantities of zinc disclosed that a number of precipitation methods have been proposed. Unfortunately cadmium seemed to interfere seriously in all such procedures. A preliminary examination indicated that the qualitative method proposed by Montequi (12) would probably be more adaptable to the determination of zinc in cadmium than any other method.

Behrens and Burgeois (6) state that the reaction of the salts of copper with mercuric ammonium thiocyanate is greatly modified in the presence of zinc salts. If the copper is present in considerable excess, irregular granules of a blackish color are produced. However, when the zinc salts predominate, the precipitate formed is crystalline and of the characteristic zinc form, but has a chocolate color. This reaction was examined by Montequi (12) who concluded that, when the mercuric ammonium thiocyanate is added to a mixture of copper and zinc salts, the latter in excess, the zinc salt has the property of forming mixed crystals with a black mercuric cupric thiocyanate. To this body is due the intense violet color of the precipitate. The composition of the crystals was found to correspond to the formula, $\text{CuZn}[\text{Hg}(\text{SCN})_4]_2$. These mixed crystals were found to be isomorphic with $\text{ZnHg}(\text{SCN})_4$. Cadmium likewise forms a violet precipitate under the same conditions, but not quite as readily as zinc.

Montequi proposed a qualitative method for the detection of as small quantities of zinc as 0.00005 gram in 2 or 3 ml. of solution. It consists essentially in the addition, to a neutral solution, of a very small amount of copper, followed by mercuric ammonium thiocyanate. After thorough mixing, an intensely violet precipitate indicates zinc. Hammond (9) adapted this method to the estimation of small quantities of zinc in storage battery electrolyte.

DEVELOPMENT OF METHOD

The most serious difficulties in the adaptation of this reaction to the estimation of zinc in cadmium rested in the precipitation of the cadmium itself and in the tendency of the cadmium solution to prevent the precipitation of the zinc compound.

The effect of concentration on the reaction was determined by treating a series of cadmium solutions with the reagents recommended by Montequi. The results showed that cadmium precipitates readily from dilute solutions (1 per cent) but more slowly as the concentration increases. At a concentration of 0.85 gram of cadmium chloride per ml., the precipitate formed is slight, even after standing overnight. The results when using other salts were not so satisfactory as with the chlorides. Free mineral acids were found to be the cause of very erratic behavior, but the addition of sodium acetate neutralizes the free acid so that reproducible results may be obtained.

To a series of solutions containing 0.5 gram of cadmium per ml. were added increasing amounts of zinc, followed by the precipitation reagents. It was found that the precipitates produced in the cadmium solutions were distinctly less in amount than in pure water solutions of equal zinc concentration. According to the statement of Behrens (5) which Montequi questions, the presence of cadmium salts interferes somewhat with the precipitation of the zinc salt. It is evident that the view of Behrens is correct, but this interference is not sufficient to prevent the formation of the zinc precipitate entirely, although it does reduce the sensitivity of the reaction from 0.00005 gram in 2 or 3 ml. to 0.0001 gram in 5 ml.

In order to use this reaction as a measure of the amount of zinc present in cadmium, it was necessary to show that regularly increasing amounts of zinc produced corresponding changes in the appearance of the precipitate formed. This was done by using zinc-free cadmium chloride, adding known amounts of zinc, and then treating with the precipitation reagents. The results were gratifying, as 5 ml. of solution containing 2.5 grams of cadmium as cadmium chloride and no zinc gave a slight, pale flesh-colored precipitate after standing 15 minutes. Other 5-ml. portions containing increasing quantities of zinc in increments of 0.0002 gram of zinc produced precipitates whose color and abundance increased regularly with the zinc concentration. Smaller increments of zinc had the same effect, but the change from one increment to the next was too small to be of value as a quantitative measure. The precipitates were allowed to stand overnight, when it was found that the intensity of color had increased noticeably. The differences in appearance were much more distinct than after the first 30 minutes. No further changes were apparent after standing 3 days.

At this point it should be noted that, under the conditions outlined below, the intensity of color increases regularly with the zinc concentration. When the reaction is carried out in dilute solutions, the color is most intense when the zinc concentration is smallest (12) although the abundance of the precipitate varies directly with the amount of zinc present.

The question of interference of other probable impurities in cadmium metal was then taken up. Copper was found to

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increase the intensity of color of the precipitate, but to have no appreciable effect upon the amount of precipitate. If, however, there is more copper present than zinc, a green precipitate, $\text{CuHg}(\text{SCN})_4$ (12), is formed in addition to the usual violet. Iron in small quantities gives a reddish color to the solution and changes the color of the precipitate slightly by occlusion. Lead, manganese, aluminum, and chromium do not interfere.

SCHEME OF ANALYSIS

ZINC

REAGENTS. Blank solution, 97.46 grams of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ dissolved in sufficient water to make 100 ml.

Copper sulfate, 0.2 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1 drop of sulfuric acid dissolved in 100 ml. of water.

Mercuric ammonium thiocyanate. Grind 8.0 grams of mercuric chloride and 9.0 grams of ammonium thiocyanate in a mortar with a small amount of water. Add water to make 100 ml., and then filter.

Zinc standard, 2.1 grams of zinc chloride dissolved in 100 ml. of water.

Sodium acetate, saturated solution in water.

METHOD. Place 12.5 grams of the finely divided sample in a 150-ml. beaker, on a piece of platinum foil. Cover with a watch glass and add 25 ml. of concentrated hydrochloric acid. Warm until nearly all the cadmium is in solution, adding more acid as necessary. Decant the solution, wash the residue, foil, and cover with a minimum of water. Discard the residue. Evaporate the solution to dryness and bake until the odor of hydrochloric acid is gone. Add 15 ml. of water, agitate, and warm until solution is complete. Cool, transfer to a 25-ml. flask, and fill to the mark.

Transfer 5.0 ml. of this solution to a small, narrow beaker or test tube. Add 1 drop of sodium acetate solution to neutralize the remaining acid. Mix thoroughly, then add 1 drop of copper sulfate solution, mix again, and finally add 0.5 ml. of mercuric ammonium thiocyanate solution. Mix thoroughly and allow to stand at least 30 minutes.

Prepare a series of standards by adding zinc solution in increments of 0.02 ml. of zinc standard to 5.0-ml. portions of the blank solution. Add 1 drop of sodium acetate solution and proceed exactly as with the sample. Match the precipitate formed in the unknown with the standards, both as to color and abundance. The precipitate settles quickly and may be gathered into the center of the beaker by swirling the liquid with a rotary motion of the arm.

Iron and copper would interfere if present, but the method of solution eliminates the copper and most of the iron. The small amount of iron that goes into solution does not influence the precipitation appreciably. Lead, manganese, aluminum, and chromium do not interfere. Free mineral acids should be absent.

The method is effective between 0.0001 and 0.003 gram of zinc in 5 ml. of solution. It is essential that the reagents be as concentrated as practicable so that their addition will not cause excessive dilution. The use of a more concentrated copper solution causes the precipitate to form more quickly, but the differences in the standard series are less distinct.

LEAD

Lead is determined by the A. S. T. M. electrolysis method (2). Dissolve 20 grams of the metal in 40 ml. of concentrated nitric acid. Boil to remove oxides of nitrogen. Dilute to 125 ml., and electrolyze with a current of 5 amperes for 45 minutes. Lead will deposit on the anode as lead oxide. Wash lightly, dip in alcohol, dry, and weigh.

$$\text{PbO}_2 \times 0.864 = \text{Pb}$$

Cadmium, iron, copper, etc., do not interfere.

COPPER

This method is based upon the xanthate method as described by Scott (14).

REAGENTS. Potassium ethyl xanthate, 0.1 per cent in water, freshly prepared.

Copper standard, 0.039 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 100 ml. of water.

Sulfuric acid, 5 per cent.

METHOD. Prepare a stock solution for the determination of copper and iron. Dissolve 5 grams of sample in 20 ml. of concentrated nitric acid. When solution is complete, add 20 ml. of sulfuric acid (1 to 1) and heat carefully until copious fumes of sulfur trioxide are evolved. Cool, add 35 ml. of water, and agitate until solution is complete, warming if necessary. Cool, transfer to a 50-ml. flask, and add water to make 50 ml.

Transfer 25 ml. of the stock solution to a 150-ml. beaker, add 40 ml. of water and 10 ml. of xanthate reagent. Mix thoroughly. Prepare a standard by adding 10 ml. of the reagent to 65 ml. of 5 per cent sulfuric acid. Then add copper standard in 1-ml. portions until the brown tints match.

Nitrates interfere with the development of the color. Other probable metals do not interfere.

IRON

Iron is determined by the method of Lyons (11).

REAGENTS. Thioglycollic acid.

Standard iron solution, 0.007 gram of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ dissolved in 100 ml. of water.

METHOD. Place 1 ml. of the stock solution prepared for copper in a small beaker or comparison tube. This represents a 0.1-gram sample. Add 10 ml. of water and 5 ml. of concentrated ammonium hydroxide. Mix, and then add 0.5 ml. of thioglycollic acid and mix thoroughly. A red or purple color shows iron. Compare this color with that produced by the standard iron solution in varying amounts in the same total volume.

Cadmium interferes unless a decided excess of ammonia is present. Oxidizing agents also interfere.

ARSENIC

Details of the construction and manipulation of the Gutzeit apparatus may be obtained from Scott (13).

REAGENTS. Mercuric chloride strips, small (12).

Hydrochloric acid, arsenic-free (1 to 1).

METHOD. Place a 10-gram sample on a piece of platinum foil in the bottom of the apparatus. Add 50 ml. of hydrochloric acid (1 to 1, arsenic-free) and close the apparatus. Omit the usual addition of zinc, since it interferes with the solution of the cadmium. Warm on a hot plate until action ceases. Do not boil. Compare the resulting stain on the mercuric chloride strip with the standard stains.

None of the probable impurities interferes.

SULFUR

An evolution method, substantially the same as that recommended by Scott (15), is used.

REAGENTS. Iodine solution, 0.02 N.

Cadmium chloride solution, 20 grams of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in water. Add ammonium hydroxide until the precipitate redissolves. Acidify with acetic acid, and add 20 ml. excess. Make up to 1000 ml. with water.

METHOD. Place 5 grams of the finely divided sample in the evolution flask on a piece of platinum foil. Then assemble the apparatus with the gas outlet in an absorption flask containing cadmium chloride solution. Add 50 ml. of hot water

to the evolution flask, followed by 50 ml. of concentrated hydrochloric acid. Warm gently until solution is complete, and then introduce carbon dioxide into the evolution flask, either as carbonate solution or as gas, to flush out the apparatus. Acidify the contents of the absorption flask with hydrochloric acid and titrate with iodine solution in the usual manner.

None of the usual impurities interferes.

ACCURACY OF RESULTS

The results on four samples by the above procedure were compared with those obtained by the following methods:

Copper was deposited from a 50-gram sample in nitric acid solution by electrolysis. The copper was redissolved and redeposited (?).

Iron, A. S. T. M. method B-38-21 using 25-gram sample (4).

Lead, A. S. T. M. method B-38-21 using 50-gram sample (3).

Arsenic. The Gutzeit method for arsenic in small amounts is considered standard. Hence the accuracy of this use of the method was not investigated.

Sulfur was determined by the oxidation method of the A. S. T. M. (1), except that the nitric acid used for dissolving the metal was saturated with bromine. Twenty grams of sample were used.

Zinc. The method of the Committee on Analytical Reagents of the AMERICAN CHEMICAL SOCIETY (8) was altered to accommodate larger samples as follows: A 25-gram sample was dissolved in hydrochloric acid with the aid of a platinum catalyst. The solution was evaporated to dryness and the excess acid driven off. The residue was then dissolved in hot water, and sulfuric acid was added at the rate of 3.5 ml. per 100 ml. of solution. Hydrogen sulfide was then passed into the solution until no further precipitation took place. The cadmium sulfide was filtered off, the filtrate was evaporated to dryness, and the excess acid again driven off. This process was repeated until no further precipitate was obtained in the solution containing 3.5 ml. of sulfuric acid per 100 ml. of solution.

The cadmium sulfide was reprecipitated to remove occluded zinc. The final solutions were combined and evaporated until nearly all the excess sulfuric acid had been driven off. The residue was dissolved in water, neutralized with sodium

hydroxide, and then acidified with 0.1 *N* sulfuric acid. The zinc was then removed as zinc sulfide, dissolved in hydrochloric acid, and precipitated with sodium acid phosphate. This precipitate was ignited and weighed as $Zn_3P_2O_7$ (10).

The following table gives a comparison of the results obtained:

SAMPLE	METHOD	ARSENIC	SULFUR	COPPER	IRON	LEAD	ZINC
		%	%	%	%	%	%
1	A ^a	0.0001+	None	0.010	0.012	0.001	0.004
	B ^b ^c	None	0.013	0.009	None	None
2	A	0.001	None	0.004	0.004	0.006	0.028
	B	None	0.011	0.007	0.002	0.025
3	A	0.0001	0.014	0.004	0.008	0.055	0.016
	B	0.006	0.003	0.007	0.059	0.019
4	A	0.0001	0.010	0.032	0.020	0.028	0.008
	B	0.004	0.036	0.016	0.030	0.010

^a Proposed method.

^b Other method as outlined.

^c Arsenic determined by Gutzeit method only.

It will be noted that the proposed procedure requires no filtrations and but one separation in the entire scheme of analysis. This is in marked contrast to the many filtrations necessary when other methods are used.

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Determination of Relative Humidities by Means of Thermocouples

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FOR certain types of work it is necessary to have a definite relative humidity in a small space such as a desiccator. Mixtures of sulfuric acid and water are usually relied upon as a means of control, but if the substance under test is constantly giving off unknown quantities of moisture, then the actual relative humidity is always somewhat in doubt. For a particular piece of work this difficulty was encountered, so it was necessary to devise a means for roughly checking the relative humidity. Wet- and dry-bulb thermometers were impractical, since the amount of moisture evaporated from the wet bulb would be sufficient to change the equilibrium between the acid solution and the air.

It was found that relative-humidity determinations can be made by means of two small thermocouples, one of which has a small drop of water surrounding it. Because of the evapora-

tion of water from this drop, a difference in temperature is produced which causes the couples to exhibit a definite potential difference, which may be measured by a sensitive instrument such as a Leeds and Northrup type K potentiometer in combination with a sensitive galvanometer. This voltage difference, when calculated to degress Fahrenheit, is not the same as the temperature difference shown by wet- and dry-bulb thermometers, but is always lower. This is probably due to the difference in transfer of heat of metals and glass, and could possibly be further minimized by the use of smaller couples than those which will be described. However, it was found that the relation between the two was practically a straight-line function, so it was a fairly simple matter to construct the curve illustrated in Figure 1 showing the relationship between millivolt differences and wet- and

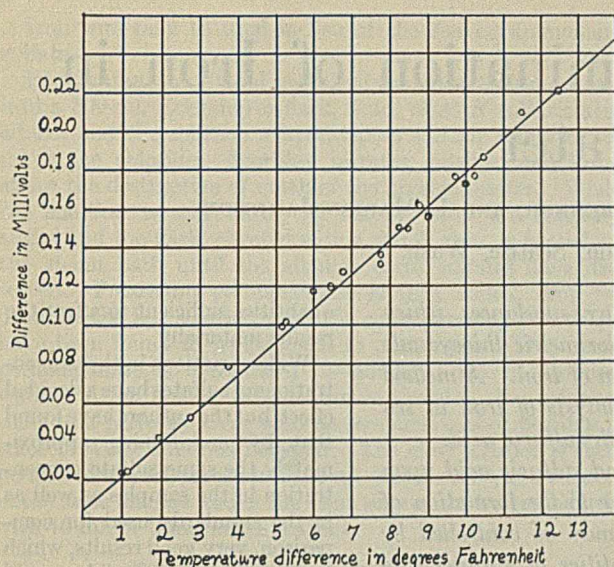


FIGURE 1. MILLIVOLT DIFFERENCES VS. WET- AND DRY-BULB TEMPERATURE DIFFERENCES

dry-bulb temperature differences at definite relative humidities.

The thermocouples are made by fusing a copper wire about 60 cm. in length to each end of a 15-cm. piece of constantan wire. These wires should be 0.02546 cm. in diameter (No. 30 B. & S. gage). This fusion is readily accomplished by holding the two wires in the flame of a Bunsen burner until the ends begin to melt, when they are brought together and fused into a small bead. The copper wires may then be covered with an insulating material and used as electrical leads.

At one of the thermocouples four small loops are made by winding the wire four times around a nail with two turns on each side of the point of fusion. When the nail is withdrawn, a small coil will remain which should be 2 or 3 mm. in diameter and which serves to hold a drop of water which will remain suspended owing to its surface tension.

TABLE I. CONVERSION OF RELATIVE HUMIDITIES TO EQUIVALENTS OF WET- AND DRY-BULB TEMPERATURE DIFFERENCES

DIFFERENCE Millivolts	RELATIVE HUMIDITY OBTAINED WITH EQUIV. IN WET- AND ACID SOLNS.		ROOM TEMP. ° F.
	RELATIVE HUMIDITY OBTAINED WITH EQUIV. IN WET- AND ACID SOLNS.	RELATIVE HUMIDITY OBTAINED WITH EQUIV. IN WET- AND DRY-BULB DIFF.	
0.023	96	1.0	75
0.024	94	1.2	67
0.041	91	2.0	75
0.052	86	2.8	65
0.078	83	3.8	73
0.101	77	5.3	76
0.089	76	5.2	70
0.117	74	6.0	74
0.127	70	6.8	72
0.119	69	6.5	67
0.131	65	7.8	70
0.150	64	8.3	72
0.155	61	9.0	72
0.149	61	8.5	69
0.136	61	7.8	64
0.161	60	8.8	69
0.176	59	9.8	74
0.176	58	10.3	76
0.172	57	10.0	72
0.186	56	10.5	74
0.209	51	11.5	73
0.220	48	12.5	73

The drop may be supplied automatically by suspending a small glass tube of water above the coil in such a manner that the water will feed into it as required. This tube must be drawn to a capillary at one end and partially sealed at the other. It is suspended so that the capillary end is immersed in the drop and is set at such an angle that some of the water

flows out. Equilibrium is soon reached and water flows from the capillary end in the amount necessary to replenish the drop.

In order to obtain the value of the voltage readings in terms of relative humidity, the following procedure was used: The thermocouples were placed in a large desiccator with a side opening and the leads brought out through this opening. A one-hole rubber stopper was inserted to separate them, and a piece of glass tubing was run through the hole to serve as a bearing for the shaft of a small fan which served to keep the air circulating around the wet couple. The fan shaft was given a thick coating of vaseline which served as a lubricant and also to make the apparatus more nearly air-tight. A cork was used as a pulley and a small electric motor furnished the driving power. The essential apparatus is illustrated in Figure 2.

The humidity within the desiccator was controlled by means of solutions of sulfuric acid and water. Approximate amounts of acid were added to the water and the specific gravity taken. From this the exact percentage of acid in the mixture and the humidity produced was ascertained by reference to tables (2). Both the solution and the air under observation were kept at as nearly the same temperature as possible.

The feed tube was filled with water and mounted so that it would feed the drop which was suspended in the coiled couple. The lid was then replaced and the fan started. The apparatus was allowed to remain undisturbed for a period of at least 30 minutes, when the voltage differences developed by the couples were determined with the type K potentiometer. After another 5 or 10 minutes, another reading was taken to make certain that

equilibrium had been reached. This procedure was carried out for a number of different values of relative humidity and the results are given in Table I. The temperatures at which the determinations were made were observed with a mercury thermometer.

The relative humidities indicated by the acid mixtures were converted to their equivalents of wet- and dry-bulb temperature differences from Table VI of Marvin's Psychrometric Tables (1), and these results are also shown in Table I. The wet- and dry-bulb temperature differences were plotted against the differences in millivolts obtained between the thermocouples, and are graphically shown in Figure 1. A working curve is thus obtained from which millivolt differences can be converted to wet- and dry-bulb temperature differences. These temperature differences can then be directly converted into relative humidity figures from psychrometric tables.

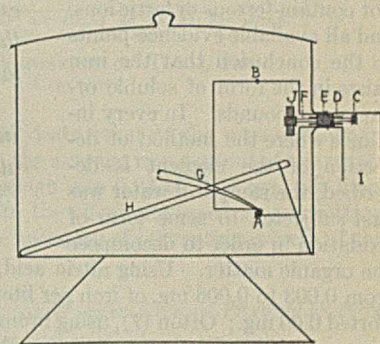


FIGURE 2. APPARATUS FOR VOLTAGE READINGS

- A. Wet thermocouple
- B. Dry thermocouple
- C. Pulley
- D. Bearing
- E. Rubber stopper
- F. Fan shaft
- G. Water-supply tube
- H. Support for water-supply tube
- I. Electrical leads to potentiometer
- J. Fan

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Occurrence and Determination of Iron in Sea Water

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IRON has frequently been detected in sea water, but very few attempts have been made to determine it quantitatively (4, 5, 7, 16, 17, 18). In many of the references to the subject, neither the method of detection nor the amount of iron found is mentioned, and no systematic study seems to have been made to show the distribution of iron with depth. Sea water does not contain ferrous or ferric ions, and all available evidence points to the conclusion that the iron exists in the form of soluble organic compounds. In every instance where the method of detection of the element is described, the sample of water was first subjected to some form of oxidation in order to decompose the organic matter. Using nitric acid, Harvey (4) obtained from 0.003 to 0.006 mg. of iron per liter; Wattenberg (18) reported 0.06 mg.; Orton (7), using bromine water, obtained 0.1 mg.; and Vernadsky (17) gave a result of 1.5 mg. Recently Braarud and Klem (1) have reported results on the Norwegian fjords varying from 0.004 to 0.023 mg.

Although bromine water and nitric acid doubtless oxidize much of the organic matter, organic acids might be formed as a result of this oxidation that would retard the usual tests for iron in much the same manner as tartrates and oxalates. Furthermore, Gautier and Clausman (2) have shown that sea water contains as much as 0.3 mg. of fluorine per liter, and it is logical to conclude that the presence of fluorides would favor the formation of the stable ferrifluoride ions, and thus hinder the usual colorimetric reactions employed in the detection of minute quantities of iron.

NATURE OF THIOCYANATE REACTION

Various reagents have been recommended for the estimation of traces of iron. After preliminary studies, the authors decided upon the use of the thiocyanate reagent because of its reliability in yielding readily reproducible results. The color produced by the thiocyanate and ferric ions has been known since 1837 (8) and has been the subject of considerable study. Recently Schlesinger and Van Velkenburgh (9) have shown by means of absorption spectra of aqueous and ethereal solutions and the electrolysis of aqueous solutions that the red color is due to the complex ion $[\text{Fe}(\text{CNS})_6]^{--}$.

Different authorities have shown that organic compounds, iodic and hydrosulfuric acids, chlorides of the alkaline earths, nitrates, nitrites, fluorides, phosphates, arsenates, and sulfates, all of which occur in sea water, prevent or considerably retard the formation of the color. However, the phosphates and arsenates are present in such small quantities that they need not be considered, if the conclusions of Leeper (6) are accepted. The chlorides of the alkaline earths occur in

Sea water contains many substances which interfere with the usual colorimetric thiocyanate method for the determination of iron. A method has been devised for the analysis of iron in sea water by removing these with sulfuric acid.

The effects of sulfates and sulfuric acid upon the thiocyanate reaction due to the formation of complex ferrisulfate ions may be controlled by the use of equivalent quantities of sulfates and sulfuric acid in the standards by utilizing a large excess of the thiocyanate reagent, and by causing the reactions in the samples and standards to take place at a constant temperature.

Surface sea water shows a seasonal variation in the iron content, which is evidently diminished at times of maximum diatom growth. Iron content generally increases with depth.

quantities sufficient to affect the results materially.

Wide variations in the concentrations of sulfates have a decided effect, but the authors have found that by maintaining approximately the same sulfate concentration in the samples as well as in the standards used for comparison, very good results, which were easily reproducible, could be obtained. Thus by treating the samples with sulfuric acid and evaporating to sulfuric fumes, all the chlorides, nitrates, nitrites, fluorides, and much of the organic matter would be removed.

The interference of the sulfate ions is due to the formation of a complex ion, probably represented as $[\text{Fe}(\text{SO}_4)_2]^-$ (10).

This is not as stable as the ferrithiocyanate complex, and therefore, by applying the law of mass action, the addition of a large excess of thiocyanate reagent greatly favors the formation of the colored compound.

DETERMINATION OF IRON

REAGENTS. The sulfuric acid used must be 36 N and iron-free.

For potassium permanganate, 6.30 grams are dissolved in water to give a solution of 1 liter. The reagent should be tested to insure the absence of iron.

To obtain bromine water a bottle of distilled water is saturated with iron-free bromine. The reagent has been found to react with the iron contained in the glass of the reagent bottle. Use of bromine water that has been stored for some time should thus be avoided.

For potassium thiocyanate, 480 grams are dissolved in water to make a stock solution of 4 liters.

For sodium sulfate, 1800 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are dissolved to make approximately 4 liters. This is equivalent to a saturated solution of the salt at 20° C. To this solution 1.5 ml. of a concentrated solution of sodium hydroxide are added and, after heating and stirring thoroughly, the solution is filtered to remove any traces of iron that may have precipitated. The filtrate is then treated with a sufficient quantity of standard sulfuric acid to just neutralize the excess of alkali. Portions of this solution are used in the preparation of standards.

To make standard iron solution 0.70 gram of ferrous ammonium sulfate is dissolved in 50 ml. of water, 20 ml. of 6 N sulfuric acid are added, and permanganate reagent introduced into the hot solution until the color persists for 5 minutes. A drop of bromine water is added to decolorize the solution which, after transferring to a volumetric flask, is made up to a volume of 1 liter containing the equivalent of 0.1 mg. of iron per ml. Before using this solution it is again diluted so that 1 ml. is equivalent to 0.01 mg. of iron.

Iron wire may be used in lieu of the ferrous ammonium sulfate.

PROCEDURE. A 100-ml. sample of the sea water is measured into a 500-ml. Erlenmeyer flask, 6 ml. of 36 *N* sulfuric acid added, and the solution evaporated to sulfuric fumes to remove the chlorides, fluorides, nitrates, nitrites, and bring about the destruction of much of the organic matter. While the solution is still warm, 85 ml. of water are carefully added and the flask, covered with a watch glass, is heated on the steam bath until the alkaline earth sulfates have dissolved. Potassium permanganate is then added, drop by drop, to the hot solution until the color persists; two drops have been found to be sufficient in most cases. The excess permanganate is decolorized by adding 1 ml. of bromine water. After boiling off the excess bromine, the solution should be perfectly clear with no sediment except possibly a trace of white siliceous material. The clear solution is then permitted to cool, placed in a 100-ml. Nessler tube, and treated in the same manner and at the same time as the iron standards with 10 ml. of thiocyanate reagent.

PREPARATION OF IRON STANDARDS

The standard iron solution is measured from a microburet into a series of 500-ml. Erlenmeyer flasks, each of which contains 22 ml. of the sodium sulfate reagent, 50 ml. of water, and 5 ml. of 36 *N* sulfuric acid. Since the usual range of iron content is 0.00 to 0.20 mg. of iron per liter and 100-ml. samples are used, the standards should contain 0.00, 0.001, 0.003, 0.005, 0.007, 0.010, 0.015, and 0.020 mg. of iron. The standards are treated with permanganate solution and bromine water as described above, and finally transferred to 100-ml. Nessler tubes. Ten millimeters of thiocyanate reagent are added to each tube. It is very important that these standards be treated with the thiocyanate at the same time as the regular samples.

The color produced by the thiocyanate fades, but in the above dilutions fading is not very rapid, especially if comparisons are made in well-diffused light. About 20 samples can be run conveniently with each set of iron standards. It has been found advisable to have the equal portions of thiocyanate reagent already measured either in a series of small graduates or in test tubes, so that the time required for adding the reagent to all the samples and standards shall be as small as possible.

The quantity of sodium sulfate used in the standards has been calculated as equivalent to the major cations of a sea water of chlorinity of 18.7 per liter at 20° C. (3, 10, 11, 13, 15, 17). Such a quantity of sulfate, together with that added as sulfuric acid, exerts a very marked effect upon the color obtained, imparting a more brownish tint and decreasing the intensity considerably below that of standards without the presence of sulfates. The color is more stable at lower than at higher temperatures. It is imperative that all of the samples and standards be at the same temperature before treating with the thiocyanate reagent.

PRECAUTIONS. Well-seasoned bottles should be used for samples of sea water to eliminate the possibility of contamination due to the leaching of iron from the glass container. It is essential that fresh samples of water be used for analysis, as the growth of diatoms will remove most of the iron from solution if the samples are permitted to stand. Waters rich in plankton should be filtered immediately upon sampling. Should it be impossible to analyze the samples for some time, they should be acidified with sulfuric acid before storing.

EFFECT OF DIATOMS UPON IRON CONTENT OF SEA WATER

In the summer of 1931, samples of sea water were collected in an estuary of the San Juan Archipelago (East Sound), from

four different depths at each of three stations. The samples were exceedingly rich in diatoms and were permitted to stand in the laboratory for a period of 2 months. At the end of that time, samples of the filtered and unfiltered sea water were analyzed with the average results for the three stations as shown in Table I. Owing to the large amount of suspended material in the unfiltered samples resulting from the growth of diatoms, several modifications of the method were necessary in

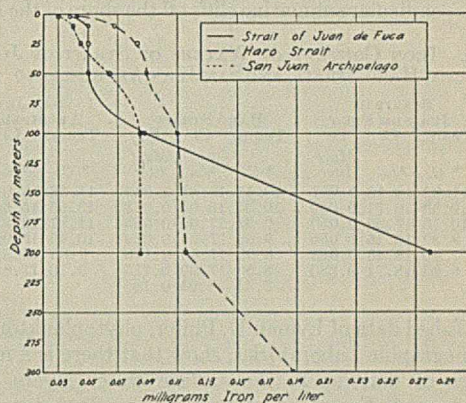


FIGURE 1. VARIATION OF TOTAL IRON CONTENT

order to insure complete destruction of the organic matter. At the time of sampling, the average iron content of the water of the San Juan Archipelago was 0.03 to 0.04 mg. per liter. The data given illustrate the effect produced by permitting samples to stand and the necessity of preventing growth of the diatoms.

TABLE I. IRON CONTENT OF WATERS RICH IN PHYTOPLANKTON (Samples stood several months before analysis)

DEPTH Meters	IRON CONTENT (Mg. Fe/liter)	
	FILTERED SAMPLES	UNFILTERED SAMPLES
1	0.00	0.04
5	0.00	0.03
10	0.00	0.05
20	0.01	0.07

IRON CONTENT OF WATERS OF SAN JUAN ARCHIPELAGO AND STRAIT OF JUAN DE FUCA

SEASONAL VARIATION. Surface samples were collected once a week for a period of 1 year beginning September, 1928, at Friday Harbor, Washington. From these weekly samples, monthly composite samples were prepared. The highest results, 0.05 mg. and 0.06 mg. of iron per liter, were obtained in March and April, but these were followed by a decrease through May to July when the lowest result, 0.032 mg. of iron per liter, was noted. A slight decrease in the iron content was likewise observed in December and February. The average for the year was 0.042 mg. of iron per liter. Because of certain imperfections in technic at the time these determinations were made, the authors believe the results to be low; it is the relative variation that is of particular interest.

The waters of Puget Sound are remarkably high in the so-called nutritive material, such as phosphates, nitrates, etc. (12, 14). This is caused by the up-welling of the deeper ocean waters, rich in nutritive salts, off the continental shelf, and also is largely due to the strong tidal-current effect in the deep, canyon-like shape of the ocean floor at the entrance to the Strait of Juan de Fuca. In the spring and summer months the waters are characterized by a rich growth of diatoms in the surface layers down to depths of approximately 25 meters.

In the summer of 1931, cruises in the San Juan Archipelago, Haro Strait, and the length of the Strait of Juan de Fuca to the Pacific were made. Table II gives a summary of the iron

content in the waters of the several stations. The chlorinities of the waters of the Strait of Juan de Fuca are greater than those of Haro Strait, and those of Haro Strait are greater than those of the San Juan Archipelago. The data represent the average of four stations in each body of water. The stations in Haro Strait were taken to the westward of San Juan Island. These stations are characterized by their greater depth and the exceedingly marked turbulence of the waters produced by the strong tidal currents striking the almost perpendicular submarine cliffs off the shore of the island.

TABLE II. IRON CONTENT OF WATERS OF STRAIT OF JUAN DE FUCA, HARO STRAIT, AND SAN JUAN ARCHIPELAGO

DEPTH	STRAIT OF JUAN DE FUCA			HARO STRAIT			SAN JUAN ARCHIPELAGO		
	Temp.	Cl	Fe	Temp.	Cl	Fe	Temp.	Cl	Fe
Meters	° C.	‰	Mg./liter	° C.	‰	Mg./liter	° C.	‰	Mg./liter
1	11.83	16.18	0.037	10.68	16.81	0.042	14.58	15.01	0.030
10	10.86	16.71	0.050	10.35	16.95	0.068	13.05	15.66	0.040
25	10.10	17.26	0.050	10.32	17.09	0.083	11.87	16.32	0.045
50	8.32	18.15	0.050	9.66	17.26	0.089	10.45	16.95	0.065
100	7.40	18.46	0.088	8.92	17.65	0.110	9.65	17.34	0.085
150-200	6.93	18.71	0.280	8.53	17.99	0.115	9.10	17.66	0.085
300				8.35	18.04	0.188			

Unpublished data of Lyman D. Phifer, phytoplanktonist for the Oceanographic Laboratories, show that there is a marked abundance of diatoms in the surface water layers of the Strait of Juan de Fuca to depths just below 25 meters. The plankton are distributed throughout the water mass in larger quantities in Haro Strait and the tidal channels of the Archipelago, and exist in still greater abundance in the estuaries of the latter.

The data in Table II indicate that the iron is actually removed from the water by microscopic plants and that iron may be an essential element for their growth. This is further substantiated by the data in Table I, which show that the iron was completely absorbed by the growth of the diatoms contained in the samples taken in East Sound.

Figure 1 shows the distribution of iron in the waters of the Strait of Juan de Fuca, Haro Strait, and the San Juan Archipelago. The bottom waters of the Strait of Juan de Fuca have a relatively greater iron content than the waters from other depths and areas. The graph illustrates the partial mixing of these waters with those of the surface layers as they reach the deeper and more turbulent condition of Haro Strait. A similar presentation of either temperature or chlorinity data would show the same result.

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Determination of Alkalinity in Boiler Waters

A Comparison of Methods

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MCKINNEY (5) questions the accuracy of the standard methods which have been used in the analysis of boiler waters and suggests a new method of calculating the distribution of the ions which he terms the "equilibrium method." In order to compare the results obtained when using the standard methods of analysis and his method, he prepared synthetic solutions and analyzed them using the A. P. H. A. and Winkler methods of analysis. In Table V, page 196 (5), he gives the results of these data and calculations, results which would indicate, especially from sample 1, that the old standard methods are open to an exceptionally large error. Since the original data are not given, one must assume that 0.02 *N* acid was used, and 100 cc. of the sample was used for titration. Based on these assumptions, the amount of acid necessary to titrate the synthetic solution, allowing for the slight increase in carbon dioxide above that actually added as sodium carbonate, would be 44.6 cc. for the phenolphthalein end point and 50.7 for the methyl orange end point. However, to obtain the values reported these would have been 94.9 cc. for phenolphthalein and 104.4 for methyl orange end point. Such errors are

certainly not probable in the regular A. P. H. A. titration using synthetic solutions.

However, if the results reported had been miscalculated so that they were actually sodium carbonate and sodium hydroxide instead of carbonate and hydroxide as reported, a recalculation would give $\text{CO}_3 = 60.8$ p. p. m. against 69 calculated to be present; and $\text{OH} = 123$ p. p. m. against 131 calculated to be present. This agreement is within reasonable limits. If this were so, the titration figures would be phenolphthalein = 41.6 and methyl orange = 47.0 cc. of acid, which agree fairly well with the values calculated for the synthetic solutions.

The use of the pH value for calculating hydrate concentration is open to much error, for this value cannot be definitely determined within an error of ± 0.1 , and often an error of 0.5 is possible. Assume that an accuracy of 0.1 is possible. Thus, with a solution having a pH of 11.75 as calculated in (e), page 195, the value for 11.75 and activity of 0.87 would be 6.507 millimoles of hydroxide or 260 p. p. m. sodium hydroxide. If the pH determined were 11.85, the result would be $7.127/0.87 = 8.18$ millimoles of hydroxide,

TABLE I. COMPOSITION OF SYNTHETIC SOLUTIONS

Soln. no.	1	1A	1B	2	2A	2B	3	3A	3B	4	4A	4B
						<i>Millimoles per liter</i>						
NaOH	2.36	2.36	2.56	7.90	7.85	8.75	14.95	14.95	16.38	39.40	39.40	41.34
Na ₂ CO ₃	0.84	0.84	0.93	1.06	1.08	1.19	3.02	3.02	3.18	14.80	14.80	14.80
NaCl	1.00	1.00	1.00	5.00	5.00	5.00	5.00	5.00	5.00	15.00	15.00	15.00
Na ₂ SO ₄	2.46	2.46	2.46	7.00	7.00	7.00	25.60	25.60	25.60	75.30	75.30	75.30
PO ₄		0.75	0.75		1.00	1.00		3.75	3.75		3.75	3.75
SiO ₂			0.50			1.95			3.00			3.88
						<i>Parts per million</i>						
NaOH	94	94	102	316	314	352	598	598	655	1575	1575	1654
Na ₂ CO ₃	89	89	99	113	115	121	320	320	338	1568	1568	1568
NaCl	58	58	58	293	293	293	293	293	293	876	876	876
Na ₂ SO ₄	350	350	350	995	995	995	3630	3630	3630	10680	10680	10680
PO ₄		71	71		95	95		356	356		356	356
SiO ₂			30			117			181			233

or 327 p. p. m. sodium hydroxide, an error of 25.8 per cent. An error of the same order of magnitude occurs in the calculation of HCO₃⁻ in this pH range. At lower pH values the CO₃⁻ calculation is similarly affected by an error of 0.1 in the pH. This would indicate that the use of this method is certainly not to be recommended until more accurate methods of determining pH values can be placed in the hands of the plant or routine laboratory operators.

It has been known for at least the last 15 years that the alkalinity values obtained by ordinary titration methods do not give all the desirable information in regard to the solution being tested and that the additional information given by the pH value is often desirable. However, for the reasons already given, it has not been considered advisable to rely entirely on the pH value. The two methods of testing solutions give supplementary data, and neither method is absolutely independent of the other.

The A. P. H. A. and the Winkler methods of determining alkalinity have been used as standard methods for years. However, if errors as large as those reported by McKinney are probable, the methods are certainly not to be considered as standard. In order to determine the relative accuracy of the A. P. H. A., the Winkler, and the equilibrium methods, tests have been made on various solutions. These solutions were not limited, as in McKinney's work, to dilute synthetic solutions, but also included boiler waters having concentrations commonly encountered in power plants.

METHODS OF ANALYSIS TESTED

The methods of analysis tested were: (1) the alkalinity (hydrate and carbonate) determination recommended by the American Public Health Association (1) with corrections applied for phosphate when present; (2) the Winkler method for hydrate and a modification of this method for carbonate (4, 6, 7); and (3) the equilibrium method, both short and complete, recently discussed by McKinney and Hecht (3, 5). The determination of phosphate by a direct titration method was also used.

SOLUTIONS USED FOR COMPARATIVE ANALYSIS

The solutions used for the comparative analysis consisted of twelve synthetic solutions of known composition similar to boiler concentrates and eleven boiler concentrates obtained from power plants in various parts of the United States and Canada which were representative of the various types of boiler waters encountered in operating plants.

The synthetic solutions were made up by using redistilled water with low carbon dioxide content in paraffined bottles, and adding the desired reagents in definite amounts. The total carbonate was determined by evolving the carbon dioxide from a known volume of the solution, absorbing it in ascarite, and weighing. The solutions contained sodium hydroxide, sodium carbonate, sodium chloride, and sodium sulfate. After four solutions of various compositions of these salts were analyzed by the test methods, definite amounts of trisodium phosphate were added, and the solutions analyzed

again. Then definite amounts of sodium silicate were added and the solutions analyzed again. Thus results were obtained with solutions free from phosphate and silicate as well as with solutions having these salts present.

The composition of the twelve synthetic solutions in millimoles per liter and parts per million is given in Table I.

PROCEDURE IN MAKING ANALYSES

The analyses of the synthetic waters were run in duplicate by three different analysts. The solutions were titrated in Erlenmeyer flasks using approximately 0.05 *N* acid. The A. P. H. A. tests were made by titrating with phenolphthalein indicator to colorless and methyl orange indicator to the first color change. When phosphate was present, 5 cc. excess of acid were added after the methyl orange end point was reached, the solution boiled for 3 minutes, cooled, and titrated with standard sodium hydroxide, until the first appearance of a reddish color similar to the alkaline color of phenolphthalein. A blank run using distilled water and carried through all of the steps of the procedure applied to the regular samples familiarized the operator with the end point and provided the correction allowance for the excess acid added. The difference between the amount of acid used and the blank was taken as a measure of the phosphate.

The Winkler test was run by adding 5 cc., and in the more concentrated solutions 10 cc., of a standard solution of sodium hydroxide containing about 10 per cent barium chloride to the sample of boiler water in an Erlenmeyer flask. The flask was then stoppered, let stand at least 15 minutes, and then titrated with the standard acid solution until colorless with phenolphthalein indicator.

The short equilibrium method tests were run using bromocresol green and thymol blue indicators with a Hellige-Klett pH comparator modified according to McKinney and Hecht (3).

The pH value was determined by use of the hydrogen electrode. Whenever the pH value was within the range of the colorimetric pH comparator, it was also determined colorimetrically.

The solutions were analyzed for sulfate, phosphate, chloride, and silica by standard laboratory methods. These determinations were made by only one operator.

The boiler waters were run by only two operators and not in duplicate. The agreement of the results obtained by the two operators was within the experimental error in the majority of the boiler water tested. Consequently duplicate analyses were not run.

CALCULATIONS OF RESULTS

A. P. H. A. METHOD. The amount of acid used to reach the phenolphthalein end point is designated as *P*, and the total required to reach the methyl orange end point as *M*. *N* represents normality of the acid, *V* the volume of solution tested, and PO₄ the phosphate content in p. p. m.

The calculations involved in the absence of phosphate are as follows:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} (M - P) \quad (1)$$

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (2P - M) \quad (2)$$

If phosphate is present, the calculations are based on the fact that when a solution containing hydrates, carbonates, and phosphates of sodium is titrated with acid to the *P* and *M* end points, the amount of acid required between the *P* and *M* end points is equal to one-half the carbonate and one-third the phosphate (2).

The calculations for hydrate and carbonate in the presence of phosphate are as follows:

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (2P - M) \quad (2)$$

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \quad (3)$$

WINKLER METHOD. If the amount of acid necessary to titrate the solution after adding a definite volume of standard sodium hydroxide solution containing barium chloride is designated as *Pw*, and *B* represents the amount of acid needed to neutralize the standard sodium hydroxide added, then

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (Pw - B) \quad (4)$$

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \quad (5)$$

During the preparation of this material, R. W. Fisher, of Baltimore, called the attention of the author to an error in this method which explains why the carbonate determined in this manner tends to be low when phosphate is present. In the ordinary titration to the *P* end point, all of the hydroxide, one-half of the carbonate, and one-third of the phosphate are supposed to be titrated. Thus, when the hydroxide determined by the Winkler method is subtracted from this amount, the remainder should be one-half of the carbonate and one-third of the phosphate. If the phosphate is determined, the carbonate can be calculated. However, unless the pH of the solution is above 12, there is less than one-third of the phosphate titrated, since it will not be completely converted to trisodium phosphate below a pH of 12. This means that

when one-third of the phosphate is subtracted, the carbonate will be low.

SHORT EQUILIBRIUM METHOD. The sodium hydroxide is determined by the equation

$$\text{pH} = \frac{\log \text{OH p. p. m.}}{17} + 11 \quad (6)$$

$$\text{NaOH, p. p. m.} = \frac{\text{OH} \times 40}{17} \quad (7)$$

The sodium carbonate is determined by the equation:

$$\text{CO}_3, \text{ p. p. m.} = (V_2 - V_1) 12.32 - 0.813 - 0.626 \text{ PO}_4 \text{ (p. p. m.)} \quad (8)$$

when $V_2 - V_1 = \text{cc. of } 0.02 \text{ N acid necessary to titrate } 100 \text{ cc. of solution from a pH of } 8.5 \text{ to } 5.0.$

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{\text{CO}_3 \times 106}{60} \quad (9)$$

The complete equilibrium method calculations are described in detail by McKinney (5). The sodium hydroxide from the pH value is calculated from the same formula as the one used in the short method, Equations 6 and 7, except that allowance is made for the fact that the activity is not equal to 1. To determine the activity, a knowledge of the composition of the solution is essential. In these tests this calculation is made only on the synthetic solutions, since there are not sufficient data available to calculate the activity in the boiler waters.

DETERMINATION OF PHOSPHATE BY DIRECT TITRATION. The amount of alkali necessary to back titrate the A. P. H. A. test sample which has had 5 cc. excess of acid added after the *M* end is reached, is designated by *A*. *B* equals the amount of acid used to back titrate the blank, and *Nc* equals the normality of caustic solution used.

$$\text{PO}_4, \text{ p. p. m.} = \frac{95 \times 1000 \times Nc}{V} (A - B) \quad (10)$$

RESULTS OF ANALYSES

The average results of the analyses on the synthetic solutions and the boiler waters are given in Table II. Table III shows the per cent error in the sodium carbonate and sodium hydrate contents for all the solutions tested.

The per cent error in the sodium carbonate content of the synthetic solutions illustrates that the A. P. H. A. and the short equilibrium method both show good agreement with the actual content. In order to check this further, the average ($V_2 - V_1$) and ($M - P$) readings were compared. This is done

TABLE II. AVERAGE Na_2CO_3 AND NaOH BY DIFFERENT METHODS IN SYNTHETIC SOLUTIONS AND BOILER WATERS (Parts per million)

SAMPLE	BY CO_2 EVOLUTION		A. P. H. A.	WINKLER	SHORT EQUILIBRIUM	LONG EQUILIBRIUM ^a	NaOH CALCD.	A. P. H. A.	WINKLER	SHORT EQUILIBRIUM	LONG EQUILIBRIUM FROM PH VALUE
	EVOLUTION	A. P. H. A.									
1	89	84	87	87	94	89	94	97	96	89	97
1A	89	86	42	42	91	89	94	96	110	127	144
1B	99	86	61	61	96	99	102	106	115	113	127
2	113	124	116	116	116	113	316	310	309	226	282
2A	115	121	70	70	120	115	314	305	321	282	330
2B	121	126	115	115	129	121	352	348	352	400	495
3	320	323	347	347	329	320	598	594	584	425	580
3A	320	323	292	292	321	320	598	596	619	588	870
3B	338	327	382	382	349	338	655	657	648	517	715
4	1568	1542	1560	1562	1562	1568	1575	1605	1595	1128 ^b	
4A	1568	1543	1485	1485	1603	1568	1575	1581	1622	1600	
4B	1568	1505	1773	1773	1592	1568	1654	1685	1593	1600	
101	16	28	3	3	27			24	39	39	
102 ^c	8	58	41	41	29			66	73	127	
103 ^c	5	28	14	14	33			43	48	49	
104	30	44	3	3	41			343	361	350	
105	26	81	49	49	50			194	199	179	
107	24	68	0	0	68			157	185	127	
108	493	506	536	536	539			1482	1472	1665	
109	6675	6865	7165	7165	7215			1797	1695	1010	
110	648	705	786	786	732			969	939	588	
111	495	536	591	587	587			573	556	310	
112 ^c	25	40	0	0	42			15	30	0	

^a About 3 per cent of the carbonate will be as bicarbonate. However, for simplicity it is included in the sodium carbonate figure. Since the sodium carbonate is calculated from the carbon dioxide obtained by evolution, results are same as those in column 1.

^b Too high a concentration of salts to calculate activity with any degree of accuracy

^c In low carbonate-ion concentrations the error is necessarily large.

in Table IV. The difference between $(V_2 - V_1)$ and $(M - P)$ is calculated in per cent of $(V_2 - V_1)$. The maximum per cent error of any one determination from the average for $(V_2 - V_1)$ and $(M - P)$ is also shown. These results show very good agreements, and indicate that for the waters analyzed the equilibrium and A. P. H. A. methods are equally satisfactory. In the synthetic solutions the $(V_2 - V_1)$ average maximum error was 1.9 per cent, whereas that of the $(M - P)$ reading was 0.6 per cent. For the boiler waters the errors were 4.4 and 3.6, respectively, thus showing that the A. P. H. A. determination with the use of much less expensive equipment gave results as close as the method involving the use of the color comparator.

TABLE III. ERROR IN Na_2CO_3 AND NaOH CONTENT FOR SOLUTIONS TESTED

WATER	ERROR IN Na_2CO_3 CONTENT			ERROR IN NaOH CONTENT		
	A. P. H. A. %	Winkler %	Short equilibrium %	A. P. H. A. %	Winkler %	Short equilibrium %
1	-5.5	-2.5	-5.5	3.2	2.1	-5.3
1A	-3.4	-53.0	2.2	2.1	17.0	35.0
1B	-13.0	38.0	3.0	3.0	13.0	11.0
2	10.0	2.7	2.7	1.9	-2.0	-28.4
2A	6.2	-39.0	4.3	-2.9	2.2	-10.1
2B	4.1	-4.9	6.6	-1.1	0.0	+29.0
3	1.0	8.5	3.0	-0.6	-2.3	-29.0
3A	1.0	-8.7	0.3	-0.3	3.5	-1.6
3B	-2.9	13.0	2.9	+0.3	-1.1	-21.0
4	-1.7	-0.1	0.1	1.9	1.2	-28.0
4A	-1.6	-5.3	2.2	0.4	3.0	1.6
4B	-4.0	+13.0	1.5	1.9	-3.6	3.3

TABLE IV. COMPARISON OF ACCURACY OF DETERMINING $(V_2 - V_1)$ AND $(M - P)$ VALUES IN ALL WATERS

WATER	$(V_2 - V_1)$ Av.	$(M - P)$ Av.	$\frac{(V_2 - V_1) - (M - P)}{(V_2 - V_1)}$ %	$(V_2 - V_1)$	$(M - P)$
				MAX. ERROR FROM Av. %	MAX. ERROR FROM Av. %
1	1.67	1.70	-1.8	4.8	4.8
1A	3.35	3.31	1.2	4.8	0.6
1B	3.42	3.27	+4.3	3.8	10.0
2	2.35	2.52	-7.0	15.0	7.0
2A	4.37	4.52	-3.2	4.1	1.7
2B	4.63	4.65	-0.4	2.6	0.0
3	3.28	3.27	+3.0	3.6	1.8
3A	7.20	7.20	0.0	7.5	2.2
3B	7.25	7.24	0.1	0.8	0.1
4	7.83	7.77	0.8	0.5	0.2
4A	9.77	9.81	-0.4	2.3	0.1
4B	9.71	9.57	-0.2	1.9	0.6
Av.			-0.6	4.3	2.5
101	1.59	1.64	-3.1	3.8	2.4
102	0.70	1.19	-70.0	0.0	0.5
103	0.67	0.57	+15.0	3.0	0.7
104	3.23	3.43	-6.1	1.2	0.9
105	1.26	1.63	-23.0	3.2	1.2
107	2.52	2.72	-8.0	7.0	4.5
108	2.90	2.55	1.4	7.0	7.6
109	14.15	13.85	2.1	1.8	1.1
110	3.65	3.55	2.7	1.3	0.6
111	2.94	2.71	7.9	10.5	4.1
112	0.83	0.80	3.8	3.8	0.0
Av.			-7.0	3.9	2.3

In order to understand why there should be such close agreement of these two methods, it is only necessary to compare the formulas for calculating the results. The A. P. H. A. method, when corrected for phosphate, gives the following equation:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \quad (3)$$

If $N = 0.02$ and $V = 100$, then:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = 21.2 (M - P) - 0.111 \text{ PO}_4, \text{ p. p. m.} \\ \text{or CO}_2, \text{ p. p. m.} = 12.0 (M - P) - 0.63 \text{ PO}_4, \text{ p. p. m.} \quad (11)$$

Equation 8 for the carbonate by the short equilibrium method is as follows:

$$\text{CO}_2, \text{ p. p. m.} = 12.32 (V_2 - V_1) - 0.813 - 0.626 \text{ PO}_4, \text{ p. p. m.} \quad (8)$$

The results tabulated in Table IV show that the $(V_2 - V_1)$ and $(M - P)$ readings are almost identical for the synthetic solutions and show good agreement in the boiler waters. The maximum difference between these two equations should come in low concentration. Thus, if the figures obtained in water 112, $(V_2 - V_1) = 0.83$ and $(M - P) = 0.80$, were substituted in their respective formula with $\text{PO}_4 = 0$, the results are as follows:

$$\text{CO}_2 \text{ by A. P. H. A.} = 22.4 \text{ p. p. m.} \\ \text{CO}_2 \text{ by equilibrium} = 23.0 \text{ p. p. m.}$$

which agrees within the experimental error. If phosphate is present as in water 1A, then:

$$\text{CO}_2 \text{ by A. P. H. A.} = 48.4 \text{ p. p. m.} \\ \text{CO}_2 \text{ by equilibrium} = 51.6 \text{ p. p. m.}$$

which agrees within the experimental error. The calculation of the carbonate by the short equilibrium method applies corrections to the older method which are less than the experimental error. Consequently, the results agree very closely with those obtained by the older method.

The carbonate as determined by the combination of the Winkler method with the P determination of the A. P. H. A. method, gave good results in the absence of phosphate and silicates. The presence of phosphate tended to decrease the amount found, whereas the addition of silicate increased the carbonate determined.

The reported carbonate in the boiler waters was very interesting. In samples 108, 109, 110, and 111, the results are fairly close to the actual carbonate present. Any one of the methods appears to give accurate results. These boiler waters contain appreciable amounts of alkalinity, low organic matter, and no phosphate. They are typical of the boiler waters found in lower pressure industrial plants. The results on all the other boiler waters showed that none of these methods gives concordant carbonate results in low concentrations.

The sodium hydroxide results obtained on the synthetic waters by the A. P. H. A. method were very accurate. The Winkler method also gave very good results. The short equilibrium method gave very erroneous results. In the absence of phosphate, the results were low. With phosphate present, the results tended to be higher. One would not expect the hydrate to be correct, since it is assumed that the activity is equal to 1, and in most of the waters tested it is less than 0.85. This would tend to give low results. At the same time a large error is introduced with only a small variation in pH determination. Thus, an error of 0.1 in pH means an error of 25 per cent. In the boiler waters 108, 109, 110, and 111, the Winkler and the A. P. H. A. methods give good results for the hydrate. These are the clean waters which gave good carbonate results. The short equilibrium method gives low results on the boiler waters 109, 110, 111, and 112. It is almost impossible to calculate the activity coefficients for these solutions with any degree of accuracy, and consequently this correction cannot be applied. In general there is nothing in these results to show that the determination of pH values gives anything more than an approximation of the hydrate content unless corrected for activity, and then in the presence of phosphate or silicate the values would be too high.

As some of the waters tested contained phosphate, the amount present was determined both by the standard laboratory procedure and by the back-titration method. It was found that in the synthetic solutions the back-titration method gave very good agreement with the standard procedure, whereas in the boiler waters the agreement was poor in most cases. It seems as though the presence of organic matter in the boiler waters influences the results obtainable by back titration and introduces errors which cannot be compensated for in the calculation of the results.

CONCLUSIONS

The conclusions to be reached from digesting the results of these analyses are:

1. The A. P. H. A. and Winkler methods give reliable hydrate content in the absence of high silica and organic matter. In the presence of organic matter the Winkler method appears to be the most reliable.

2. The determination of hydrate from the pH value gives erroneous results.

3. The carbonate determined by the A. P. H. A. method is accurate in the absence of organic matter. However, in boiler waters having the sodium carbonate below 50 p. p. m. this method is not reliable.

4. The determination of carbonate using the short equilibrium method gave results which averaged about the same as those obtained by the A. P. H. A. method.

5. The carbonate determined by the carbon dioxide evolution method gave the most reliable results for carbonate.

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An Inexpensive Low-Temperature Thermostat

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THE low-temperature thermostat described in this paper, although inexpensive to construct and to operate, has been found to be accurate and reliable. Liquid ammonia is used as the cooling agent for temperatures between 7° and -25° C. This substance is cheap, readily available, and because of its exceptionally large heat of vaporization per unit weight, cools economically. Ice is used to cool the bath for temperatures between 7° and room temperature. The method of applying the cooling agent differs from the usual practice in that the heat is conducted away from the bath to the cooling agent by means of a copper rod soldered through the wall of the bath, which is constructed of copper. The cooling of the bath liquid is thus accomplished by transfer of heat to the container wall, rendering the use of a cooling coil or other device in the bath itself unnecessary.

DESCRIPTION OF APPARATUS

The bath and its associated apparatus are illustrated diagrammatically in Figure 1. The bath itself consists of a copper tank, *a*, made by soldering one end of a section of copper tubing 7.5 inches (19.05 cm.) long and 3.5 inches (8.89 cm.) inside diameter into a groove turned in a copper disk 4.5 inches (11.43 cm.) in diameter. The walls and bottom of the bath are 0.125 inch (0.32 cm.) thick. A 1-inch (2.54-cm.) hole is drilled in the wall of the bath 2.5 inches (6.35 cm.) from the top, and through this hole is soldered a 1-inch (2.54-cm.) copper rod, *b*, so that it extends 0.5 inch (1.27 cm.) into the bath. The rod is bent

downward 2.5 inches (6.35 cm.) from the wall of the bath, passes through a cork, *c*, and extends down 8 inches (20.32 cm.) below the bend. The bath and that portion of the rod between it and the cork are carefully lagged with 1.5 inches (3.81 cm.) of hair felt (not shown). The lagging is somewhat thinner between the rod and the bath to allow clearance for the vacuum bottle. Kerosene is used as the bath liquid.

The bath is cooled continuously by inserting the copper rod into a 500-cc. silvered vacuum bottle, *d*, containing liquid ammonia, or into a beaker of ice and water. The cork, *c*, fits loosely into the neck of the bottle. Heat is supplied

intermittently by one or two 21-candle power automobile headlight bulbs, *f* and *f'*, as conditions may require. The switches, *o* and *o'*, are arranged to permit the use of one or both bulbs. The bulbs, which are lighted by a standard 6-volt storage battery, are mounted with special clamps of brass strap, *g* and *g'*, which pass around the base of the bulb and are soldered to the 0.125-inch (0.32-cm.) copper rod, *h*, which passes through the cork, *i*, and forms one side of the lamp circuit. Copper wires, *j* and *j'*, are soldered to the other contact of the bulbs and pass through the cork to the insulating bracket, *k*. The lamp circuit is controlled by the 250-ohm relay, *l*, the primary circuit of which is operated by a conventional gas type thermoregulator which consists of a gas-filled 20-cc. bulb, *m*, connected by a small-bore capillary to a closed-end manometer of slightly more than barometric height, which was carefully boiled out after being filled with

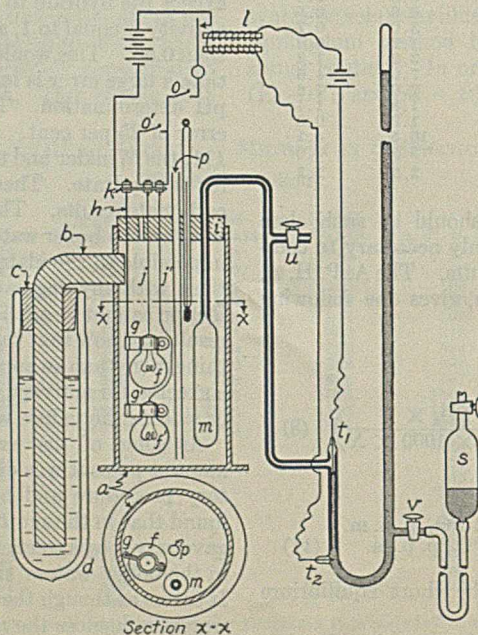


FIGURE 1. DIAGRAM OF LOW-TEMPERATURE THERMOSTAT

pure mercury. Tungsten leads tipped with platinum are sealed through at t_1 and t_2 . The circuit is made and broken by the rise and fall of the mercury in the capillary at the tip of t_1 . The dead space above the mercury at t_1 and in the connecting capillary is so small that variations in room temperature do not perceptibly affect the setting of the thermoregulator. The cross section at $x-x$, shown immediately below the bath in Figure 1, shows the arrangement of parts in the other plane. Most of the bath space is left free for other apparatus.

Figure 2 is a photograph of the bath, vacuum bottle, and wooden stand used to support them. The bottle rests on a movable shelf which may be removed at any time to permit lowering of the bottle. The picture shows the lagging and the method of securing it with metal straps ordinarily used for fastening lagging to steam pipes. The large cork, i , which closes the top of the bath and through which the lead wires, tubes, etc., pass, is bolted to a horizontal cross-piece (not shown) which forms part of the frame which supports the manometer and other equipment. The cork and other apparatus are thus supported independently of the bath which can be lowered to expose the apparatus by simply removing the stand.

Because of the small size of the bath, no mechanical stirrer is used, but instead dried air is passed in through the tube p and allowed to bubble up through the bath liquid. This has been found quite satisfactory. Precooling of this air would make it possible to operate at somewhat lower temperatures with a given cooling agent.

The operation of the apparatus is as follows: The bath is brought to the desired temperature by immersing the rod in liquid ammonia or ice while the cock, u , is open. The height of the mercury in the manometer is then adjusted by means of the leveling bottle, s , until it makes contact at t_1 , the cocks, u and v , are closed, and the heaters turned on. The bath will then hold the desired temperature. Additional ammonia or ice can be added at any time without interfering with the operation of the thermostat. In cooling the bath initially to temperatures below 0°C ., some time and liquid ammonia can be saved by precooling the bath liquid. This is done by immersing the kerosene in an ice bath before it is poured into the thermostat.

DISCUSSION

The bath as described has been used only with liquid ammonia and ice, but there is no apparent reason why it could not be used equally well with other cooling media, for example, liquid air or carbon dioxide snow in acetone, and thus be made to operate at lower temperatures than are possible with liquid ammonia. The practical lower limit, using ammonia, is about -25°C ., but the limit would not approach the temperatures of liquid air and carbon dioxide snow as closely as it does that of liquid ammonia, owing to increased heat losses at lower temperatures. The bath has been operated at several temperatures between 0° and -25°C . using liquid ammonia, and at 6.75° , 9° , and 19°C . using ice. The range between room temperature and -25°C . is thus readily covered with the two cooling agents, ice and liquid ammonia. No change in the apparatus is required when cooling agents are changed. The highest practical operating temperature with any cooling medium is reached when the bath cools so rapidly that the heaters must operate almost continuously to maintain that temperature. With two bulbs in use, it is possible to operate at higher temperatures with a given cooling agent, and by using one or two bulbs as necessary the heating and cooling periods can be made more nearly equal.

The ammonia consumption is small, 400 cc. being sufficient

to cool the bath from 15° to -15°C . and maintain it at the latter temperature for 5 hours. Starting with the bath already down to temperature, a single filling suffices for a day's run of about 7 hours. The apparatus is being used under a fume hood and the ammonia fumes have given no trouble. For operation in the open air the cork, c , should be made to fit tightly and a tube passed through it at the side through which the ammonia fumes could be carried off as desired. Care must be exercised when placing the bottle of ammonia around the copper rod, as the ammonia boils violently when it first touches the warm rod.

The temperature change of the bath during its heating or cooling period was imperceptible on a pentane thermometer, and an attempt was made to follow it with a copper-constantan thermocouple. The couple was made of fine wire

and was placed in direct contact with the bath liquid to reduce the lag as much as possible. The e. m. f. readings were made with a Leeds and Northrup Type K potentiometer and galvanometer to 1 microvolt. Although these readings could hardly have an absolute accuracy of 1 microvolt, if all errors affecting the instrument are assumed constant over the brief interval of a heating or cooling period, then the change in e. m. f. should be accurate to about 1 microvolt (0.027°C .). Of thirteen readings taken with the bath operating at -10°C ., a readable difference was observed in only one case in which the e. m. f. changed 1.5 microvolts between the start and end of a heating period (67 seconds). Similar results were obtained with the bath operating at -19°C . Out of eleven determinations one readable difference of 5 microvolts was observed, all the others showing no perceptible variation between the start and end of a heating or cooling period. The two observations showing variation were probably due to some extraneous cause, especially since both showed a change of e. m. f. in the direction opposite to that which would be expected. The twenty-four determinations were made under a variety of conditions, with the vacuum bottle half filled with ammonia, with the bottle full, with one bulb in use, with both in use, with the thermocouple junction near the top, and with the junction near the bottom.

The bath was explored with the thermocouple junction to determine whether adequate stirring was being obtained. Of five readings taken at widely separated points in the bath, a variation of ≈ 1 microvolt was observed, corresponding to a temperature variation of $\approx 0.03^\circ\text{C}$. Although this could perhaps be improved by mechanical stirring, it is entirely adequate for many purposes.

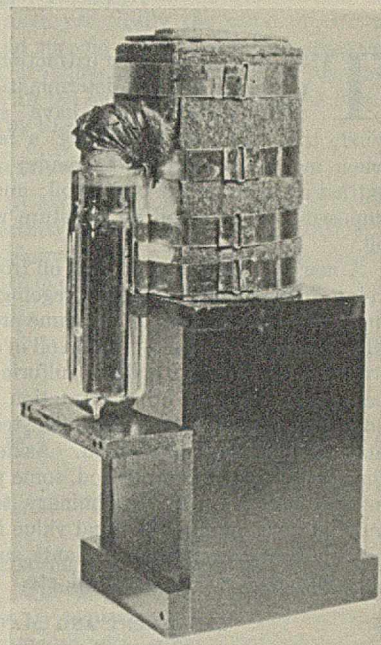


FIGURE 2. THERMOSTAT BATH AND STAND

Determination of Oil Content of Pecans

New Sulfuric Acid Digestion Method

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THE gravimetric ether extraction methods now used for the quantitative determination of the oil or fat content of pecans have several disadvantages. First, they are time-consuming, a factor to be considered when many tests are to be made; second, ether solvents extract other materials besides oil; and third, it is practically impossible to drive off all moisture without oxidizing some oil.

A new method for extracting oil from pecans has been developed which overcomes the foregoing disadvantages, at least in part. It is based upon the same procedure as is applied in the Babcock cream test. Pecan oil in a pure state is liberated from the nut meats by dilute sulfuric acid at a certain temperature. With the ether extraction method, from 21 to 22 hours are necessary for making the test, as compared with 30 minutes with the new method. Aside from the considerable time saved by the new method, some progress has been made in overcoming error. Preliminary tests indicate that the method gives promise of equal value in the determination of oil in nuts and seeds of other plants, such as peanuts, walnuts, coconuts, cotton seed, flax seed, etc.

EQUIPMENT AND MATERIALS

1. Fifty per cent, 9-gram, so-called "6-inch cream-test" bottles, used in the Babcock cream test. They have a bulb capacity of approximately 45 cc.
2. A centrifugal machine equipped with a Babcock-test attachment and geared to a speed of 800 to 1000 revolutions per minute.
3. A constant-temperature bath, large enough to hold all the bottles used in one run, deep enough to come within 0.5 inch (1.27 cm.) of the top of the test bottle, and capable of maintaining temperatures of 55° and 65° C.
4. Sulfuric acid, with a specific gravity of approximately 1.84, diluted 1.5 to 1 part of water.

EXPERIMENTAL PROCEDURE

The pecans used for this work were collected from orchards in Texas and Louisiana and consisted of several of the more common varieties. These nuts were cracked and stored in tightly sealed bottles; then, as needed for experimental purposes, were very finely ground with the nut-butter cutter in a Russwin food chopper, and used immediately.

Moisture determinations were made on all samples of nuts by placing a 10-gram sample of finely ground nut meats in the vacuum oven at 65° C. for 5 hours at approximately 12.55 pounds vacuum. All calculations were based on oven-dried samples.

All oils used for comparison were tested for oxidation, using Kreis' test for detection of oxidation. Any oil found to be oxidized was discarded.

Four grams of the finely ground nut meats were weighed and transferred into a dry cream-test bottle (this can be accomplished by cutting off the stem of a 4-inch (10.16-cm.) glass funnel and holding it in position over the test bottle). Next 35 cc. of dilute (1 to 1.5) sulfuric acid were added and the bottle placed in the water bath for 15 minutes at 65° C. (a higher temperature will give a dark color to the oil). The bottle was shaken occasionally to aid digestion of the nut meats, and was then transferred to the centrifuge, counter-

balanced, and after the proper speed (800 to 1000 r. p. m.) had been attained, whirled 5 minutes. The bottle was filled to the neck with dilute sulfuric acid and whirled 3 minutes. More acid was added until the liquid column approached near the top graduations of the scale, and the bottle whirled 1 minute. The bottle was transferred back to the water bath for 10 minutes at 55° C. With the aid of dividers or calipers, the spaces occupied by the oil column from its lower surface to the top of the upper meniscus were measured.

The per cent oil can quickly be calculated using the formula:

$$\frac{\text{Spaces oil occupied in test bottle}}{\text{Spaces 1 gram oil occupied} \times \text{wt. of sample}} \times 100 = \% \text{ oil}$$

As the cream-test bottles used are graduated to read in terms of butter fat and not pecan oil, it was necessary to determine the spaces occupied by 1 gram of oil and calculate the per cent of oil from the factor found. The spaces occupied by 1 gram of oil were determined as follows: a cream-test bottle was filled to the neck with sulfuric acid (1 to 1.5) and pecan oil was added to the first graduation of the bottle, then the bottle was placed in the water bath for 10 minutes at 55° C., transferred to the centrifuge, and whirled 3 minutes. The bottle was again placed in the water bath at 55° C. for 10 minutes and the space occupied by the upper meniscus of the oil read. Now the test bottle was placed on the analytical balance and 3 grams of oil accurately weighed into it; then it was placed in the water bath for 10 minutes at 55° C., transferred to the centrifuge, and whirled for 1 minute after the proper speed had been attained, and again placed in the water bath for 10 minutes at 55° C. With the aid of calipers, the spaces occupied by the 3 grams of oil were measured from its lower surface to the top of the upper meniscus. The spaces occupied by the 3 grams of oil divided by 3 equals the space occupied by 1 gram of oil. By using the factor thus obtained, the per cent oil is readily calculated.

TABLE I. SPACES OCCUPIED BY OIL FROM DIFFERENT VARIETIES OF PECANS

(1 gram of oil at 55° C.)	
VARIETY OF PECAN	SPACES OCCUPIED
Schley	11.15
Moneymaker	11.16
Pabst	11.17
Success	11.22
Stuart	11.23

TABLE II. COMPARATIVE RESULTS BY PETROLEUM ETHER EXTRACTION AND NEW METHOD

VARIETY OF PECANS	OIL BY NEW METHOD	OIL BY PETROLEUM ETHER EXTRACTION
	%	%
Schley	77.20	77.80
	76.34	76.93
Success	74.35	74.10
	75.04	74.20
Stuart	73.77	73.11
	75.10	74.40
Pabst	72.52	72.89
	73.96	74.43
Moneymaker	76.39	76.25
	77.58	77.73

The space factor is not the same for all varieties of pecans. Table I shows the spaces occupied by 1 gram of oil at 55° C.

for several varieties of nuts. From this table it is evident that the spaces in the cream-test bottle occupied by 1 gram of oil vary slightly with each variety. The average of all the tests was 11.18 spaces occupied by 1 gram of oil. Using the factor 11.18 gives results very near to those obtained by the gravimetric method, as seen in Table II. Greater accuracy, however, can be obtained by using the individual factor for each variety of nuts, but this does not seem necessary for most work. More work needs to be done at this point and will be undertaken when time permits.

TABLE III. CHEMICAL AND PHYSICAL CHARACTERISTICS OF PECAN OIL EXTRACTED BY EXPRESSION, PETROLEUM ETHER, AND NEW METHOD

(Stuart variety)					
METHOD OF EXTRACTING	IODINE NO. (WIJS METHOD)	REFRACTIVE INDEX (ABBÉ REFRACTOMETER)	SAPONIFICATION NO.	SPECIFIC GRAVITY (WESTPHAL BALANCE)	COLOR
Expressed	102.86	1.4670	189.89	0.9190	Light golden
Petroleum ether	103.27	1.4670	187.80	0.9190	Light golden
New method	103.83	1.4670	189.95	0.9190	Colorless

The percentages of oil as determined by the petroleum ether extraction and the new method are shown in Table II. Samples of each variety were collected from two different localities and the determinations made in duplicate. The results are found to compare favorably.

Table III shows a comparison of the physical and chemical characteristics of pecan oil extracted by expression and by the two foregoing methods. This table shows the oil from the different methods to have practically the same properties. The refractive index and specific gravity were the same with all three methods. The iodine number and saponification number were highest with the new method, indicating that a purer oil was obtained by this method.

ACKNOWLEDGMENT

The author wishes to express his indebtedness to A. O. Alben, Pecan Soil Fertility Laboratory, U. S. Bureau of Chemistry and Soils, Shreveport, La., for valuable suggestions and kind assistance in connection with this work.

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Graphic Calculations in Water Analyses

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THE facts that the existing methods for calculating the elements and radicals present in mineral waters into certain hypothetical combinations are many and diverse, rendering the results of such calculations confusing and not readily comparable one with the other, and that modern chemical knowledge fully justifies no such calculations, are diverting the general tendency toward the ionic form of stating the results of water analysis.

The practice of combining the ions, however, still finds extensive application in industry, and various schemes have been evolved whereby these calculations are reduced to a routine applicable by the operator with limited chemical training.

The use of milligram equivalents (or reacting values) in water analyses has long been practiced (1, 4), and an elaboration on the use of equivalents has been made by graphically representing the results of analysis (2, 3). These graphic representations have been employed for a number of years in publications of the U. S. Geological Survey. The use of equivalents may be further extended to the length of integrating the hypothetical combinations by mechanical methods.

In the method herein advocated, a determination of calcium, magnesium, carbonate, sulfate, and chlorine is made. The results, stated as parts per million, are converted to the milligram equivalents per kilogram (Stabler's reacting values, 4) by multiplying by the reciprocals of the combining weights of the respective ions. The results being thus con-

verted, any ion may be combined with any other ion in numerically equal quantities. The advisability of determining the sodium and potassium is contingent upon the accuracy desired, and when sodium and potassium are not determined, such an amount of sodium is "written in" as will cause the sum of the equivalents of the acid radicals to be exactly equal to the sum for the bases. The probability of the two sums balancing when all of the ions are determined is very small, and the small difference usually existing is distributed so as to effect a balance.

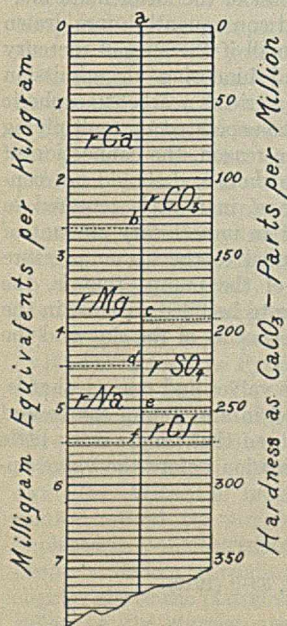


FIGURE 1

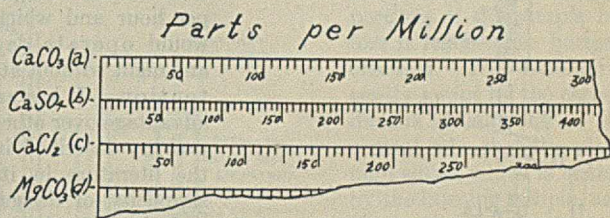


FIGURE 2

The equivalents of the positive and negative radicals, being thus adjusted, are then consecutively laid out on prepared coordinate paper (calibrated in milligram equivalents) on either side of a central line (Figure 1). The length on the graph representing an ion may be called the "reacting length" of that ion. Since linear distance on the graph is quantitatively proportional to the equivalents of the ions, it is also proportional to the equivalents of the compounds. All radicals lying laterally contiguous are combined, and the compounds supposedly present in the sample may thus be instantly visualized. The failure of two radicals to lie laterally adjacent connotes the absence of the compound composed of those two radicals.

The results as read from this graph are in terms of milligram equivalents and necessitate a conversion into the desired units. A series of graphic scales, one for each possible compound, are constructed for this purpose (Figure 2) and may be used indefinitely.

To convert the calcium carbonate, distance ab (Figure 1), the reacting length of the calcium carbonate, is transferred to scale a (Figure 2) by means of a pair of dividers, and the result is read directly in terms of parts per million of calcium carbonate. The length representative of 1 part per million of calcium carbonate (scale a) may be called the "factor length," and bears a ratio to the length representing 1 milligram equivalent on the graph, equal to the reciprocal of the factor for converting the milligram equivalent of calcium carbonate into p. p. m. of that compound. The factor length is determined by dividing the reacting length unit by this combination factor. Foulk (4) presents a discussion and a list of these combination factors. All other scales are made and the conversions executed in accordance with the foregoing procedure. The scales may be adjusted to give results in any unit desired, such as grains per gallon, pounds per 1000 gallons, etc.

When the linear counterpart of 1 milligram equivalent is a suitable length, for example 2 or 3 cm., the method may be applied without resort to graph paper. The numerical react-

ing values of the ions may be converted into the reacting lengths by the use of a vernier slide micrometer. These lengths are plotted on either side of a straight line drawn on a clean sheet of paper, and the conversion to the desired units made with dividers and the scales as usual.

The method is, of course, independent of the system or order of combining the radicals, the order employed above being arbitrarily selected for the purpose of demonstrating the method. The accuracy of this method varies directly with the length taken as unity in the graph.

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Pressure Pump for Circulating Gases in a Closed System

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IN AN investigation of the action of oxygen on low-temperature tar when recirculated through the material in a closed system, it was necessary to devise a pressure pump able to overcome the strong resistance created by the viscous column of tar through which the gas was to be forced. To this end, a non-mechanical pump operated by an external

water-pump through a mercury medium was constructed which would circulate 6 to 20 liters of gas per hour and which would operate day and night without attention. It has an advantage over other pumps described in the literature in its simplicity of design, or in its lack of solid moving parts and bearing surfaces. The underlying principle is somewhat similar to that of the pump described by Maass (1), but the construction is more compact and the operation less complicated.

The water-pump is connected to e , as in Figure 1. The suction produced reduces the pressure in f , a , and b which causes the mercury to rise in a and b and to go down in c and d .

When the level of the mercury in c reaches point i in b , a difference of pressure between atmospheric and that obtaining in voids of f , a , and b greater than the height of the mercury slug in b , is quickly established. The result is that the slug is shot forcibly into f , thus relieving the vacuum in e , f , and a . The mercury level in a therefore drops suddenly, forcing the level in d upward. At the same time the air intake is cut off by c 's filling with mercury as before, and the cycle repeats itself. The pulsating motion of the mercury level in d , together with the valve arrangement g and h , makes circulation of the gas through the closed system possible. Tube e is filled with glass beads and glass wool to trap stray globules of mercury.

The capacity of the stroke in d is affected by changes in diameter of a ; for a larger diameter of the latter more mercury is raised per unit height and consequently more drawn from d . Tube b is necessarily small if the slug of mercury is to be kept from breaking and hindering air admission through c . The return to atmospheric or nearly atmospheric pressure of voids in a and c can be expedited by multiplying b by two or more. For the same reason, the connection of e with the water-pump should be short and should not contain a safety-trap in series. None, in fact, is required in this apparatus. The presence of an unnecessary amount of space to be evacuated and returned to the higher pressure merely lowers the effectiveness of the pump—that is, the larger this space the more there is to be filled with air in the short time elapsing between the shooting of the slug and the cut-off of air-intake through c .

Likewise the space between the valves and pump—that is, the space above the mercury level in d at top of stroke and connecting line—should be small, so that only a very little of the stroke is wasted in compression before the valve operates.

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RECEIVED January 29, 1932. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

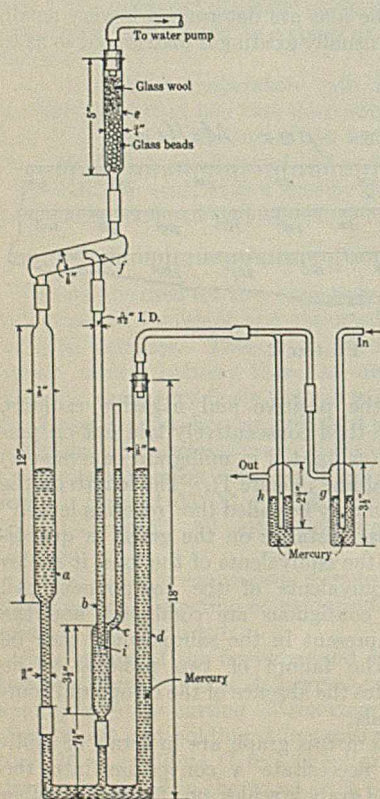


FIGURE 1. PUMP FOR CIRCULATION OF GASES IN CLOSED SYSTEM AGAINST BACK PRESSURE

Ashing Apparatus for Samples Containing Traces of Iodine

GEORGE M. KARNS, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

IN THE preparation of large samples of organic material for the determination of traces of iodine, recognition of the advantages of ashing samples in systems in which iodine may be recovered from the vaporized combustion products as well as from the ash has led to the development of closed systems for ashing in an atmosphere of oxygen. Most of the devices used for this purpose are based upon the appliance proposed by McClendon (1) and subsequently developed by him and his co-workers.

Although valuable data have been accumulated by the use of apparatus of this well-known type, the operation is often attended with difficulty. With such apparatus it is usually necessary for oxygen to be swept through at a comparatively high rate in order that no loss of products from the sample occurs by expansion during combustion. The rapid rate of this gas stream, from which, of course, the iodine must be recovered, necessitates in turn the employment of a high-capacity washing train involving the use of large amounts of water and reagents which must be eliminated before the final determination is made. Then, too, in apparatus of this type some part of it is subjected to intense heat, either from the burning sample or from external application, and hence its life is short. The apparatus described in this paper has been designed to ash samples slowly if desired. During such slow ashing the oxygen utilization is quite efficient, making it unnecessary to handle a large excess of oxygen and therefore enabling the use of a comparatively simple collecting train. The apparatus is also capable of giving a good ash without the aid of outside heat, and during its operation no destructible part of it becomes so excessively heated as to cause damage.

Figure 1 shows the essential parts of the new apparatus. In carrying out a combustion, the sample is either molded into cylindrical form in a manner similar to that suggested by McClendon and Remington (2), or placed in a paper cylinder fitting the Pyrex glass inner tube *T*. A small amount of suitable fuse material, such as cotton, is put on top of the sample. With the brass ramrod retired, the sample is placed in position, being properly held protruding slightly above the platinum and rod. The tube is then set

in position in the bulb and, with the collecting train in place, the desired adjustment of the slight vacuum under which the system is to operate is made, with the oxygen speed regulated to its proper rate. For convenience, the oxygen-inlet tube from a convenient flowmeter is attached at *O*. Carbon dioxide is admitted at *C*, the speed of admission being the minimum of continuous flow through a needle valve. When the system is so arranged, the inner tube is removed from the apparatus, the fuse material is ignited, and the tube is quickly replaced, being held there by rubber bands about the appropriate lugs. As the sample burns, the brass rod is used to push fresh portions of it gently into the flame area, where it is consumed as oxygen becomes available. The globular design of the combustion chamber causes circulating gases to direct the incoming oxygen toward the sample. The rate of burning is adjusted by the oxygen speed. The apparatus illustrated will hold samples of from 35 to 60 grams, depending upon the type of material under consideration. Such sizes of samples are adequate for determinations on most materials, but, if it is desired to analyze large samples, additional cylinders of material may be ashed without interrupting the oxygen flow. When the tube is to be removed to enable the addition of a second portion of sample, the ash may be shaken down into the cup about the central tube, which is provided for that purpose.

As the top portion of the sample burns, radiated heat distills off some of the volatile constituents from lower portions of the sample before it reaches the burning chamber. This distillate is gently swept by the carbon dioxide stream out of the central tube past the platinum collar, which is heated by the burning sample, and through the flame area, where ignition takes place. The carbon dioxide stream also serves to prevent the migration of the flame down into the glass portion of the apparatus, thereby precluding the early destruction of the latter. The combustion products pass into the collecting train through the outlet tube *D*.

The apparatus as illustrated has been used with several sizes of inner tube, but the size shown has been found to be more convenient in general than those of smaller diameter. Little difference in operating the apparatus has been found

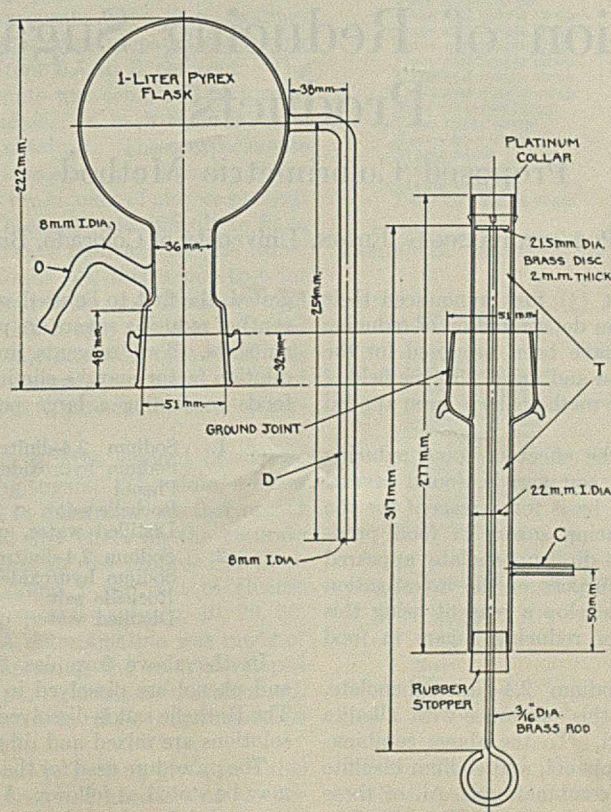


FIGURE 1. ASHING BULB

in working with samples of leafy vegetables, dried milk, mixed cattle foods, tankage, fish scrap, and commercial ground meat. Ground beef containing some fat has been successfully ashed without being previously dried. Using an oxygen speed of 1 liter per minute, a good iodine recovery was made by a simplified collecting train consisting of one condensing tube containing glass wool moistened with sodium bisulfite solution immersed in an ice bath, a Cottrell precipitator 30 cm. in length, and a single Milligan wash bottle containing caustic solution. Operating at the low rate, the average sample is consumed at approximately 25 grams per hour. Although designed to make possible the ashing of samples with a simplified collecting train, the ashing bulb will operate equally well with trains capable of handling the products from a more rapid combustion.

In comparing the apparatus with others previously described, its chief advantage is in its smooth and governable operation. The burning of the sample being complete and controllable, little difficulty is encountered from the development of back pressure from the ignition of accumulated combustibles. It is therefore unnecessary to handle the rapid stream of gas that is usually recommended. It is possible to obtain satisfactory combustion without the usual application of heat from supplementary burners or coils outside or inside the apparatus. Heat-flow direction, distribution, and dissipation make special cooling devices, such as water-circulating coils, unnecessary either in the apparatus or about the feed mechanism. The behavior of the apparatus in this respect also makes it capable of prolonged use when constructed almost entirely of glass.

The above-mentioned features, whose simplicity is readily recognizable by the experienced operator, are difficult to evaluate quantitatively in a procedure which is laborious at

best. However, analysts have developed satisfactory technic using the ashing bulb in four or five trial runs. Since the ashing device is used in the preparation of the sample, recovery is important only as the total procedure is influenced by the device in question. It suffices to say that using the ashing bulb with collecting trains described by McClendon and Remington, the recovery of iodine is equivalent to that obtained by them. When compared with the McClendon and Remington ashing tubes, it is more convenient to clean on account of its size, shape, and lack of internal coils, and on account of the fact that no ash can fuse into the bulb as it sometimes does with glass or silica tubes. The bulbs have been used for approximately one hundred runs without becoming noticeably affected in their hotter portions, a considerably longer life than that of the ashing tube made of Pyrex, which must be used at temperatures approaching its softening point. These, in the hands of operators of some experience, are often in bad condition after five or six runs. The bulb is better in this respect than the more expensive silica tubes, which often crack after alkaline ash fuses into them, even when special precautions are taken.

Experience has demonstrated that the smooth operation of the ashing process in this apparatus makes available dependable types of collection hitherto unutilized in analyzing commodities for iodine.

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RECEIVED December 30, 1931. Presented before the Division of Agricultural and Food Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Determination of Reducing Sugars in Food Products

Proposed Colorimetric Method

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SINCE Lewis and Benedict (4) first announced their colorimetric method for the determination of reducing sugars, several methods have been proposed for the estimation of these sugars in blood and urine. In the field of food chemistry these colorimetric methods have been applied but little.

The authors (?), in testing the effect of some reducing sugars on certain organic nitro compounds, found several compounds which might form a basis for a reagent for the quantitative estimation of reducing sugars in food products. Among these sodium 2,4-dinitrophenolate appeared to be very satisfactory. The purpose of the investigation reported in this paper was to develop a reagent using this compound for the estimation of reducing sugars in food products.

While experimenting with sodium 2,4-dinitrophenolate, many different combinations of this substance with alkalis and alkali carbonates were tried. To the above combinations were added Rochelle salt, phenol, and sodium bisulfite separately and then in various combinations. All of these reagents were tested for the development of color with dextrose. As a result, two different reagents have been sug-

gested, the first to be used when small amounts (1 to 10 per cent) of reducing sugars are present, and the second for larger amounts. Two reagents are suggested in order that the dilution factor may be eliminated as far as possible with the foods containing a large percentage of reducing sugars:

- | | | |
|----|------------------------------|-----------|
| 1. | Sodium 2,4-dinitrophenolate | 8 grams |
| | Sodium hydroxide, 5 per cent | 200 cc. |
| | Phenol | 2.5 grams |
| | Rochelle salt | 100 grams |
| | Distilled water, q. s. | 1000 cc. |
| 2. | Sodium 2,4-dinitrophenolate | 8 grams |
| | Sodium hydroxide, 5 per cent | 200 cc. |
| | Rochelle salt | 100 grams |
| | Distilled water, q. s. | 1000 cc. |

In the above formulas the sodium 2,4-dinitrophenolate and phenol are dissolved in the sodium hydroxide solution. The Rochelle salt is dissolved in about 700 cc. of water. The solutions are mixed and diluted to 1 liter.

The procedure used for the estimation of the reducing sugars may be stated as follows: A given amount of the food product containing the reducing sugars is weighed and the necessary dilution made. One cubic centimeter of this dilution

is placed in a Folin-Wu sugar tube, and 3 cc. of the proper reagent (depending upon the amount of reducing sugar present) are added. The tube is heated in a beaker of boiling water for 6 minutes, then cooled in running water for 3 minutes, and finally diluted to the 25-cc. mark with cold distilled water. Then this solution is compared in a colorimeter with a standard made by treating a given amount of pure glucose in the same manner as the unknown. The side of the colorimeter containing the unknown is set at 20, and the standard varied until the colors match. An average of five readings is taken and the percentage of the reducing sugars calculated.

TABLE I. READINGS FOR 1 PER CENT GLUCOSE IN SOLUTION WITH DIFFERENT AMOUNTS OF SUCROSE

(Per cent sucrose)									
At 0	At 5	At 10	At 20	At 30	At 40	At 50	At 60	At 70	
20.0	20.2	19.8	20.0	20.0	20.0	20.0	19.8	20.0	
20.2	19.8	20.2	19.8	20.2	19.8	19.8	19.8	20.2	
20.3	19.9	20.0	20.1	20.1	20.2	20.0	20.0	20.0	
19.8	20.0	20.0	20.0	20.0	19.8	20.0	20.0	19.8	
19.9	20.1	20.2	19.8	20.0	19.9	20.2	20.0	20.0	
Av. 20.04	20.00	20.04	19.94	20.06	19.94	20.00	19.92	20.00	

With the ordinary sirups, jellies, jams, and fruit juices, the color present did not interfere with the accuracy of the method. In products very high in coloring matter, such as molasses, preliminary clarification was necessary. The use of neutral lead acetate as directed in the Methods of Analysis of the Association of Official Agricultural Chemists (6) was satisfactory. This clarification could also be accomplished with alumina cream, fuller's earth, decolorizing carbons, and dry basic lead acetate without interfering with the accuracy of the method.

Because of the fact that the percentage of reducing sugars in the original food product is not known, readings are often obtained which are not very close to the standard reading of 20. This brought up the question as to whether or not the colorimetric method was accurate when these readings were rather far apart. Solutions were prepared containing glucose in varying amounts from 0.5 to 3 per cent. The color developed by these amounts was compared to a solution containing 1 per cent glucose. In each case, the correct theoretical readings were obtained. These experiments showed that with the proposed reagents, the intensity of the color is directly proportional to the amount of glucose present. This is a distinct advantage, because it is difficult to have the standard and unknown always read exactly the same. According to Rothberg and Evans (8), this is not true for the Folin and Wu method; and Folin and Denis (3) and Bierman and Doan (2) state this is also the case with the picric acid method. Sumner (9), however, found with his method that 1 mg. of glucose compared to 0.5 to 2 mg. of glucose without error. Benedict (1) made the same observations with his method.

Many food products contain a large amount of sucrose and a small amount of reducing sugars. Therefore, a series of experiments was conducted to determine whether or not a large amount of sucrose had any effect on the accurate estimation of the reducing sugars by the proposed method. Solutions were prepared containing 1 per cent of glucose with varying amounts of pure sucrose—namely, 10, 20, 30, 40, 50, 60, and 70 per cent. A determination was made of each of these solutions by comparing the color developed with a 1 per cent solution of pure glucose as the standard. Table I gives the reading found in these determinations when the standard was set at 20.0.

As may be seen from the average reading given in Table I, the different amounts of sucrose had no effect on the accuracy of the determination of glucose by the proposed method.

Since reducing sugars in food products usually contain levulose, the reducing equivalent was determined for this sugar. With the proposed method, it was found to have exactly the same reducing power as dextrose.

Frequently, when colors are developed by reducing sugars in alkaline solutions of organic nitro compounds, their intensities are either changed according to the length of the time of heating, or fade upon standing. Eight tubes, each containing the same amount of glucose, were heated with the reagents for varying lengths of time—namely, 5, 7, 10, 12, 15, 20, and 25 minutes. The results indicated that the time of heating up to 25 minutes caused no difference in the color produced. Subsequent work has shown in every case that 6 minutes is ample time for complete reduction to take place. Similar experiments were conducted differing only in that the various tubes, after having been heated for 6 minutes, were allowed to stand from 5 to 20 minutes immediately after the dilution of their contents. No change in the color was noted up to 20 minutes' standing.

The proposed colorimetric method was used to determine the reducing sugar in a number of food products. Table II gives the results for pure maple sirups, cane and maple sirups, and maple sugars. Table III includes the results when fruit juices, jams, and jellies were analyzed. Table IV gives the results of the analysis of milk for lactose. In all of the food products, the reducing sugar was also estimated by the official Munson and Walker method (5).

TABLE II. ANALYSIS OF SIRUPS AND MAPLE SUGAR FOR REDUCING SUGARS

FOOD PRODUCT	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Pure maple sirup	6.23	6.08
Pure maple sirup	3.40	3.24
Pure maple sirup	1.83	1.94
Pure maple sirup	6.62	6.58
Pure maple sirup	2.56	2.48
Pure maple sirup	2.29	2.22
Cane and maple sirup	2.22	2.03
Cane and maple sirup	1.66	1.61
Cane and maple sirup	2.20	2.12
Cane and maple sirup	4.82	4.65
Cane and maple sirup	2.29	2.22
Cane and maple sirup	1.16	1.05
Beet molasses sirup	0.52	0.61
Cane sugar sirup	1.42	1.31
Beet sugar sirup	1.22	1.21
Maple sugar	6.50	6.49
Maple sugar	5.68	5.60
Maple sugar	5.66	5.72
Cane and maple sugar	0.95	0.83

TABLE III. ANALYSIS OF FRUIT PRODUCTS FOR REDUCING SUGARS

FOOD PRODUCT	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Apple juice	9.60	9.54
White grape juice	13.45	13.39
Pineapple juice	9.00	8.91
Orange juice	5.03	5.10
Loganberry juice	9.05	8.92
Grapefruit juice	30.87	30.92
Apple jelly	16.45	16.61
Grape jelly	23.81	23.92
Raspberry jelly	16.96	17.12
Currant jelly	48.78	48.92
Plum jam	48.80	48.90
Strawberry jam	48.88	48.81

TABLE IV. ANALYSIS OF MILK FOR LACTOSE

MILK	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Raw	4.63	4.60
Raw	4.80	4.74
Pasteurized	4.35	4.29
Pasteurized	4.73	4.68

From Tables II, III, and IV, we see that the proposed method checks very closely with the Munson and Walker method. The latter, however, in some cases gives slightly lower results, but the proposed method has the advantage

over the Munson and Walker method in that it is much more rapid.

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Measurement of Surface Hardness of Cellulose Derivatives

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FOR many purposes the surface hardness, including resistance to abrasion and indentation, of films and plastics formed from cellulose derivatives is of equal importance with the mechanical strength of the material in the mass. Various methods of measuring the hardness and resistance to abrasion have been suggested at one time or another. In this laboratory there has been developed and used for some time a method of measuring the resistance to scratching which gives quantitative results and which seems of interest as furnishing another criterion of the physical properties of cellulose derivatives.

moving point starting from zero load, the load increasing steadily up to the desired limit. In the operation of the scratch dynamometer, the sample is placed in the holder at *A* so that the face is parallel to the base and turned downward. The material is best used in the form of thin, uniform films coated on glass although, where desired, coatings may be on metals or other rigid supports, or skived plaques of sufficient rigidity may be taken. Point *A* is fitted on a slide weight, *S*, which is drawn from its initial position of zero load (in counterpoise) by the weight *C* back toward a pivot, *P*. Traction is effected by the cable *D* running over a pulley driven by a constant-speed motor. Movement is started by the release *R*, and a scratch is produced by the point

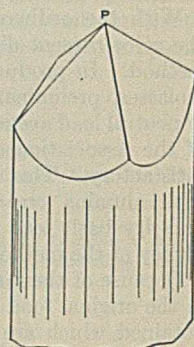


FIGURE 2. SHAPE OF POINTS

under a load increasing according to the equation: $L = \frac{dW}{b-d}$

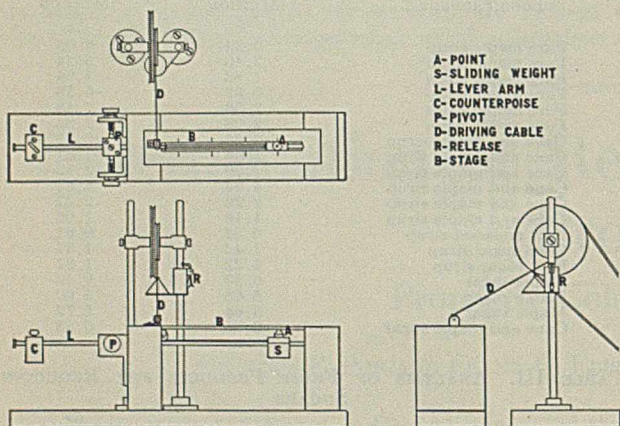


FIGURE 1. DIAGRAM OF SCRATCH DYNAMOMETER

The comparison of the findings obtained by this apparatus with the results of direct abrasion tests comes properly under the subject of testing materials, particularly the testing of paints, lacquers, and varnishes, and this phase of the work will be discussed in another place.

APPARATUS AND METHODS OF MEASUREMENT

The apparatus used consists essentially of two instruments. One of these is a scratch dynamometer and the other a scratch-observing instrument. Scratch dynamometers may be divided into two types: (1) a series of scratches is produced, each made with a constant load, the load increasing from one scratch to another; (2) a single scratch is made under a load increasing at a definite rate. Instruments have been designed for both purposes, but most of the work described here was carried out with an instrument of the second type, whose construction is shown in Figure 1.

The apparatus is devised to produce a scratch by a

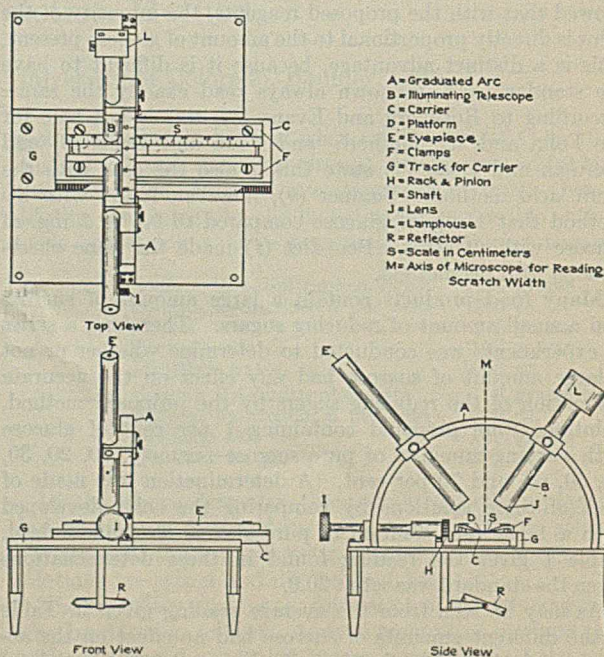


FIGURE 3. DIAGRAM OF ILLUMINATOR FOR SCRATCH TESTER

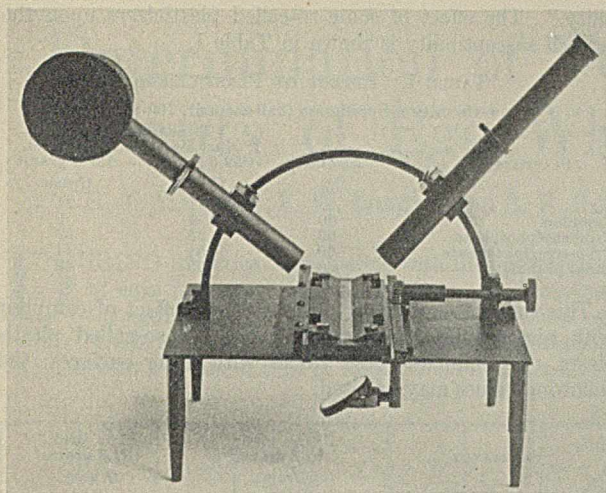


FIGURE 4. ILLUMINATOR FOR SCRATCH TESTER

where L = load on point
 W = weight of S
 b = original distance of point from pivot
 d = distance traveled by point

Thus in a specific instance,

$$W = 145 \text{ grams}$$

$$b = 25 \text{ cm.}$$

$$\text{hence } L = \frac{145 d}{25 - d} \text{ grams}$$

A straight scratch ready for examination in the illuminator is produced.

The type of scratch and the scratch susceptibility depend on the kind of point chosen. Not only will the material of the point affect the results, but also the shape of the point or style. In the experiments described, a hardened steel point shaped to an inverted tetrahedron of 45 degrees was used (Figure 2).

OBSERVATION AND MEASUREMENT OF SCRATCH SUSCEPTIBILITY

Measurement of scratch susceptibility may be expressed either as the threshold load just producing a scratch, or by a curve expressing the relation between the magnitude of the scratch and the load.

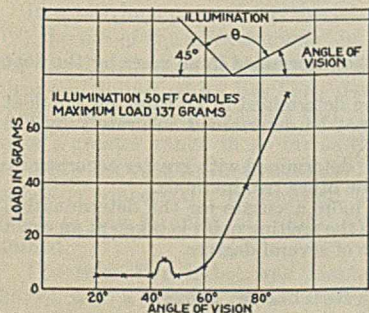


FIGURE 6. THRESHOLD VALUE AS FUNCTION OF ANGLE OF VISION

The illuminating tube, L , and the observing tube, E , are movable on a graduated circle, A , the scratch being on a line passing through the center of the circle and perpendicular to its plane. The appearance of the scratch at any point along its length can be examined, the scratch being moved forward by a rack and pinion at H and I . The carriage is graduated as shown at

Measurements of both kinds have been made. For measuring the threshold load, the carriage holding the test piece is removed from the dynamometer and slid into the stage of the illuminator, whose general construction is shown in the diagrams of Figure 3 and by photographs in Figures 4 and 5.

The illuminating

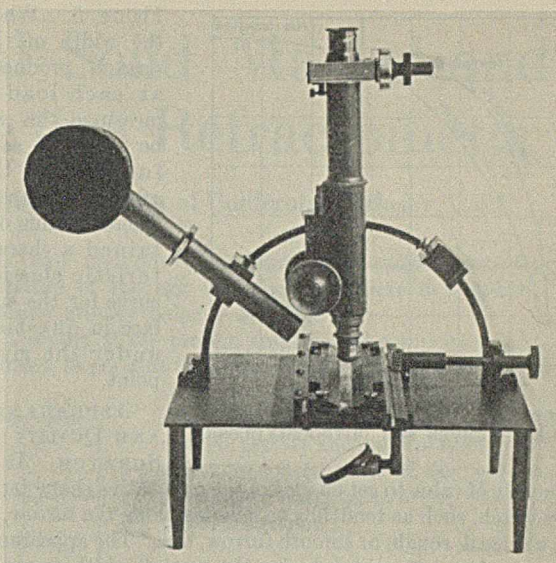


FIGURE 5. ILLUMINATOR IN POSITION FOR SCRATCH-WIDTH MEASUREMENT

S , the graduations corresponding to different loads, according to the equation already given. The illuminator, L , is adjusted to give a constant level of illumination, and the scratch may be examined either by reflected light or by light transmitted by the mirror, R .

The least load making a perceptible scratch will depend upon the visibility conditions, and therefore upon the amount and angle of illumination. The scratch illuminator is operated in a dark room or dark cabinet. Experimentally it was found that an angle of approximately 30 degrees was most satisfactory, avoiding both specular reflection and grazing incidence of the light. It will be seen from the curves

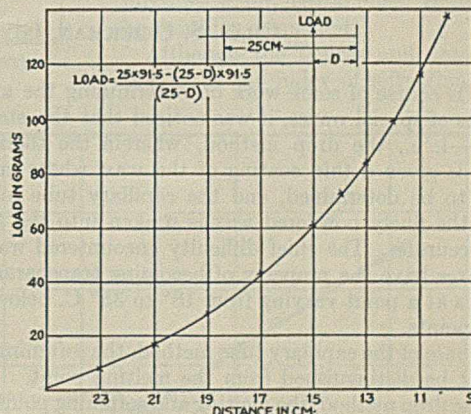


FIGURE 7. SCRATCH-LOAD CALIBRATION CURVE

in Figure 6 that the angle chosen is in a flat portion of what may be termed the "angular visibility" curve, and the glare and reflected image which occur at specular reflection at 40 degrees are avoided. In Figure 7 is given a scratch-load calibration curve, by which intervals along the scratch are converted to effective loads. The illumination level at the scratch used in the present work was 50 foot-candles, corresponding to an average indoor illumination.

SCRATCH-WIDTH MEASUREMENTS. The magnitude of the scratch is best determined by measurements of the width of the scratch at a given load. To measure this, a microscope is mounted on the graduated circle, A , carrying a filar eye-piece micrometer. The arrangement of this is shown in

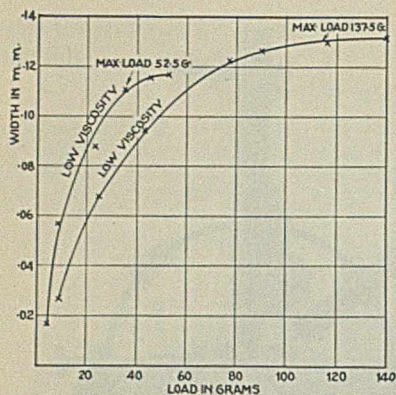


FIGURE 8. CHARACTERISTIC SCRATCH-WIDTH CURVES FOR NITROCELLULOSE

frequently of value to get an idea of the qualitative character of the scratch, such as tendency to splinter along the furrow, to give a ragged, rough, or smooth furrow, etc. The appearance can, of course, be noticed during the scratch-width measurement, but a permanent record can be obtained by substituting a small camera for the eyepiece micrometer and taking a photograph at low magnification.

EXPERIMENTAL RESULTS

The experimental data presented at this time are given by way of illustration. In Figure 8 are given curves of scratch-width, illustrating the behavior of a low-viscosity nitrocellulose film. It can be seen that the scratch seems to start from finite value of the load, which would be practically identical with what has been termed the "scratch suscepti-

bility." The effect of some so-called plasticizers upon the scratch susceptibility is shown in Table I.

APPEARANCE AND QUALITY OF SCRATCH.

It is thus obtained a characteristic abrasion curve for the surface in question under the given point.

TABLE I. EFFECT OF PLASTICIZERS
(Low-viscosity nitrocellulose (half-second), 100 parts)

PLASTICIZER	AMOUNT %	THRESHOLD VALUE	
		Max. load, 52.5 grams Grams	Max. load, 137.5 grams Grams
Camphor	60	17	21
Triphenylphosphate	60	4	9
Tri- <i>o</i> -cresylphosphate	60	25	32
Ethyl phthalate	60	34	41
	60	35	47

This shows the distinctly characteristic effect of camphor with nitrocellulose, compared with other so-called plasticizers. To compare these values with other surfaces, the following values may be cited:

SUBSTANCE	THRESHOLD VALUE	
	Max. load, 52.5 grams Grams	Max. load, 137.5 grams Grams
Nitrocellulose (low viscosity)	17	21
Nitrocellulose (high viscosity)	14	20
Spar varnish	32	28

The characteristic action of plasticizers actually requires measurement at different proportions, giving a characteristic curve for each plasticizer.

ACKNOWLEDGMENT

Thanks are due G. Willis, formerly of these laboratories, who helped materially in the construction of the dynamometer.

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Determination of Melting Points of Special Waxes

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IN THE course of some work on determining the melting points of special waxes, it was noticed that the standard methods—i. e., the drop method, wherein the thermometer bulb is given a thin coating of the wax whose melting point is to be determined, and the capillary tube method, wherein the finely powdered wax is shaken into the tube—were inaccurate. The chief difficulty encountered was that these waxes have the property of becoming transparent and gelatinous at a point varying from 18° to 35° C. below their melting points.

In the case of the capillary tube method, the softening point could not be distinguished from the melting point. In the case of the drop method, the melting and softening points were more easily distinguishable. Nevertheless, neither of the methods was adequate, and, therefore, a method which is applicable to these special waxes and also to other waxes was worked out.

Fill a 4-inch (10.16-cm.) length of 0.25-inch (0.62-cm.) tubing having a $\frac{3}{16}$ -inch (0.58-cm.) bore to a depth of 2 inches (5.08 cm.) with the wax by sucking it up into the tube while molten. Hold the thumb over the unfilled end of the tube and blow on the filled end until the wax has cooled sufficiently to retain its position in the tube. Then lay it down and allow to remain for a half hour to cool to room temperature, leaving it open at both ends. Fasten it to a thermometer so that the upper level of the wax is on a level with the water in the beaker. Raise the temperature at the rate of about 3° C. per minute, and make readings as follows:

1. Softening point = temperature at which wax becomes transparent.
2. Melting point = point at which mass first starts to rise in tube.

Taking Table I as a basis for comparison, in which tests were made on three samples of special waxes and three other standard waxes, the results obtained by all three methods show that:

1. Softening points can be determined in all cases by the float method.
2. Melting points can be determined in all cases by the float method, whereas they cannot be determined accurately by the capillary tube method.
3. Melting points can be determined with greater accuracy by the float method than by the other two methods.
4. The float method is more accurate for the determination of the melting point because the melting point is taken at an exact point rather than at a range of several degrees.

TABLE I. RESULTS OF TESTS

WAX	DROP METHOD		CAPILLARY TUBE		FLOAT TEST	
	S. P. ° C.	M. P. ° C.	S. P. ° C.	M. P. ° C.	S. P. ° C.	M. P. ° C.
I. Paraffin	...	56-58	..	54-56	..	56
II. Carnauba wax	...	85-87	..	84-86	..	86
III. Carnauba wax, refined	...	84-86	..	83-85	..	86
IV. Gelowax 1	60	78	?	56-58	59	78
V. Gelowax 2	60	95	?	55-57	60	95
VI. Gelowax 3	56-60	79-87	?	56	60	90

S. P. = softening point; M. P. = melting point.

RECEIVED March 22, 1932.

Determination of Total Solid Matter and Density of Egg White by Refractometer

H. J. ALMQUIST, F. W. LORENZ, AND B. R. BURMESTER, University of California, Berkeley, Calif.

DURING investigations dealing with the deterioration of eggs it became desirable to have a rapid method for estimating the total solid matter in natural egg white. It was found possible to use the index of refraction, obtained with a common type of refractometer, as a measure

the two methods was found to be satisfactory. Specific gravities of the egg white samples were determined by a specific gravity balance at 25° C.

The sum of the protein and mineral components has been plotted, as per cent total solids, against the index of refraction.

The relationship appears to be linear, as is also true for the relationship between specific gravity and index of refraction. To enable reconstruction of the graphs, the following points, taken accurately from the plots, are given:

INDEX OF REFRACTION n_{25}^D	TOTAL SOLIDS %	SPECIFIC GRAVITY d_{25}^{25}
1.3520	10.55	1.0312
1.3600	14.55	1.0442

Egg white may be considered to be protein, mineral, and water only, the mineral component of the white being a small and nearly constant fraction of the total (the ash obtained from the white amounted to 0.80 per cent on the average). For this reason the system behaves as a binary mixture. A linear variation such as that found is required by the Lorenz-Lorentz formula (1) for the specific refraction of binary mixtures where partial molal volumes may be considered constant.

Although the figures and data suggest that both the index of refraction and the

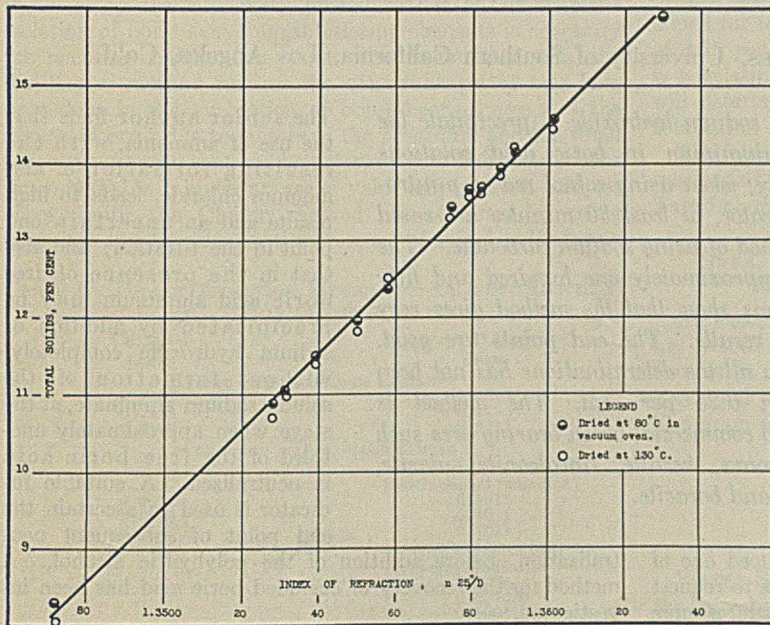


FIGURE 1. RELATIONSHIP OF TOTAL SOLIDS, DETERMINED BY TWO METHODS, TO INDEX OF REFRACTION IN NATURAL EGG WHITE

of this solid matter. Since many agricultural research stations about the country are engaged in studies of egg problems, it appeared that the method to be described might be of general interest and value.

In a previous paper from this laboratory (2) the use of the refractometer in studying the distribution of total solids between firm and liquid white has been described. This work has been repeated and extended over a greater range in so far as the relationship between refractive index and total solids is concerned. In addition, the densities of the samples of white were obtained.

The refractive index was measured at 25° C. with a Spencer refractometer, Abbé type. This may be done in a few seconds. The total solid matter in the samples of egg white was found in two ways—by drying in an oven at 130° C. and one atmosphere, and by drying at 80° C. under a vacuum of 29 inches of mercury. In each case the drying was continued until successive weighings showed a negligible decrease in weight. The agreement between

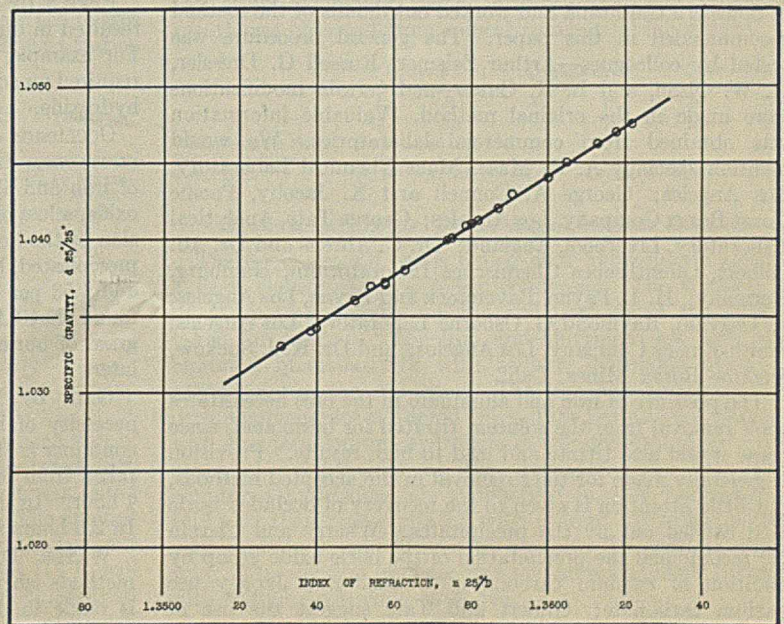


FIGURE 2. RELATIONSHIP OF SPECIFIC GRAVITY TO INDEX OF REFRACTION IN NATURAL EGG WHITE

specific gravity may serve with nearly equal accuracy as a measure of the total solids content, the use of the former proves much more convenient, as it may be determined with greater ease and speed and with only a drop or two of the sample. In conclusion, we wish to point out that it is fundamentally unsound to apply this method to a study of egg yolk or whole egg, since these mixtures contain more than two major components. This condition makes possible an

indefinite series of mixtures all of which may have the same refractive index.

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RECEIVED January 9, 1932. Contribution 15, Division of Poultry Husbandry, Agricultural Experiment Station, University of California.

Rapid Method for Determination of Boron

Suggested Procedure for Evaluation of Boron-Bearing Ores for Boron Content

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SOME years ago the senior author published a method for the evaluation of boron-bearing ores in his work on "Standard Methods of Chemical Analysis." The procedure followed the generally accepted principles for the evaluation of boronatrocalcite, borocalcite, boracite, and boron-bearing ores decomposed by hydrochloric acid, but was not adapted to higher grades of ore now found in California, or to concentrates. Considerable contrary opinions exist on the details for an exact and rapid method for the commercial evaluation of these ores, which induced one of the large shippers of the ore and ore concentrates to request the senior author to investigate the existing procedures more generally accepted as standards. The matter being of personal interest, the senior author undertook the work and carried out a series of tests in his laboratory at the University of Southern California and worked out details of the method recommended in this paper. The general procedure was tested by colleagues—Arthur Zeismer, Russell G. Dressler, H. W. Olson, and L. K. Gates—and certain modifications were made in the original method. Valuable information was obtained from commercial laboratories. We would mention specially A. R. Maas, Maas Chemical Laboratory, Los Angeles; George A. Connell and K. Jacoby, Pacific Coast Borax Company, Los Angeles; George Tate, Analytical Laboratory, Liverpool, England; Dr. C. Ahrens and Dr. Ad. Gilbert, Offentliches Chemisches Laboratorium, Hamburg, Germany; H. L. Payne, Baverstock and Payne, Los Angeles; A. Osgyani, Raymond G. Osborne Laboratory, Los Angeles; Smith-Emery Company, Los Angeles; and Dr. K. J. Suckow, Suckow Borax Mines, Calif.

The presence of iron and aluminum in the ores necessitates their removal from the solution titrated for boric acid, since these would also titrate and lead to high results. Provision is generally made for their removal in the accepted methods, but little attention is given to the recovery of occluded boric acid carried out by the precipitates. Wherry and Chapin (2) recommend the precipitation of the boric oxide group by addition of calcium carbonate; Connell and Jacoby use barium carbonate; Gilbert and Tate suggest the use of sodium carbonate. Ammonium hydroxide, magnesium carbonate or oxide, and sodium hydroxide have been used.

By using sodium hydroxide to precipitate the iron and aluminum in boric acid solutions quantitatively, when using sofrol red or p-nitrophenol indicator, at least 30 minutes are saved over the method of using sodium carbonate. The results of approximately one hundred and fifty determinations show that the method gives very satisfactory results. The end points are good. The error in all the determinations has not been greater than 0.25 per cent. The method is applicable to commercial boron-bearing ores such as crude borax, kernite, tinalconite, ulexite, colemanite, and boracite.

The senior author finds that the use of ammonia, with the resulting formation of ammonium chloride, leads to high results and an uncertain end point in the titration; and also that in the presence of free boric acid aluminum may be precipitated by addition of sodium hydroxide completely, without formation of the soluble sodium aluminate, at the stage when approximately one-third of the free boric acid is neutralized. A suitable indicator is used to ascertain the end point of subsequent neu-

tralization, before addition of the polyhydric alcohol. A method for the recovery of occluded boric acid has been investigated.

RECOVERY OF OCCLUDED BORIC ACID

EFFECT OF IRON AND ALUMINUM SALTS. A positive error resulted in direct proportion to the amount of salts present. For example, 1 gram of aluminum chloride (aqua) added required an additional titration of 25.3 ml. of 0.552 *N* sodium hydroxide.

OCCLUSION OF BORIC ACID BY IRON AND ALUMINUM PRECIPITATES. In a sample of "tincal" containing 1.9 per cent of iron and aluminum oxides and over 44 per cent of boric oxide, a loss of 1.15 per cent of boric oxide occurred by occlusion of the boric acid by the iron and aluminum hydroxides precipitated, by sodium carbonate solution washed six times; and 1.53 per cent by the precipitate washed twice. It was found that 0.2355 gram of aluminum hydroxide held 0.1922 gram of boric oxide, washed twice. Further results appear later.

GAIN OF MOISTURE IN BORATE CONCENTRATES. The necessity of keeping the representative sample in a closed container is shown by the following tests: A 5-gram sample taken from material as received was exposed to the air for 1 hour. In this time the sample gained 24.5 mg. of moisture. In 2.5 hours it had gained 66.1 mg., or over 1 per cent.

WATER DISPLACEMENT OF CLAY RESIDUE. In rapid methods where the clay is allowed to settle and the solution is made to definite volume, an allowance is made for the volume occupied by the residue in the flask. The senior author found that 10.08 grams of this residue in the analysis

of "tincal" occupied a space of 4.8 ml., or approximately 0.5 ml. per gram of residue.

PRECIPITATION OF ALUMINUM HYDROXIDE BY SODIUM HYDROXIDE IN PRESENCE OF FREE BORIC ACID. The sample from the acid extraction of the borate concentrate was titrated in the presence of phenolphthalein indicator to a faint pink color (the polyhydric alcohol being omitted), aluminum hydroxide was completely precipitated, and no evidence of sodium aluminate in the filtrate was obtained. It was found that approximately one-third of the boric acid in the solution was neutralized at this stage, and the free boric acid evidently prevented the formation of the soluble sodium aluminate.

RAPID METHOD VS. CHAPIN'S DISTILLATION METHOD. Some doubt has been expressed regarding direct titration methods by the customary procedure. It is felt that the isolation of boric acid from interfering elements is necessary for accurate results. Any one who is familiar with the distillation method realizes the disadvantages of this long procedure in the evaluation of boron-bearing ores and the danger of error due to factors in the procedure and the small amounts of boron that can be determined. The comparisons given in Table I, however, are of value and interest. Better checks with the Chapin method are obtained by using mannitol and titration in the presence of sofnol indicator.

TABLE I. DIRECT TITRATION METHOD VS. CHAPIN'S DISTILLATION METHOD^a

CHAPIN'S Gram	DIRECT TITRATION Gram
BORIC OXIDE, 0.5-GRAM SAMPLE ^b	
0.2195	0.2221
0.2189	0.2228
0.2199	0.2213
PURE BORIC ACID, 0.1-GRAM SAMPLE	
With glycerol and <i>p</i> -nitrophenol indicator	
0.0972	0.1012
0.0966	0.1011
0.0967	0.1011
With mannitol and sofnol indicator	
	0.0996
	0.0996+
	0.1005
	0.1002

^a Data by H. W. Olson.

^b In Chapin's method, 0.5 gram of ore; in direct titration method, aliquot portion of sample equivalent to 0.5 gram.

The results of tests reported in Table II show the degree of precision in checks that can be expected by direct titration of the solution containing the borate.

TABLE II. COMPARISON OF RESULTS OF DIRECT TITRATION OF SOLUTION CONTAINING BORATE

CRUDE CRUSHED ORE 30-gram sample %	COARSE DUMPLINGS 10-gram sample %	FINE DUMPLINGS 10-gram sample %	CONCENTRATE 10-gram sample %	CONCENTRATE AT MINE 10-gram sample %
25.00	13.40	28.28	44.30 ^a	48.20
25.52	13.45	28.80	44.12	48.38
			44.10	
			44.38	
			44.42 ^b	
			44.54	
			44.25	

^a Data by Russell G. Dressler.

^b Data by H. W. Olson.

OCCLUSION OF BORIC ACID. In studying the occlusion of boric acid by aluminum hydroxide when precipitated with sodium hydroxide, which has been mentioned, it was found that definite amounts of the acid are occluded. The amount depends on the concentration of the solution and the per cent of aluminum present. From the data in Table III it will be seen that if the amount of aluminum present is less than 0.2 per cent, the occluded boric acid need not be run when the concentration of the sodium hydroxide reagent is above 0.5 normality.

TABLE III. OCCLUSION OF BORIC ACID BY ALUMINUM HYDROXIDE^a

SAMPLE	(0.6184-gram sample taken)			AVERAGE H ₂ BO ₃ OCCLUDED %
	ALUMINUM ADDED %	H ₂ BO ₃ OBTAINED %	H ₂ BO ₃ OCCLUDED %	
1	None	100.00 ^b	0.00	0.00
2	None	100.00 ^b	0.00	0.00
3	0.2	99.75	0.25	0.25
4	0.2	99.75	0.25	0.25
5	0.5	99.25	0.75	0.62
6	0.5	99.50	0.50	0.62
7	1.0	98.55	1.45	1.45
8	1.0	98.55	1.45	1.45
9	2.0	97.34	2.66	2.78
10	2.0	97.10	2.90	2.78

^a Data by Arthur Zeisler.

^b Standard solution.

In the analysis of ten synthetic samples, including two blanks, the occluded boric acid was recovered and the amount added for total percentage of boric acid. A maximum error of 0.25 per cent was obtained. Since aluminum hydroxide is a gelatinous substance, the amount present in a sample will determine the length of time required in filtering the solution in order to obtain all of the occluded boric acid.

The following report of analysis of a California concentrate received at Liverpool, England, was received from the George Tate Laboratory:

	SCOTT'S METHOD	METHOD BY TATE
Lot A, % B ₂ O ₃	42.40	42.50
Lot B, % B ₂ O ₃	42.50	42.25

An excess of acid used in the original digestion of the ore has practically no effect on results, this excess being taken care of in the procedure. The following results from the Raymond G. Osborne Laboratory supports the statement. Ten-gram samples were examined.

AMT. OF N HCl Cc.	BORIC OXIDE %
50	43.94
75	44.15
100	44.15

WATER-SOLUBLE BORATES. It may be desired to evaluate the ore by determining its water-soluble content. The California deposits of sodium borates are largely water-soluble. The residue must be examined also if total borate is desired. The water extraction is made in a covered beaker, the reflux condenser being unnecessary.¹ The following report was obtained from a local commercial laboratory.

	SCOTT'S METHOD		GILBERT'S METHOD		OSBORNE'S METHOD	
	A	B	A	B	A	B
Water-soluble B ₂ O ₃	46.35	46.24
B ₂ O ₃ in residue	1.32	1.65
Total B ₂ O ₃	47.70	47.89	48.04	48.08	48.05	47.84

DETERMINATION OF TOTAL ACID-SOLUBLE BORATE

The finely ground ore is boiled with hydrochloric acid in a flask connected to a reflux condenser. The solution is made up to a definite volume and portions of the filtrate taken for analysis. The iron and aluminum are first precipitated quantitatively with sodium hydroxide using *p*-nitrophenol as the indicator. The iron and aluminum hydroxide precipitate is filtered off, and the boric acid is titrated with standard sodium hydroxide in the presence of glycerol, using phenolphthalein as the indicator. The iron and aluminum hydroxides are redissolved in 6 *N* hydrochloric acid and then reprecipitated with sodium hydroxide added very cautiously, and filtered to separate the occluded boric acid. The solution from the iron and alumina is now titrated with sodium hydroxide as above.

¹ Even in the presence of acid practically no loss of boron occurs at temperatures just below boiling. This confirms the results of Dodd and Scott (1).

ACID EXTRACTION. The method is applicable for the determination of total boric acid in borates of sodium, calcium, and magnesium in materials such as crude borax, tincalconite, kernite, boracite, ulexite, colemanite, etc. Silicoborates required a preliminary fusion with sodium carbonate. The acid residue should be examined for these. Iron, aluminum, ammonium salts, and substances other than boric acid should be absent from the solution if they react with sodium hydroxide.

REAGENTS

1 or 0.5 *N* HCl
 1 or 0.5 *N* NaOH (carbonate-free)
 6 *N* HCl (acid of constant boiling point is satisfactory)
 50% solution of NaOH (carbonate-free)
 Indicators: *p*-Nitrophenol (saturated water solution)
 Sofnol red No. 1
 Phenolphthalein (1% in 50% alcohol solution)
 Mannitol or glycerol
 Water, carbon dioxide-free

A five-gram sample, finely ground, is placed in a 250-cc. volumetric flask, 15 to 20 cc. of 6 *N* hydrochloric acid are added, together with an equal volume of water, and the flask connected to a reflux condenser. The mixture is heated to boiling and boiled for 20 to 25 minutes. After allowing to cool slightly, 75 cc. of water are poured into the flask through the condenser tube, the solution mixed, and then the heating and boiling repeated for 10 to 15 minutes. The flask is again allowed to cool slightly and about 50 cc. of water poured through the condenser tube into the flask. The condenser is disconnected, and the flask placed in a cold water bath and cooled.² Water is now added to the 250-cc. mark, and if necessary an additional amount to allow for the volume occupied by the residue.³ After the residue has settled, the clear solution in the quantity desired is decanted through a dry filter into a dry, clean beaker, and portions of this filtrate taken for analysis. Fifty cubic centimeters are equivalent to 1 gram of the original sample.

Of the filtrate, 50 or 100 cc. are taken, according to the strength of the reagents used, and placed in 400-cc. beakers.

REMOVAL OF IRON AND ALUMINUM. To the boric acid solution in a beaker are added 3 to 4 drops of sofnol red or *p*-nitrophenol indicator. Standard sodium hydroxide is added cautiously until the yellow color of the indicator remains. All the iron and aluminum will be precipitated at this point. The solution is heated gently, then allowed to stand for several minutes. The iron and aluminum hydroxide are filtered off and washed with hot water, and the filtrate and washings titrated for boric acid according to the procedure given under titration of boric acid below.

RECOVERY OF OCCLUDED BORIC ACID. The iron and aluminum hydroxide carry out very appreciable quantities of boric acid when precipitated in the presence of a large excess of this acid. If the amount of these hydroxides is appreciable, the recovery of boric acid is essential for accurate results.

The hydroxides are dissolved in the filter by addition of 6 *N* hydrochloric acid, added in sufficient excess. The acid solution is caught in a beaker together with hot washing of the filter. Three to four drops of sofnol red or *p*-nitrophenol are added to the solution, and sodium hydroxide (50 per cent solution) is now added dropwise until about neutral, then 0.5 *N* sodium hydroxide until the yellow color of the indicator remains. The solution is heated gently, then allowed to stand for several minutes. The iron and aluminum hy-

droxides are filtered off, and the precipitate is washed with warm water. The filtrate is acidified with 0.5 *N* hydrochloric acid, the solution neutralized to sofnol red or *p*-nitrophenol indicator by addition of sodium hydroxide drop by drop, and the boric acid determined by titration with sodium hydroxide in the presence of mannitol or glycerol with phenolphthalein indicator. Time is saved by carrying out this titration separately from the main solution.

TITRATION OF BORIC ACID. The solution from the precipitation of iron and aluminum is acidified with hydrochloric acid and then just neutralized cautiously with standard sodium hydroxide to the yellow color of sofnol red or *p*-nitrophenol. About 10 drops of phenolphthalein indicator and 25 to 50 cc. of neutral glycerol or mannitol (according to the amount of boric acid titrated) are added, and then the standard alkali added until a distinct reddish pink color appears. The true end point for boric acid is pH 11.

NOTE. The boric acid in the solution recovered from the iron and aluminum precipitate is determined also as directed above, and the amount added for total percentage of boric oxide.

1 cc. of *N* = 0.03482 g. B₂O₃; or 0.9536 g. Na₂B₄O₇ · 10H₂O; or 0.0618 g. H₂BO₃
 1 cc. of 0.5 *N* NaOH = half above amounts

The acid extraction generally effects complete solution of the borates available in crude borate minerals. Should silicoborates be present, a fusion of the acid residue should be made with sodium carbonate flux, and the fusion examined for borates.

The reflux condenser is used to avoid loss of the boric acid by volatilization. (The 6 *N* hydrochloric acid is approximately acid of constant boiling point.) This is unnecessary in water extractions for water-soluble borate.

The removal of iron and aluminum from the extract is necessary, as iron and aluminum salts lead to high results for boric acid by the action of their combined acid with the standard base.

Definite amounts of borate are invariably carried out by the iron and aluminum hydroxides, so that a recovery must be effected if the precipitates are present in appreciable amounts.

The isoelectric point of aluminum is between pH 6 and 7.5, and it is at this point that the aluminum compound is least soluble. Some aluminum hydroxide will go into solution if too much sodium hydroxide is added to precipitate the aluminum.

Therefore, care must be exercised in exactly neutralizing in the presence of a suitable indicator.

The end point in the presence of phenolphthalein is a combination of the two colors yellow and pink, and is a distinct reddish pink color. The sofnol red or *p*-nitrophenol gives a distinct yellow color in alkaline solutions. Both indicators are colorless in acid solutions.

A concentrated solution of sodium hydroxide is used to neutralize the 6 *N* hydrochloric acid so as not to increase the volume for filtering. Other strengths or concentrations may be used.

Neutral glycerol is prepared as follows: To 1000 cc. of glycerol add 4 to 5 cc. of phenolphthalein and neutralize with regular sodium hydroxide reagent. Owing to the formation of acid, the color will fade, but addition of sodium hydroxide from time to time will keep the color pink. A sharper end point is obtained with mannitol.

If end points are run over, back titrations are possible with either indicator.

If a carbonate is used in the precipitation of iron and aluminum, it should be removed by acidifying the solution and gently heating at a "simmering" temperature for 10 to 15 minutes in a covered beaker. Loss of boron occurs if the beaker is not covered. The presence of carbonic acid in the solution leads to an error in the boric acid titration.

The use of sodium hydroxide in place of sodium carbonate in the precipitation of iron and aluminum avoids the necessity of removing carbon dioxide from the solution.

LITERATURE CITED

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- (2) Wherry, E. T., and Chapin, W. H., *J. Am. Chem. Soc.*, 30, 1687 (1908).

² The addition of 2 to 5 grams of sodium chloride hastens settling of the suspended material. The salt does not interfere with the accuracy of the method.

³ One gram of the residue occupies a volume slightly less than 0.5 cc. Generally the amount is so small that this additional water is unnecessary.

Determination of Carbon Dioxide and Titratable Base in Sea Water

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THAT carbon dioxide and carbonate salts play an important role in numerous chemical reactions and equilibria of sea water has long been recognized by oceanographers. As a consequence the quantities and chemical relations of these substances in sea water have been investigated during many years by a number of workers and many methods for the determination of carbon dioxide and titratable base have been proposed. In spite of this, the existing methods for the direct determination of carbon dioxide in sea water are too cumbersome and time-consuming, especially when it is realized that most oceanographic investigations require numerous analyses, often under difficult working conditions. Many titration methods have been used for determining the titratable base content and, in some cases, carbonate and bicarbonate, but these methods have not been sufficiently standardized and there is no unanimity of opinion as to the exactness and significance of the results obtained.

At the Scripps Institution information concerning the free and combined forms of carbon dioxide in the adjacent sea was desired in connection with studies of the biological environment and in the course of investigations of the calcium carbonate equilibrium of sea water. The authors have found that of the factors governing this equilibrium, the titratable base and the total carbon dioxide, together with the hydrogen-ion concentration, seem to be most readily susceptible of exact measurement. In a subsequent article (7) it will be shown that a distinct advance in the solution of the carbonate equilibrium problem has been made by expressing the buffer mechanism of sea water in terms of pH, carbon dioxide, and titratable base.

Accordingly, during the past several years, work has been carried out in this laboratory to develop a relatively simple and rapid method for the determination of total carbon dioxide in sea water, and we believe that this has been accomplished by adapting the Van Slyke (23) manometric method to the purpose. At the same time a critical study has been made of a method for measuring the titratable base content and of a differential titration method for determining the different forms of carbon dioxide.

DETERMINATION OF TOTAL CARBON DIOXIDE

Up to the present the total carbon dioxide in sea water has been determined, in practically all cases, either by titration

A semi-micromethod for determining the total carbon dioxide content of sea water with the portable manometric apparatus of Van Slyke is described. It is relatively simple, rapid, and suitable for work on board ship, and gives results reproducible to 1 per cent or better. A table of factors for converting the analytical data into milliliters, milligrams, or millimoles per liter of sea water is given.

The results of critical studies of the differential titration method for determining carbonate, bicarbonate, and free carbon dioxide in sea water are reported. When phenolphthalein and methyl orange are used as indicators and when the titrations are carried to end points in accord with theory, this method gives results reproducible to within 1 per cent, and the total carbon dioxide found agrees to about 1 per cent with that obtained with the Van Slyke apparatus.

It is shown that for sea water more alkaline than pH 7.8, the difference between the base titration value and the total carbon dioxide gives the carbonate content.

or by acidifying the water and expelling the gases by boiling or aerating, the quantity of carbon dioxide in the expelled gases being ascertained by one of several methods. The boiling-out method was used by Tornøe (20), who acidified the water with sulfuric acid and caught the carbon dioxide in a solution of barium hydroxide of known strength. Wells (25) determined carbon dioxide in water from the Gulf of Mexico by boiling 250 ml. of acidified water for some time and washing out the residual gas with a stream of carbon dioxide-free air, the carbon dioxide evolved being trapped in soda-lime weighing tubes. Thompson and his co-workers (19) used 4-liter samples of water which were acidified with hydrochloric acid and the carbon dioxide expelled into standard barium hydroxide solution by aerating for 24 hours. In more recent determinations in Thompson's laboratory (18), the gas was

driven off by boiling, but the volume of the sample used is not stated. The principle of the Toricellian vacuum was introduced by Petterson (15) who also added the feature of washing out the residual carbon dioxide with a stream of hydrogen generated within the water sample itself. Subsequently many investigators, among whom may be mentioned Dittmar (3) and Fox (5), have modified and improved Petterson's method. The best method of this type is probably that developed by Fox.

The above methods all suffer from one or more defects which render them impracticable for use in most oceanographic investigations. The apparatus required is complicated and consequently the technic difficult or, on board ship, perhaps impossible; the time needed for a determination is too great to permit numerous analyses, the minimum time required, that of Fox's method, being a half hour or more; and finally, large water samples, ranging from 100 to 4000 ml. are necessary.

In many instances the necessity of using large samples of water is perhaps of no moment, but where analyses are to be made on water from below the sea surface or where many substances are to be determined on each sample, it becomes decidedly important to keep the volume of water required for each analysis down to a small figure. It is obvious that before we can expect adequate information concerning the variation with depth, season, and other factors of the quantity of carbon dioxide in various parts of the sea, a relatively simple and rapid method of analysis of the micro type must be developed. This is in keeping with the trend of development

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of other chemical methods employed in oceanographic studies.

A start in this direction was made by McClendon (13) who adapted the Van Slyke volumetric blood gas apparatus to sea water, making use of a 10-ml. sample. With this apparatus the dissolved gases are liberated by forming a vacuum, and their volume is subsequently measured at atmospheric pressure. This method falls far short of the criterion of simplicity, however, as is shown by the following quotation from McClendon (13, p. 259).

With careful manipulation, an accuracy of 0.5 per cent was attained. In order to accomplish this, a large number of corrections had to be applied, and since these corrections vary so much for different determinations, . . . they cannot be combined in a table such as Van Slyke has made for blood, . . .

The new manometric blood gas apparatus of Van Slyke and Neill (23), in which the gas is liberated in a Toricellian

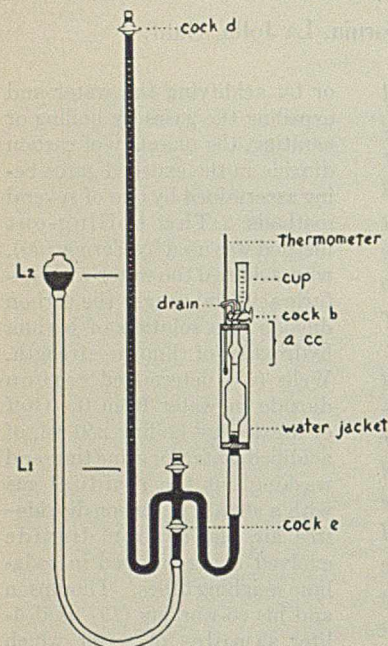


FIGURE 1. DIAGRAM OF GLASS PARTS OF APPARATUS

vacuum, then reduced to a constant volume and its pressure determined, instead of measuring its volume at atmospheric pressure as in the old type of apparatus, offered the possibility of being adapted to the determination of carbon dioxide in sea water with sufficient speed and accuracy to meet the requirements of oceanographic work. Experiments with this apparatus were begun in this laboratory several years ago, and since then several hundred carbon dioxide determinations on sea water have been made. The apparatus, technic, and correction factors used are described below.

The apparatus used is the portable model (22), with a 50-ml. reaction chamber. A working diagram of the glass parts is shown in Figure 1. Before adding the sample, the cup is filled to the 6-ml. mark with an approximately normal solution of lactic acid. After lowering the mercury bulb to the position L_1 , cock e is opened and then the lactic acid slowly admitted into the reaction chamber by opening cock b . Cock b is again closed and sealed with a few drops of mercury before air is drawn into the apparatus, then the mercury is lowered until it fills only about half the reaction chamber, when cock e is closed. The chamber is then shaken slowly for about a minute and the lactic acid expelled by placing the mercury bulb at the level L_2 , and opening cock e and then cock b to the drain. Care is taken to close b before the mercury overflows. The washing is then repeated with an equal volume of distilled water. At the end of this washing a little mercury is allowed to run into the drain tube to make a mercury seal.

The apparatus is now ready for introducing the sample. About 1 ml. of mercury is caused to run into the cup by opening cock e , placing the mercury bulb at L_2 , and opening b carefully. Any water entering the cup with the mercury is removed with a piece of filter paper. For measuring and introducing the water sample, a 10-ml. pipet, accurately calibrated to deliver between marks and with a stopcock sealed to either the upper or lower end, is used (see Figure 2). This pipet is rinsed twice with the water to be analyzed and filled to above the 10-ml. mark. A rubber tip like that shown in Figure 2 is placed on the end of the pipet, and the level of the sample adjusted to the upper calibration

mark. The stopcock is then closed and, if a drop of water hangs from the tip, it is wiped off. The tip of the pipet is now introduced into the cup beneath the mercury, and fitted firmly against the bottom to make an air-tight seal. If an air bubble is trapped during the insertion of the pipet, it can be observed in the capillary portion of the cup and should be removed by gently manipulating the leveling bulb with cocks e and b open.

The mercury bulb is now placed at L_1 , cock e is opened, and then the stopcock of the pipet. Lastly cock b is carefully opened and the sample allowed to run slowly into the reaction chamber until the lower calibration mark of the pipet is reached, when cock b is closed. The pipet is then closed and quickly removed without allowing the tip to touch the sides of the cup. One milliliter of carbon dioxide-free 0.2 *N* lactic acid² is now run into the cup on top of the mercury. If air bubbles are noticed in the capillary part of the cup, they are removed by means of a wire, and then the mercury and acid are carefully lowered into the reaction chamber by opening cock b . The leveling bulb is at L_1 and cock e is open.

With a pipet a few drops of mercury are introduced into the cup to make a leak-proof seal. The leveling bulb is lowered until the mercury in the reaction chamber reaches the 50-ml. mark. Cock e is then closed, the leveling bulb placed at L_1 , and the mechanism which shakes the reaction chamber is started. Shaking is discontinued after 3 minutes when, with the mercury bulb still at L_1 , cock e is opened and the mercury allowed to rise, rapidly at first and then more slowly, until the liquid is exactly on the 2-ml. mark. Cock e is then closed and the manometer reading is taken. This reading is recorded as p_1 . Oscillation of the gas is to be avoided (23).

After reading the manometer, 0.2 ml. of 5 *N* sodium hydroxide is introduced into the cup over the mercury seal, and after making sure that no gas bubbles are in the capillary, is run into the reaction chamber by opening cock b , cock e remaining closed. After introducing the alkali, a new mercury seal is made, cock e is opened, and the mercury in the chamber lowered to about the 25-ml. level. Cock e is then closed and the reaction chamber agitated gently for about 1 minute, after which e is again opened and the liquid allowed to ascend to the 2-ml. mark, when the manometer is read, the reading being recorded as p_2 .³ The thermometer in the water jacket surrounding the reaction chamber is now read. The two manometer readings and the thermometer reading comprise the experimental data required for calculating the carbon dioxide content of the sea water analyzed.

From the manometer readings and the corresponding temperature, the quantity of carbon dioxide in the sample analyzed can be computed by means of the following equation, taken from Van Slyke and Neill (23):

$$V_{0^{\circ}, 760} = P \times \frac{ai}{760(1 + 0.00384t)} \times \left(1 + \frac{S}{A - S} \alpha'\right)$$

where $V_{0^{\circ}, 760}$ = volume of carbon dioxide measured under standard conditions; P = partial pressure of carbon dioxide—i. e., $p_1 - p_2$; a = volume of gas at which the pressure is measured; i = reabsorption coefficient of the gas in the liquid in the reaction chamber; t = temperature at which the manometer readings are made; S = volume of sample and reagents; A = volume of extraction chamber; and α' = the distribution coefficient of carbon dioxide between the gas and liquid phases.

Table I. FACTORS FOR CALCULATING CO₂ CONTENT OF SEA WATER

(When $A = 50$ ml., $S = 11$ ml., $a = 2$ ml., and sample = 10 ml.)

TEMP. ° C.	α'	FACTORS FOR CO ₂ PER LITER OF SEA WATER		
		Ml.	Mg.	Millimoles
15	0.946	0.3209	0.6341	0.01442
16	0.922	0.3176	0.6279	0.01427
17	0.901	0.3151	0.6228	0.01416
18	0.8815	0.3125	0.6178	0.01404
19	0.864	0.3103	0.6134	0.01394
20	0.848	0.3079	0.6086	0.01383
21	0.829	0.3057	0.6042	0.01373
22	0.812	0.3033	0.5995	0.01362
23	0.794	0.3011	0.5950	0.01352
24	0.772	0.2984	0.5899	0.01341
25	0.756	0.2962	0.5854	0.01331
26	0.737	0.2940	0.5810	0.01321
27	0.720	0.2918	0.5765	0.01311
28	0.701	0.2896	0.5723	0.01301
29	0.683	0.2873	0.5676	0.01290
30	0.665	0.2854	0.5641	0.01282

² The carbon dioxide is removed in the Van Slyke apparatus after which the solution is kept under oil. (See Van Slyke and Neill, 23.)

³ To this reading Van Slyke and Neill (23) apply a correction, c , for the effect of the absorbent solution, but when only 0.2 ml. of sodium hydroxide solution is used the effect becomes negligible and no correction is necessary.

When the determination is made according to the procedure described above—i. e., when $A = 50$ ml., $S = 11$ ml., $a = 2$ ml., and the sample analyzed = 10 ml.—the factors given in Table I can be used for making the calculations. Volumes other than those given may be used provided the ratios $A:S:a$: sample remain unchanged. Multiplying $p_1 - p_2$ by the appropriate factor for the temperature at which the manometer readings were made will give the quantity of carbon dioxide per liter, in terms of milliliters, milligrams, or millimoles, respectively, in the sea water analyzed.

In computing the factors in this table, the value of i was taken as 1.017 (24) and applies only when the gas pressure is measured at one-twenty-fifth the volume of the reaction chamber—i. e., at 2 ml. in a 50-ml. chamber. The values for α' were computed from data given by Bohr (1) for the solubility of carbon dioxide in sodium chloride solutions, and are considered sufficiently accurate for sea water. In order to facilitate the computation of factors for apparatus for which the factors in the table cannot be used, Table I also gives values of α' for temperatures between 15° and 30° C.

Determinations of carbon dioxide in sea water by the procedure outlined above are readily reproducible to within 1 per cent, and the results obtained agree well with those obtained by other methods (see Tables II and III). Approximately 15 minutes are required to complete an analysis. The apparatus can readily be mounted on board ship, thus providing a means for making accurate and rapid determinations of carbon dioxide on extended cruises.

TABLE II. COMPARISON OF VAN SLYKE AND TITRATION METHODS ON SAMPLE TAKEN FROM SCRIPPS INSTITUTION PIER

TITRATABLE BASE	CARBON DIOXIDE BY TITRATION			Δ CO ₂	
	Carbonate	Bicarbonate	Total	CO ₂ BY VAN SLYKE	TITRATION
Milliequivalents	Mg./liter	Mg./liter	Mg./liter	Mg./liter	
2.291	11.89	77.03	88.92	89.59	0.67
2.279	11.37	77.55	88.92	89.66	0.74
2.279	11.37	77.55	88.92	88.95	0.03
2.291	11.89	77.03	88.92	89.78	0.86
2.291	12.20	76.41	88.61	89.78	1.17
2.279	11.89	76.52	88.41	89.49	1.08
2.303	12.20	76.93	89.13	89.31	0.18
2.303	11.68	77.96	89.64	90.02	0.38
2.284	11.89	76.72	88.61		
2.279	11.89	76.52	88.41		
2.303	12.20	76.93	89.13		
Mean	2.289	11.86	77.01	88.87	0.64

TABLE III. COMPARISON OF VAN SLYKE AND TITRATION METHODS ON SAMPLES FROM DEPTHS INDICATED 10 MILES OFF SCRIPPS INSTITUTION PIER ON AUGUST 20, 1931

DEPTHS Meters	TITRATABLE BASE	CARBON DIOXIDE BY TITRATION			Δ CO ₂	
		Carbonate	Bicarbonate	Total	CO ₂ BY VAN SLYKE	TITRATION
Milli- equivalents	Milli- equivalents	Mg./liter	Mg./liter	Mg./liter	Mg./liter	
0	2.244	8.07	82.70	90.77	90.19	-0.58
5	2.232	7.76	82.80	90.56	90.77	+0.21
10	2.232	7.76	82.80	90.56	90.77	+0.21
15	2.237	7.76	83.01	90.77	91.45	+0.68
20	2.232	8.28	81.76	90.04	90.44	+0.40
25	2.232	7.76	82.80	90.56	90.76	+0.20
30	2.232	8.07	82.18	90.25	90.83	+0.58
35	2.232	7.76	82.80	90.56	90.68	+0.12
40	2.244	6.21	86.42	92.63	91.40	-1.23
50	2.244	5.69	87.46	93.15	94.46	+1.31
60	2.244	4.14	90.56	94.70	95.64	+0.94
75	2.249	2.58	93.87	96.45	96.61	+0.16
100	2.256	2.07	95.22	97.29	97.86	+0.57
150	2.256	1.04	97.29	98.33	99.71	+1.38
200	2.279	0.00	100.39	100.39	101.20	+0.81
		Free CO ₂				
250	2.291	0.80	100.91	101.71	102.35	+0.64
300	2.291	2.00	100.91	102.91	101.98	-0.93
400	2.298	2.00	101.22	103.22	104.05	+0.83
500	2.303	3.60	101.43	105.03	105.06	+0.03

MEASUREMENT AND SIGNIFICANCE OF TITRATABLE BASE OF SEA WATER

One of the most readily determined chemical properties of sea water is the amount of base which can be titrated with a strong acid to the turning point of some appropriate in-

dicator. Such titrations have long been in use, but there still remain many disputed points as regards both the methods and the significance of the results.

Even the names that have been given to the titratable base of sea water are at present not wholly satisfactory. By Tornøe (20), Fox (5), Ruppin (16), Buch (2), Kändler (10), and others it is designated as the "alkalinity," a term which would ordinarily suffice were it not that it is sometimes applied to the hydroxyl-ion concentration of sea water. McClendon (14) uses the expression "alkaline reserve," but this has a specific meaning in blood chemistry which is not equivalent to the titratable base of sea water. In a recent article, Thompson and Bonnar (18) propose the term "buffer capacity," but we feel that this may be confused with Van Slyke's (21) "buffer value" or "buffer index," which is defined as the rate of change of pH with the addition of alkali or acid and is obviously not comparable to the titratable base. Since none of the above terms appears to be entirely satisfactory, we are using the expression "titratable base" to designate the base combined with weak acid radicals in sea water, or, stated in another way, the quantity of base which can be titrated with a strong acid when the titration is carried to a point at which all the weak acid radicals have been replaced by the acid added.

We may now turn to a consideration of the methods in use for determining the titratable base. These may be grouped into back titration and direct titration methods. In the back titration methods a measured quantity of strong acid, in excess of the amount required to break up the salts of the weak acids, is added to a sample of sea water, the carbon dioxide liberated from the carbonates is boiled off, and the excess acid is titrated. For this titration, Tornøe (20) employed sodium hydroxide, and Fox (6) barium hydroxide, both using phenolphthalein as indicator. Ruppin (16) determined the excess acid by titrating the iodine liberated on the addition of a mixture of potassium iodide and potassium iodate. Thompson and Bonnar (18) have recently described a method whose principle is "to add a measured quantity of standard acid to a known amount of freshly sampled sea water, determine the hydrogen-ion concentration of the resultant solution, using special standards for comparison, and calculate the amount of acid neutralized." The pH is determined colorimetrically, the standards being prepared by adding known quantities of standard acid to neutralized sea water of the same chlorinity as the water analyzed.

In the case of the direct titration methods, standard acid is added to the turning point of an appropriate indicator, usually methyl orange. McClen-

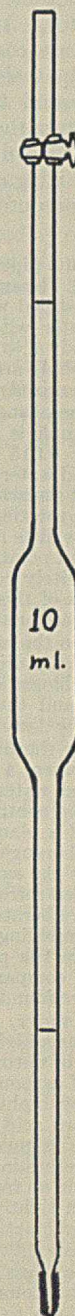


FIGURE 2. PIPET FOR MEASURING AND INTRODUCING WATER SAMPLE

don (14) modified this procedure by boiling off the carbon dioxide during the titration and using bromocresol purple as indicator. McClendon states that his method gives slightly higher results than does the usual back titration to the turning point of phenolphthalein.

DETERMINATION OF CARBON DIOXIDE BY TITRATION

The classical procedure, based on the work of Lunge (12) and of Küster (11), for determining the carbonate and bicarbonate content of natural water, is to titrate with standard hydrochloric or sulfuric acid to the turning point of phenolphthalein, then to add methyl orange (or a similar indicator), and continue the titration to the turning point of the latter indicator. According to the theory of this method, the carbonate content of the water can be computed from the phenolphthalein titration and the bicarbonate content from the second titration, whereas the total titration gives a measure of the titratable base. This method has been used by Dole (4) and for some years at the Scripps Institution for determining carbon dioxide in sea water. In this laboratory the procedure is as follows:

With a pipet a 100-ml. sample of sea water is measured into a 250-ml. Florence flask which has been rinsed with carbon dioxide-free distilled water, care being taken to keep the contact of the sea water with air at a minimum. While the pipet is being emptied, 4 to 6 drops of phenolphthalein (1 per cent solution in alcohol) are introduced into the flask, so that the indicator will be mixed with the sample without additional stirring.

If the phenolphthalein shows more than a faint trace of color, the sample is titrated with standard hydrochloric acid, approximately 0.015 *N*, using for comparison a blank of 100 ml. of distilled water in a flask similar to the one containing the sample. At first the acid is added rapidly and is mixed with the sample by gently rotating, rather than by shaking the flask, in order to have as little contact as possible between the air and the sample. The end point is taken as the last faint color before the solution is definitely colorless. A number of times we have determined the pH of this end point and found it to be 7.70 ± 0.05 , when corrected for salt effect.

When the sample is acid to phenolphthalein, it is titrated with standard sodium carbonate of about the same normality as the hydrochloric acid. This titration is carried to the same end point and the same precautions against contact with air are taken as described for the hydrochloric acid titration.

After the buret reading for the phenolphthalein titration has been taken, 4 drops of methyl orange solution (0.05 per cent in distilled water) are added to the sample in the flask and the titration continued until the color of the methyl orange matches that of a blank. This blank is prepared by adding 4 drops of methyl orange to 100 ml. of a sodium chloride solution of approximately the same concentration as the sea water to be titrated, and then introducing about the same quantity of carbon dioxide that is liberated in the sample during the titration. It appears that bubbling air from the lungs through the solution will produce the proper concentration of carbon dioxide. The use of this comparison solution was introduced by Küster (11), and we have found its pH to be close to 4.5.

Sea water, such as may be used for experimental purposes, that has a higher or lower carbon dioxide content than ordinarily found in nature, should be sampled under oil to prevent loss or gain of carbon dioxide through contact with air. When making the phenolphthalein titrations of such water, a portion of the standard acid or alkali should be added to the flask before the sample is measured into it. It need not be stated, perhaps, that determination of carbon dioxide or titratable base should be made on freshly sampled water, because when water is stored, even in tightly stoppered bottles with practically no air space, biological activity will soon alter the carbon dioxide content, and basic substances may dissolve from the glass.

Since these titrations involve no abrupt changes in pH, the indicator colors must be judged very accurately if reproducible results are to be expected. It is essential, also, that the end points be in close agreement with those deduced from the theory of titration for the respective substances determined. It has already been stated that the end points to which we titrate occur at about pH 7.7 for the phenolphthalein titration and at pH 4.5 for the methyl orange titration. It can readily be shown

that these values agree well with theory. The reactions involved in the titration with hydrochloric acid are:



For Reaction 1 the titration, to give correct results, should be carried to the pH of a solution of bicarbonate in sea water. The mass law equation obtained by combining the two dissociation steps, is:

$$K_1' \cdot K_2' = \frac{[\text{H}^+]^2 [\text{CO}_3^{--}]}{[\text{H}_2\text{CO}_3]}$$

In a solution containing only bicarbonate, $\text{CO}_3^{--} = \text{H}_2\text{CO}_3$, and

$$[\text{H}^+] = \sqrt{K_1' \cdot K_2'}, \text{ or } \text{pH} = \frac{1}{2} (\text{p}K_1' + \text{p}K_2')$$

In a following paper (7) it is shown that for sea water the dissociation constants of carbonic acid, in the usual logarithmic terms, are close to the values of $\text{p}K_1' = 6.0$ and $\text{p}K_2' = 9.0$. According to the above equation, these constants would lead to a pH of 7.5 for the theoretical end point of Reaction 1, whereas we titrated to a pH close to 7.7.

The theoretical end point for the methyl orange titration, according to Reaction 2, is given by the relation,

$$[\text{H}^+] = \sqrt{K_1' \cdot [\text{H}_2\text{CO}_3]} \text{ or } \text{pH} = \frac{1}{2} (\text{p}K_1' - \log [\text{H}_2\text{CO}_3])$$

If the value of the carbonic acid is taken as the amount of carbon dioxide ordinarily present in sea water—namely, about 2.2 millimoles per liter, then:

$$\text{pH} = \frac{1}{2} (6.0 + 2.7) = 4.35, \text{ as against } 4.5 \text{ found}$$

There is thus an excellent agreement between the end points deduced from theory and those developed experimentally. These end points also have the advantage of being easily identified during titration.

A number of objections have been leveled against titration methods for determining carbonates and carbon dioxide, especially of sea water. The most serious objection is usually against the phenolphthalein part of the titration, but Thompson and Bonnar (18) also question the titration to methyl orange as a means of determining the titratable base. Their objection is based on a comparison of results obtained by their own method with results obtained by titrating to methyl red, methyl orange, and bromophenol blue. As shown in Table IV of their paper, the agreement between their method and the methyl orange titration is better than in the case of the other methods tested, and the departure is significant only in the first and last samples of the six listed. Johnston (9) states that the methyl orange titration of the titratable base is reproducible and accurate when the Küster comparison method for determining the end point is employed. Admittedly the color changes of the whole titration procedure outlined are difficult to judge, and considerable training is required to obtain concordant results. However, the Küster comparison method almost automatically leads to a proper end point, and we have already pointed out the excellent agreement between the theoretical and measured pH of the end point.

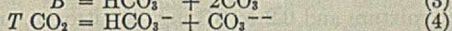
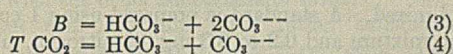
The objections to phenolphthalein as an indicator for the titration of carbonate have been summed up by Johnston (9, p. 961), who says:

Direct titration with acid and phenolphthalein is not to be recommended. For the results depend greatly on what one chooses as the point at which the solution is considered to have become colorless.

This effect, Johnston points out, depends upon the slow rate of neutralization of carbonic acid, which occasions the repeated vanishing and reappearing of the color. Another factor of importance in all titrations of the salts of carbonic acid is the loss of carbon dioxide when this gas is in excess of the partial pressure of the gas phase. Thus Johnston notes that

Seyler (17) found that errors in the phenolphthalein titration are due chiefly to loss of carbon dioxide, so that by carrying out the titration in a closed flask, sharper end points and better results were obtained. For determining carbonate and bicarbonate in a mixture of these salts, Johnston recommends first titrating to the methyl orange end point and then determining the bicarbonate by precipitation with an excess of alkali and barium chloride, the excess of alkali being measured by back titration. This method is obviously not applicable to sea water because of the magnesium and calcium present.

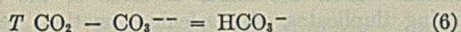
Although our experience indicates (see Tables II and III) that titration to phenolphthalein, provided the proper precautions are taken, will give results of a satisfactory order of accuracy for sea water, a substitute method may at times be useful, especially for checking the titration method. Such a method is provided by the fact that from the total carbon dioxide, as determined by the Van Slyke apparatus, and the titratable base, the respective amounts of carbonate and bicarbonate can be computed. In sea water which contains only negligible amounts of carbonic acid and certain other substances to be mentioned later, the following are the equations for titratable base and total carbon dioxide:



where B is the titratable base in milliequivalents or other appropriate units, and $T \text{ CO}_2$ is the total carbon dioxide expressed in comparable terms. Then, subtracting 4 from 3, we obtain,



The bicarbonate is obviously given by the relation



We thus have a means of determining the carbonate and bicarbonate carbon dioxide fractions of certain sea waters even when titration with phenolphthalein is not practicable, and we also have a method for testing the validity and accuracy of the differential titration method. The results of such a test series are given in Table IV, where carbonate and bicarbonate values determined by titration are compared with values obtained according to Equations 5 and 6. It will be noted that the agreement between the two methods is consistently good.

TABLE IV. COMPARISON OF CARBONATE VALUES DETERMINED BY TITRATION AND COMPUTED FROM TITRATABLE BASE AND TOTAL CO₂

(Data given in Table II used)

TITRATABLE BASE EXPRESSED AS CO ₂ (B)	TOTAL CO ₂ BY VAN SLYKE (T CO ₂)	CARBONATE CO ₂ BY B - T CO ₂	CARBONATE CO ₂ BY TITRATION	DIFFERENCE
Mg./liter	Mg./liter	Mg./liter	Mg./liter	
100.81	89.59	11.22	11.89	0.67
100.30	89.66	10.64	11.37	0.73
100.30	88.95	11.35	11.37	0.02
100.81	89.78	11.03	11.89	0.86
100.81	89.78	11.03	12.20	1.17
100.30	89.49	10.82	11.89	1.07
101.33	89.31	12.02	12.20	0.18
101.33	90.02	11.31	11.68	0.37

The evaluation of carbonates and bicarbonates from the total carbon dioxide and the titratable base is possible only when negligible quantities of carbonic acid are present, and this would be the case in water containing CO₃⁻⁻, and when the titratable base occurs solely as salts of carbonic acid. That there are traces of other substances in sea water which are capable of forming weak acids has long been known. These are chiefly silica, boron, and phosphorus. The amount of phosphorus is known to be too small to be a factor, and in this and many other localities the same is true of silicon.

Concerning boron in sea water there is practically no information available, but it is thought that the quantity is negligible. Irving (8) goes to the length of maintaining that about half the buffer value of sea water is due to factors other than the salts of carbonic acid. Thompson and Bonnar (18) "are of the opinion that the buffer capacity is also a function of some inherent basic property of the sea."

However, experimental data seem to disprove both of these contentions, at least as far as certain parts of the ocean are concerned. If the contribution of the "nonvolatile" buffer—i. e., salts other than those of carbonic acid—to the titratable base of sea water were of numerical importance, the total carbon dioxide as determined by a direct method should be consistently lower than that determined by titration. That this is not the case can be seen from Tables II and III which show that the agreement between the two methods is as good as the agreement between different determinations by either method. In this connection, reference should be made also to the work of Dole (4) and of Wells (25) on water from the Gulf of Mexico. Dole determined carbon dioxide by titration and his results were corroborated by Wells who used a direct method already mentioned.

Moreover, when the pH of sea water is increased by removing carbon dioxide, the nonvolatile buffer effect should increase very appreciably and reach a value of about 20 per cent of the base titration at pH 9.5. In a following paper (7) the results of some experiments will be reported in which the pH of sea water was brought to this figure by the removal of carbon dioxide. Even on this water excellent agreement was obtained between carbon dioxide values determined directly and by titration.⁴ As a result we are led to the conclusion that the nonvolatile buffers are of no practical significance in natural sea water and that the titratable base is determined almost entirely by the quantity of salts of carbonic acid.

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⁴ Some weeks after this was written, carbon dioxide values obtained by titrating this water were too high and later analysis indicated that this was due to silica dissolved from the bottle containing the water.

Improved Direct Nesslerization Micro-Kjeldahl Method for Nitrogen

Determination in Organic Compounds and Biological Fluids

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LAURO (5) has recently described the use of selenium as a catalyst in macro-Kjeldahl digestions. He found that it is much superior to either copper or mercury. These results suggested to the writers the possibility of improving the micro-Kjeldahl method as it is applied in determining the nitrogen of biological fluids and of compounds.

The phosphoric-sulfuric acid digestion of Folin and Wu (2) has the disadvantage of severely attacking the digestion tubes and materials used to prevent bumping, leading to breakage and some difficulty in obtaining clear nesslerized solutions. The hydrogen peroxide-sulfuric acid digestion of Koch and McMeekin (4) is rather free from these objections, but there is the danger of spattering and loss of sample upon addition of peroxide to the hot digestion mixture, and there may be appreciable nitrogen in the peroxide which must be determined and corrected for. Also, the necessity of interrupting the digestion and adding the peroxide is an inconvenience.

It has been found that blood filtrates and urines are rapidly and completely digested by 1 to 1 sulfuric acid containing approximately 0.2 per cent selenium, and the nitrogen values are similar to those found by the peroxide method of Koch and McMeekin. The selenium does not interfere with nesslerization. By using a digestion mixture of 1 to 1 sulfuric acid saturated with potassium sulfate and 0.2 per cent selenium, the rate of digestion is increased, and such a mixture is preferable in the analysis of substances difficult to oxidize, although quite unnecessary for blood filtrates and urine.

EXPERIMENTAL PROCEDURE

REAGENTS. Selenium digestion mixtures:

1. Without potassium sulfate. One cubic centimeter of selenium oxychloride (Eimer & Amend) is added to 500 cc. of 1 to 1 sulfuric acid and mixed. This mixture is recommended for the determination of blood N. P. N., the nitrogen of urine, and other biological fluids. The solution should be kept stoppered when not in use to prevent taking up water and precipitation of selenium.

2. With potassium sulfate. One volume of sulfuric acid is mixed with an equal volume of saturated potassium sulfate solution, and to 500 cc. of this mixture 1 cc. of selenium oxychloride is added. A small amount of potassium sulfate separates overnight. The solution is decanted from this.

Nessler reagent: This was prepared according to Bock and Benedict (3) and then diluted with an equal volume of 10 per cent sodium hydroxide. This formula has been found quite satisfactory.

Hydrogen peroxide: Three per cent hydrogen peroxide from Parke Davis, and Merck's Superoxol. This was found to be practically nitrogen-free.

METHOD. A quantity of solution representing approximately 0.2 to 0.3 mg. of nitrogen (5 cc. of Folin-Wu blood filtrate or 1 cc. of urine diluted 1 to 40) is pipetted into a Pyrex digestion tube¹ (25 by 200 mm.) calibrated at the 50-

¹ Tubes constricted to about one-third diameter at the graduation mark were used. This enables more accurate dilution and also tends to minimize the loss of sulfate.

cc. level. To this 1 cc. of the digestion mixture and 2 dry glass beads (2 are better than 1) are added, and the tube covered with a glass bulb or light short-stemmed funnel with the stem sealed. The solution is rapidly evaporated over a microburner until all water is driven off, the mixture chars, and sulfate fumes appear. The flame is then reduced, the mixture gently boiled until it becomes clear and colorless (usually 1 to 2 minutes), and the boiling continued a further 4 minutes. The digest is cooled, diluted with 25 cc. of water, and 15 cc. of Nessler's reagent are added quickly.² The tube is diluted to the mark, stoppered with a rubber stopper, and mixed. A standard is prepared using 1 cc. of the digestion mixture and 0.2 to 0.3 mg. of nitrogen, nesslerized and diluted to 50 cc. Colorimetric readings and calculations are made in the usual way.

RESULTS

Table I records data obtained on tungstate filtrates of blood and diluted urines using 1 to 1 H₂SO₄ + 3 per cent H₂O₂, 1 to 1 H₂SO₄ + 30 per cent H₂O₂, and 1 to 1 H₂SO₄ + 0.2 per cent Se as the digestion mixtures. The values are identical within the limits of error of the methods. In running duplicates, the selenium method seems to give somewhat better checks than the peroxide method, possibly because of loss by spattering with the latter procedure.

TABLE I. DATA ON TUNGSTATE FILTRATES OF BLOOD AND DILUTED URINES

(All determinations in duplicate)

DIGESTION MIXTURE	1 to 1 H ₂ SO ₄ + 3% H ₂ O ₂ Mg. N/100 cc.	1 to 1 H ₂ SO ₄ + 30% H ₂ O ₂ Mg. N/100 cc.	1 to 1 H ₂ SO ₄ + 0.2% Se Mg. N/100 cc.
Blood filtrates:			
Sheep blood	50.5	50.5	50.5
Pig blood	37.7	37.0	37.0
Urines:			
Sample 1	1240	1220	1240
Sample 2	1120	1200	1140
Sample 3	1120	1120	1100
Sample 4	693	690	695

TABLE II. NITROGEN VALUES

(All determinations in duplicate)

NITROGEN FOUND IN:

DIGESTION MIXTURE	K ₂ SO ₄ + H ₂ SO ₄ + 3% H ₂ O ₂	K ₂ SO ₄ + H ₂ SO ₄ + 30% H ₂ O ₂	K ₂ SO ₄ + H ₂ SO ₄ + 0.2% Se	N CALCD.	REMARKS
	%	%	%	%	
Urea	46.3	45.9	45.9	46.66	
Uric acid	33.3	33.3	33.3	33.33	
Alanine	17.1	17.0	17.0	15.73	Unpurified
Acetanilide	10.47	9.45	10.47	10.36	
Phenacetin	7.30	7.76	7.70	7.82	
Creatine	20.90	21.70	23.60	28.17	29.20% by macro-Kjeldahl using 0.2 gram of Se + 0.5 gram of sucrose
Creatine	23.20	25.00	29.40	28.17	2 mg. sucrose in each digestion
Creatinine	29.00	30.05	36.5	37.13	2 mg. sucrose in each digestion
Cystine	11.66	11.66	2 mg. sucrose in each digestion

Table II gives nitrogen values on several compounds. Inasmuch as only comparative results were desired, the compounds used, with one or two exceptions, were commercial samples and not specially purified. For these

² Nessler's reagent must be added quickly after water to prevent separation of elementary selenium with resulting cloudiness.

determinations the K_2SO_4 - H_2SO_4 -Se and K_2SO_4 - H_2SO_4 -peroxide digestion mixtures were used for comparison. Results with the 1 to 1 H_2SO_4 + Se mixture are quite comparable on these compounds to those obtained by using the K_2SO_4 - H_2SO_4 -Se mixture, as are also the 1 to 1 H_2SO_4 -peroxide mixtures, although the digestion may require a few minutes longer.

The nitrogen of creatine and creatinine is not given completely by any of the above digestions. However, recovery is attained by using the K_2SO_4 - H_2SO_4 -Se mixture + 2 mg. of sucrose. Here the presence of potassium sulfate, by raising the boiling temperature, markedly speeds up the rate of digestion; in fact, without it and using sucrose, not all of the nitrogen of creatine or creatinine was recovered. Neither 3 nor 30 per cent peroxide combined with sulfuric acid and potassium sulfate + sucrose gave all of the nitrogen of either creatine or creatinine. It seems, therefore, that the selenium method combined with sucrose is a little more effective on resistant compounds than the peroxide method. It should be noted that the addition of sugar with K_2SO_4 - H_2SO_4 -Se gives the same nitrogen values for urine as H_2SO_4 -Se. The creatinine is completely determined by the ordinary methods when admixed with the other substances of urine.

One-tenth per cent selenium gives rather satisfactory digestion but not quite as good as 0.2 per cent. Four-

tenths per cent is very little better than 0.2 per cent. The selenium digestion gives correct values in the presence of chlorides.

It was noted that there is much less tendency toward bumping in the selenium digestions than the others, probably because of the separation of elementary selenium (which redissolves as the acid becomes concentrated).

This work confirms that of Davenport (1) that 3 per cent peroxide may satisfactorily, and preferably from the standpoint of handling and cost, be substituted for the Superoxol recommended by Koch and McMeekin.

From the experience of the authors, the selenium method seems to be essentially free from the annoyances of the other methods and gives a little more consistent results than the peroxide method. The cost of the catalyst is insignificant, about 4.5 cents for 500 cc. of digestion mixture.

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The Photovoltaic Cell as Indicator in Precise Titrometry

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IN PREVIOUS communications (2-4), various methods employing the photoelectric cell for following titrations have been described or mentioned. Because of the feeble photoelectric currents obtained under most conditions, amplification has been necessary. In order to obtain increased sensitivity, gas-filled cells were usually employed and possibilities of instability and electrical leakage were sometimes troublesome to obviate. Obviously a method which would retain most of the advantages and a minimum of the disadvantages of former methods would be highly desirable. The dry types of so-called "photronic" cells which have been commercially obtainable for a few months, because of their favorable characteristics, have been chosen for use in the present method.

Although these cells are said to be "electronic" in action, their output is dependent upon the photovoltaic e. m. f. developed (1). For this reason, the author prefers to call them "photovoltaic" cells.

CELL CHARACTERISTICS

A few simple experiments conducted with one of these cells showed that in one respect, at least, it was far superior to the photoelectric cell—namely, stability. Also, the fact that its resistance under working conditions is comparable with that of medium-sensitivity portable galvanometers makes possible simple yet sensitive electrical arrangement. Simple experiments with filters showed that, spectrally, the

Because of its inherent stability and simplicity of operating requirements, the photovoltaic cell is admirably suited to precise titrometry, especially where the use of small samples is necessary. In the method herein described, precision of one part per thousand is obtained with three titrations. Under the most favorable conditions only five readings for each determination are necessary, and the end point is obtained by extrapolation.

cell was most sensitive in the yellow-green portion of the spectrum. It was also noted that some response was obtained in the near infra-red and ultraviolet. Later publication of technical data by the manufacturers giving relative spectral sensitivity bears out these conclusions, but unfortunately the makers do not state whether or not these values are based on

equal-energy considerations or are dependent on the intensity distribution of a particular type of source.

To gain further knowledge of the electrical characteristics of the cell under convenient working conditions, a 6-volt, 21-candle power, concentrated-filament, nitrogen-filled lamp was mounted on an optical bench, and the cell was mounted so that it might be moved with respect to the source. The data given in Table I were obtained as follows:

- D = distance between cell and source, cm.
- E = photovoltaic e. m. f., millivolts, measured by conventional Hildebrand potentiometric method.
- I = calculated current, microamperes, which would flow with cell short-circuited.
- R = corrected resistance of cell obtained by deducting resistance of measuring instruments from total circuit resistance.
- W = calculated power, millimicrowatts, dissipated by cell when short-circuited.

In order to understand better the relations between e. m. f., current, and power, respectively, with light intensity, their logarithmic values were plotted as shown in Figure 1. At the values of distance from the source corresponding to the lower

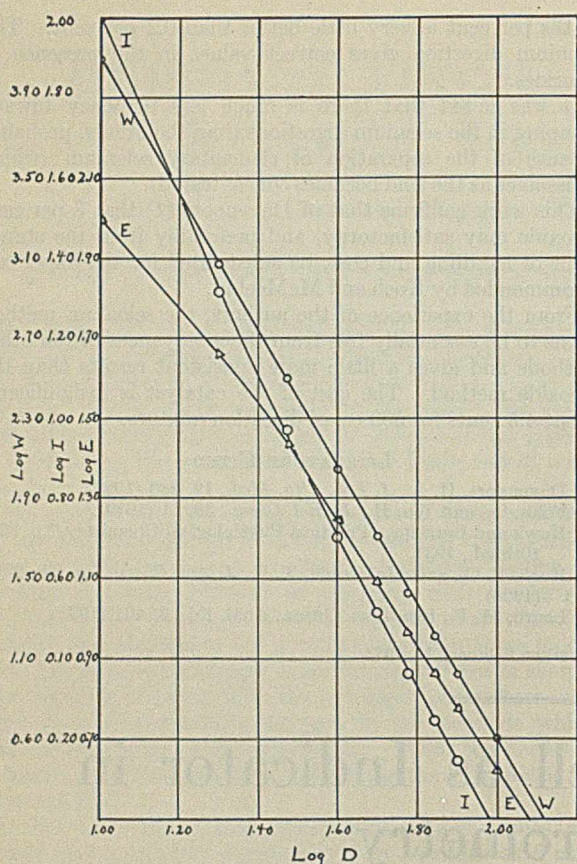


FIGURE 1. LOGARITHMIC VALUES OF E. M. F., CURRENT, AND POWER

light intensities, it will be noticed that all curves have a constant slope, and, since under these conditions we are justified in assuming the applicability of the inverse square law, the values in the second column of Table II may be considered approximately correct.

After considering the various usable characteristics, the next problem was to select the most convenient one for use in the proposed method. If a high level of illumination were possible, the current characteristic would be most suitable. Under actual conditions, however, instead of having available a strong intensity of white light, the filters used reduce the illumination to from 1 to 10 per cent of the original value in a narrow spectral band. Currents would thus be obtained which would require exceedingly delicate measuring instruments. The e. m. f. characteristic, besides being independent of cell resistance, makes possible the use of a null method which may employ a comparatively rugged portable galvanometer.

Instead of actually measuring the cell potential, it is evident that a definite fixed opposing potential may be pre-selected, and the light intensity falling on the cell may be varied until for each desired measurement the opposing potential is exactly equaled by the cell. Besides being convenient and economical, this method allows great flexibility. Its use is limited, of course, to the requirement of measuring a change rather than an absolute value. If reference standards are used, the method may be applied to absolute measurements when the proper precautions are taken.

APPARATUS AND ELECTRICAL CONSTANTS

To try out the method, the apparatus shown in Figure 2 was assembled as follows: *L* is a galvanometer illuminator containing a 64-candle power, concentrated-filament, nitro-

gen-filled lamp operating at 6 volts and supplied by a storage battery, *B*, of approximately 100 ampere hours capacity. The approximately parallel light from *L* passes through diaphragm *D* which is arranged so that its aperture may be read on scale *S* by means of vernier *V*. *S* is a 200-mm. galvanometer scale, and *V* is arranged to read it to a tenth of a millimeter. Cell *C*, containing the material to be titrated, and the indicator (if one is used) are next in the light path, followed by filter *F* and the light-sensitive cell *P*. Voltage divider *O* is arranged so that a small portion of the potential difference of *B* (about 100 millivolts, maximum) may be used to oppose the photovoltaic cell *P*. Galvanometer *G* indicates whether the balance has been obtained when tapping key *T* is closed. *G* has a sensitivity of about 150 mm. per microampere and is of the portable lamp and scale type.

To obtain an idea of the uniformity of response with scale reading, the values shown in Figure 3 were obtained. No filter or absorption cell (*C*) was used, and the potentials were obtained by the Hildebrand method. Values for lower scale readings are not given because their use in actual work is exceedingly limited, owing to the small photovoltaic response obtained.

ACIDIMETRY TITRATIONS

METHOD OF OPERATION. As a preliminary trial, the titration of sulfuric acid with 0.1 *N* sodium hydroxide was attempted. Phenolphthalein was chosen as the indicator, and a reasonably good square bottle of 150 ml. capacity was used as the titrating cell, *C*. Stirring was accomplished by carbon

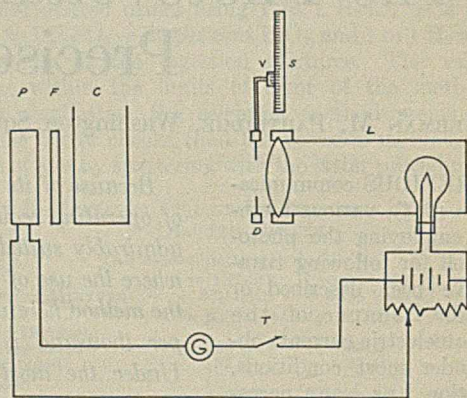


FIGURE 2. SCHEMATIC DIAGRAM OF APPARATUS AND ELECTRICAL CIRCUIT

dioxide-free air. The filter was chosen in the manner illustrated in Figure 4 of a previous communication (4). In this case, since phenolphthalein absorbs selectively in the green region, a green filter is necessary. Of the filters available, that designated by the Corning Glass Works as "Sextant Green" of 3.86 mm. thickness and transmitting between $840\mu\text{m}$ and $580\mu\text{m}$, was selected as most suitable.

A sample of acid was pipetted into the titration cell *C* by means of a 5-ml. Bureau of Standards calibrated pipet. To this 100 ml. of carbon dioxide-free distilled water and 5 drops of 1 per cent phenolphthalein in alcohol (previously found to be the most desirable amount) were added. The first few titrations were made using a 50-ml. buret and some standard sodium hydroxide made up from commercially prepared standards. The apparatus seemed to function consistently, but fading of the end-point color and inability to get a definite equivalence value were traced to carbonate in the alkali. A new standard solution prepared in such a manner as to be practically carbon dioxide-free gave good results, but it was immediately noted that more accurate buret readings were necessary if the full benefits of the method were to be attained.

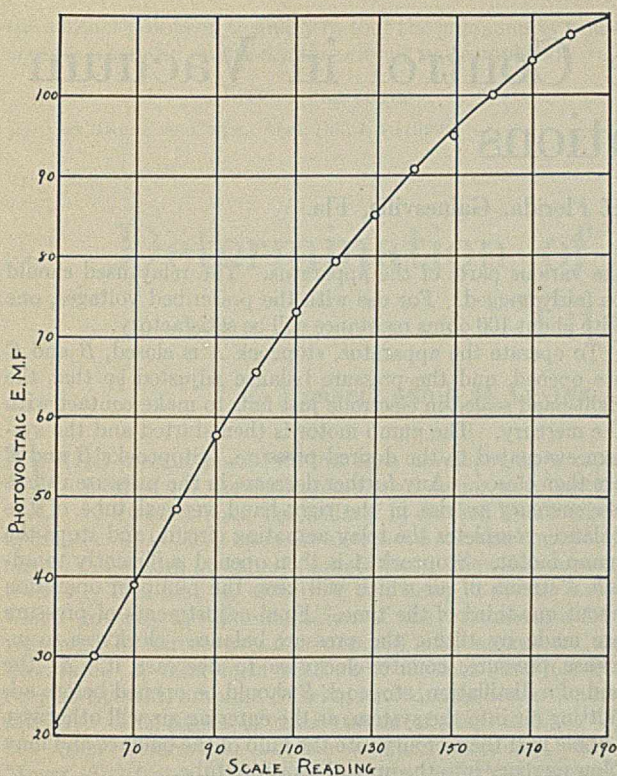


FIGURE 3. RELATION BETWEEN SCALE READING AND PHOTOVOLTAIC E. M. F.

A 5-ml. buret from which additions of 0.002 ml. could be estimated was substituted for the larger one, and five titrations, illustrated in Figure 4, were carried out. In each case, the opposing potential was set by O at such a value that the colorless solution caused the photovoltaic e. m. f. to equal the opposition when the scale reading was set between 80 and 90. Scale readings for additions of alkali were taken as shown in Figure 4. (Titration 5 was accidentally run by the end point so far that the color produced gave an off-scale value for the scale reading.) The results obtained on different days and by different observers are in very fair agreement and will not be discussed.

TABLE I. PHOTRONIC CELL CHARACTERISTICS

D Cm.	E Millivolts	I MAX. CALCD. Microamperes	W MAX. CALCD. Millimicro-watts	R CELL Ohms
10	98.7	100.4	9910	983
20	45.7	20.7	946	2221
30	27.3	9.38	256	2910
40	17.7	5.05	89.4	3400
50	12.4	3.28	40.6	3780
60	9.2	2.31	21.2	3980
70	7.3	1.77	12.9	4180
80	6.0	1.41	8.47	4250
100	4.2	0.97	4.08	4310

TABLE II. RELATIONS OBTAINED FROM FIGURE 1

$$E = K_1 \frac{1}{D^{1.55}} \quad E = K_4 C^{0.78}$$

$$I = K_2 \frac{1}{D^{1.36}} \quad I = K_5 C^{0.92}$$

$$W = K_3 \frac{1}{D^{3.39}} \quad W = K_6 C^{1.70}$$

$C = \text{light intensity}$

ERRORS AND PRECAUTIONS. The usual difficulties caused by buret and pipet drainage must be carefully considered. Temperature changes during the period of manipulation are to be avoided. Reagents and water must be carbon dioxide-free. The titration curves are probably not true straight lines, but may be considered so for these experiments. A typical curve is shown in Figure 3 of a communication by

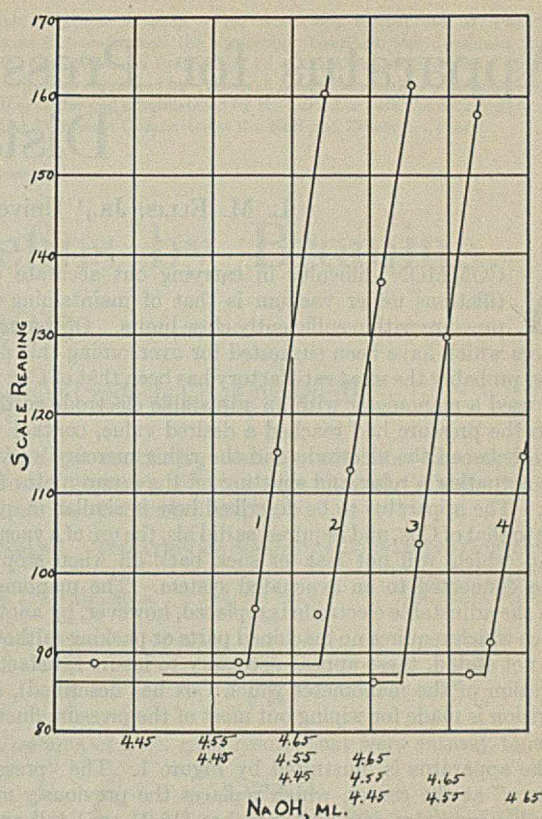


FIGURE 4. TITRATION MADE USING PHOTOVOLTAIC CELL

TITRATION	END POINT, NaOH ML.
1	4.595
2	4.585
3	4.587
4	4.595
Av. 4.590 ± 0.0025	

Müller and Partridge (2), but owing to the enormous change at the end point, no curvature could be detected. It will also be noted that the slopes of the vertical portions are not the same. This is due to the fact that different starting points were selected and the illumination level was slightly different on different days. The light source should be constant during the period between successive readings. This was accomplished in a simple manner by allowing the storage battery B to be charged at a 5-ampere rate while being discharged by the lamp at the rate of 7.5 amperes. Under these conditions the source was remarkably constant over a period of several hours.

The efficiency of the optical system can be improved, and such improvement will make the device more sensitive in the red and violet regions than is the present model.

Many other determinations, both macro and micro in nature, have been undertaken and will be described in later communications.

ACKNOWLEDGMENT

The author wishes to express his indebtedness to R. A. Smith of this laboratory for his assistance in making many of the observations contained herein.

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RECEIVED March 3, 1932.

Apparatus for Pressure Control in Vacuum Distillations

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A COMMON difficulty in carrying out accurate distillations under vacuum is that of maintaining the pressure within sufficiently close limits. Of the many devices which have been suggested for overcoming this difficulty, probably the most satisfactory has been that of Cox (1), who used a manometer with an adjustable electrode so that, when the pressure had reached a desired value, contact was made between the electrode and the rising mercury surface, thus actuating a relay and shutting off the pump motor current. The apparatus to be described here is similar in principle to that of Cox, and requires, as did his, the use of a vacuum pump which will not leak or suck back oil when stopped while connected to an evacuated system. The manometer with the adjustable electrode is replaced, however, by another device which requires no machined parts or packing (although it is not stated, these appear necessary to insure satisfactory operation of the manometer which Cox has described), and provision is made for wiping out most of the pressure fluctuations.

The apparatus is illustrated by Figure 1. The "pressure balance" at the center, which replaces the previously mentioned manometer, is about 6 inches (15.24 cm.) tall and 7 inches (17.78 cm.) wide. The bulb on the left-hand vertical arm is about 1.5 inches (3.81 cm.) in diameter, the tube just below it 1 inch (2.54 cm.), and the rest of the tubing 7 mm. inside diameter. The relative positions of the sealed-in

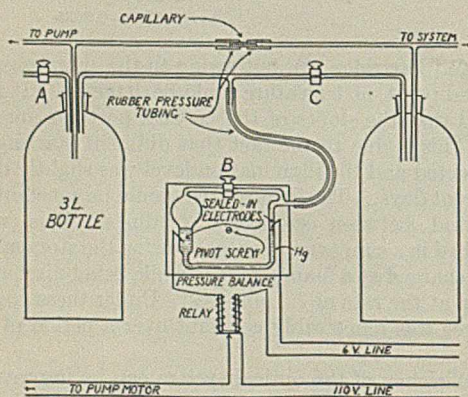


FIGURE 1. DIAGRAM OF APPARATUS

electrodes and the height to which the balance is filled with mercury are correct as illustrated. These electrodes must be gas-tight, and stopcock *B* must be kept well lubricated with a good grade of stopcock grease. The lower end of the right-hand electrode should be fairly accurately centered in the tube. The pressure balance is mounted on a board of suitable size, and the board itself supported by a screw or bolt through its center which allows it to be rotated slightly in its own plane, but which should be tight enough to prevent any accidental jarring from altering the position of the balance. Stopcock *A* should have a rather small bore; stopcock *C* should be of 3 mm. inside diameter. Glass tubing of 5 mm. inside diameter is used for making the connections between

the various parts of the apparatus. The relay used should be fairly rugged. For use with the prescribed voltages, one with about 100 ohms resistance will be satisfactory.

To operate the apparatus, stopcock *A* is closed, *B* and *C* are opened, and the pressure balance adjusted so that the right-hand sealed-in electrode just fails to make contact with the mercury. The pump motor is then started and the system evacuated to the desired pressure. Stopcocks *B* and *C* are then closed. Any further decrease in the pressure causes the mercury to rise in the right-hand vertical tube of the balance, completes the relay actuating circuit, and stops the pump motor. Stopcock *A* is then opened sufficiently to admit a stream of air which will keep the pump in operation about one-third of the time. Final adjustments of pressure are made by tilting the pressure balance—clockwise to increase pressure, counter-clockwise to decrease it. At the end of a distillation, stopcock *B* should be opened before admitting air into the system, as the entering air will otherwise bubble past the mercury into the bulb of the balance and may blow mercury into the upper horizontal tube.

The inertia of the moving pump and motor parts causes the pump to operate an additional stroke or so after the motor current is shut off, and these additional strokes of the pump are believed to be the main cause of the pressure fluctuations which occur in the apparatus. Presumably these could be overcome by using a sufficiently large volume in the system, but the arrangement illustrated gives exactly enough regulation with reservoirs of moderate volume. The introduction of the section of capillary tubing cuts down the rate of diffusion of the gas in the system so that a decrease in pressure in the left-hand bottle only slowly affects the pressure in the right-hand one, and when the apparatus is in operation such changes in pressure are compensated by the air admitted through stopcock *A* before any noticeable pressure change occurs in the right-hand bottle. The effect of the capillary is illustrated by the fact that only faint pressure changes can be detected when 250-cc. flasks are used instead of the size bottles specified.

The higher the pressure at which the system is operated, the greater the effect of the additional strokes of the pump, and hence the smaller the bore of the capillary used. For the usual range of distillation pressures, 10 to 150 mm., a 3-inch (7.62-cm.) section of 1.5-mm. bore capillary is satisfactory. For pressure in the neighborhood of 300 mm., a similar section of 0.3-mm. bore capillary has been used. At very low pressures, stopcock *C* can be left open.

Although leakage across stopcock *B* prevents satisfactory operation of the apparatus, the pressure difference between the two sides is so slight that this never occurs if a well-ground stopcock is used and kept well lubricated.

This type of control apparatus has been employed quite successfully in a number of installations in this laboratory. When the apparatus is properly adjusted, the pressure deviations are too small to be detected on an ordinary manometer, or to affect the rate or temperature of the distillation. Presumably the only changes needed to adapt the device to the control of pressures above atmospheric, up to the limit of the strength of the glass parts, would be the substitution of a suitable pressure pump for the vacuum pump and the reversal of

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the contact points on the relay so that the pump motor would operate when the relay actuating circuit was completed.

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RECEIVED March 3, 1932. This work was carried out at The Johns Hopkins University, and the apparatus described was developed in connection with Research Project No. 28 of the American Petroleum Institute. The work was supported by a research fund of the Institute donated by John D. Rockefeller and administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

Determination of Olefins by Bromine Titration

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THE present procedure has been developed as a rapid method for the determination of olefins in a mixture of hydrocarbons, particularly in cracked hydrocarbon distillate. It is based upon the idea that a solution containing olefins will absorb bromine in proportion to the olefin concentration. This idea is, of course, not new; it is the factor which governs the determination of the bromine number. Instances of direct bromine titration also appear in the literature. A chloroform solution of ice-cold nerol (4) has been so titrated, bromine entering both double bonds quantitatively. The degree of unsaturation of ethyl stilbene (5) has been determined in like manner. Similarly, Kurt Meyer (8) titrated a keto-enol mixture (methyloxaloacetate) for the determination of the enol portion. Although the application to nerol and ethyl stilbene is satisfactory, the method has potential sources of error which prevent its general adoption. The errors involved, as a result of substitution, incomplete additions, etc., have vitiated the usefulness of the bromine or iodine number as applied to cracked petroleum distillate (2).

Some of the objections are overcome when the olefin concentration of an oil is calculated from the ratio of its bromine titer to that of a standard solution containing a known concentration of known olefins. This is the basis of the present work.

PROCEDURE

The titration of the experimental standard and unknown is carried out under the same conditions of light and heat in the following manner:

The oil (2 cc. or a volume which requires 1 to 5 cc. of the bromine solution) is diluted with olefin-free naphtha to a volume of 10 cc., and a 4 per cent solution by volume of bromine in carbon tetrachloride is added from a buret, five drops (0.1 cc.) at a time, stirring after each addition. The end point of the titration is that point where a definite orange color persists for 30 seconds. This end point is one which each operator has to fix in his own mind. The titration should be carried out in diffused light, since direct sunlight causes the production of excessive hydrogen bromide.

All values of concentration in this paper are expressed in terms of volume per cent.

For the case in which the standard and unknown solution contains the same single olefin, Equation 1 is used to calculate the olefin content of the solution.

$$U = \frac{T_1}{T_2} S \quad (1)$$

where U = olefin content of solution
 S = olefin content of standard
 T_1 = titer of solution
 T_2 = titer of standard

Solutions containing various amounts of octylene in olefin-free cleaner's naphtha were titrated. Tables I and II indicate the results obtained.

TABLE I. TITRATION OF SOLUTIONS CONTAINING OCTYLENE

VOL. 12% C ₈ H ₁₈ SOLN. Cc.	VOL. BR ₂ SOLN. Cc.	VOL. BR ₂ SOLN.
		VOL. C ₈ H ₁₈ SOLN.
10	5.1	0.51
5	2.6	0.52
4	2.2	0.55
3	1.5	0.50
2	0.98	0.49

A volume of 1 cc. gave results that were entirely too low.

TABLE II

C ₈ H ₁₈ IN SOLN. %	VOL. TITRATED Cc.	VOL. BR ₂ SOLUTION USED	VOL. BR ₂ SOLN. FOR 2 CC. OF 1%
		(TITER) Cc.	C ₈ H ₁₈ Cc.
31.84	1	2.6	0.163
22.2	2	3.7	0.166
16.7	2	2.7	0.162
11.1	2	1.9	0.171
5.55	5	2.3	0.166

The amount of bromine that can be absorbed by 2 cc. of a 1 per cent octylene solution is 0.00664 cc. This corresponds to 0.166 cc. of a 4 per cent solution. The average quantity of bromine solution actually used is 0.166 cc.

The standard may also consist of an oil which contains the same type of olefin mixture as that in the oil under investigation. Equation 1 will apply in this case also. In a concurrent paper it is shown that the olefins in cracked gasolines are probably of the same type in approximately the same relative proportion. Thus a cracked gasoline in which the olefin content has been accurately determined may be used as a standard. Results are shown in Table III.

TABLE III. COMPARISON OF BROMINE AND SULFUR MONOCHLORIDE METHODS

No.	VOL. BR ₂ SOLN. Cc.	OLEFINS	
		BR ₂ method %	S ₂ Cl ₂ method (2) %
1	6.74	29.6 standard	29.6
2	6.14	27.0	28.0
3	8.72	38.2	35.0
4	6.90	30.4	29.8
5	13.0	57.0	61.4

These analyses indicate that the distribution of various olefins (including those of various types, as well as of different molecular weights) is the same in cracked distillate from various charging stocks and operations.

Equation 1 has also been found to give good results when small concentrations of olefins are to be determined. In cases of this kind larger samples are used for analysis.

The method may also be used where the solution contains known olefins different from that contained in the standard. In this case the specific gravities and the molecular weights of the olefins must be known. If the solution contains a

mixture of olefins, the average molecular weights and specific gravities will apply. The olefin content is then calculated by use of the equation

$$U = \frac{T_1}{T_2} S \cdot \frac{(N_s M_1 D_s)}{(N_1 M_s D_1)} \quad (2)$$

M_1 , D_1 , and N_1 are the actual or average molecular weight and density of and number of olefin bonds in the olefin or mixture being determined, while M_s , D_s , and N_s are the corresponding properties of the standard olefin.

If the olefin in the standard and solution is octylene and amylene, respectively, the expression $\frac{T_1}{T_2} S$ in Equation 2 gives the concentration of amylene in the solution in terms of octylene, while the expression in the brackets is the amylene equivalency of octylene.

To test Equation 2, solutions of 2-pentene, pinene, and allyl sulfide were titrated. An octylene solution was used as a standard with the results shown in Table IV. In the process of titration of the allyl sulfide, the tetrabromide was precipitated as fine white needles. Solids were deposited from solutions of pinene (and limonene) also, but they are more or less gummy.

TABLE IV. TITRATION TO TEST EQUATION 2

OLEFIN	AMT. PRESENT %	$\frac{T_1}{T_2} S$	OLEFIN EQUIV. OF OCTYLENE	OLEFIN FOUND %
Amylene	4.8	7.2	0.69	5.0
	7.0	10.9	0.69	7.5
	15.0	22.6	0.69	15.6
Pinene	2.95	5.5	0.51	2.8
	3.9	7.04	0.51	3.6
	7.4	14.7	0.51	7.5
	14.6	25.3	0.51	12.9
Allylsulfide	10.0	23.8	0.41	9.8

TABLE V. PER CENT OLEFINS IN MIXTURE

No.	OCTYLENE %	LIMONENE %	PINENE %	AMYLENE %	ALLYL SULFIDE %	CALCD. AS OCTYLENE	
						FOUND %	FOUND %
1	4.56	4.39	13.0	12.7
2	10.18	3.67	17.2	16.8
3	17.60	5.69	28.4	28.4
4	8.33	5.0	20.5	19.8
5	9.72	..	1.23	12.1	12.1
6	6.85	..	6.28	5.32	..	26.9	28.0
7	19.34	..	3.14	2.66	..	29.3	28.4
8	3.42	..	4.61	2.66	..	16.3	16.6
9	3.42	..	3.14	2.66	5.0	25.6	24.0

The two double bonds in allyl sulfide and the two potential double bonds in pinene are thus saturated quantitatively, as they are in nerol. Under the conditions of the titration, no bromine is added to the sulfur in the allyl sulfide. This inactivity is analogous to the nonreplacement of the hydroxyl group in nerol. According to Faragher, Gruse, and Garner (1), diolefins absorb halogen very rapidly in the beginning. This was observed also in this work. For example, a pinene solution absorbed 60 per cent of the needed bromine before a yellow color appeared which persisted for 30 seconds, whereas an octylene solution of double the concentration of the pinene became yellow almost from the beginning. It is of interest to note that the cracked gasolines behave as if they contained a large concentration of polyolefins, since a considerable proportion of bromine reagent was added before a yellow color was produced.

It is sometimes useful to determine the value of a mixture of olefins in terms of a standard olefin such as octylene. To determine if interfering reactions arise, Equation 3 has been applied.

$$U_s = U_1 \frac{(N_1 D_1 M_s)}{(N_s D_s M_1)} + U_2 \frac{(N_2 D_2 M_s)}{(N_s D_s M_2)} + \dots \text{etc.}$$

$$= \frac{M_s}{N_s D_s} \frac{(U_1 N_1 D_1)}{(M_1)} + \frac{U_2 N_2 D_2}{M_2} + \dots \text{etc.} \quad (3)$$

where U_s is the olefin concentration in terms of the standard, and U_1 , U_2 , etc., are the concentration of the various olefins in the mixture.

The factors for amylene, pinene, limonene, and allyl sulfide in terms of octylene as the standard are calculated to be 1.44, 1.97, 1.92, and 2.43, respectively.

DETERMINATION OF OLEFINS AND TERPENES

The bromine titration method cannot be used for olefin mixtures unless the average molecular weights and specific gravities of the olefins are known. If in a simple mixture containing two known olefins one of the olefins may be removed, however, the concentration of each olefin can be determined by this means. Mixtures of octylene and limonene were analyzed by titrating the oils before and after removal of most of the limonene.

The limonene was separated from the octylene by selective polymerization. The reagents tried were metallic sodium and the following acids: nitric, phosphoric, phosphorous, mono-, di-, and trichloroacetic, and sulfuric. All except the last polymerized limonene to a limited extent only. Table VI shows the proportions of the terpene remaining in the oil after a 9.36 per cent solution of limonene in olefin-free cleaner's naphtha was treated with the various reagents and distilled to the original end point. Phosphoric, phosphorous, and the chloroacetic acids polymerized only 30 per cent of the limonene as determined by bromine titration (the original solution being used as a standard) or by observation of the refraction of the distillate.

TABLE VI. TERPENE IN OIL AFTER TREATMENT

REAGENT	REFRACTIVE INDEX OF DISTILLATE	LIMONENE POLYMERIZED %
49% HNO ₃	1.4157	87
89% H ₃ PO ₄	1.4179	27
H ₃ PO ₃	1.4179	23
ClCH ₂ CO ₂ H	1.4176	..
Cl ₂ CHCO ₂ H	1.4179	..
Cl ₃ C.CO ₂ H	1.4167 (terpineol formation noted)	..

Sulfuric acid gave much better results. The best results were obtained as follows: The oil was shaken with three-tenths its volume of sulfuric acid of 80 per cent concentration for 30 minutes, allowed to stand for 1 hour, the acid layer withdrawn, and the oil distilled to the original end point. The distillate from the treatment of the limonene solution retained an olefin content equivalent to 7 per cent of the limonene in the untreated oil. This residual olefin is not limonene, since it is not further reacted upon by retreatment, but for the sake of calculation it may be so considered.

Under the same conditions 11.0 per cent of octylene is removed. That the relative proportion of octylene remaining after treatment is almost independent of the octylene concentration is shown in Table VII.

TABLE VII. EFFECT OF OCTYLENE CONCENTRATION

CONCENTRATED OCTYLENE Before treatment %	After treatment %	OCTYLENE UNAFFECTED %
5.17	4.63	89.5
5.26	4.68	89.0
12.25	10.5	86.0
15.67	13.82	88.2
22.8	20.75	91.0

The average proportion of the octylene remaining after treatment is 89 per cent.

According to Equation 3, the olefin concentration, M , of a mixture of octylene and limonene in terms of octylene is given by the expression

$$M = E + 1.92 L \quad (4)$$

where E and L are the volume percentages of octylene and limonene, respectively.

TABLE VIII. ANALYSIS OF MIXTURES FROM TABLE V

MIXTURE %	M	D	OLEFIN FOUND %
4.56 octylene	12.7	4.6	4.7 octylene
4.39 limonene			4.2 limonene
10.18 octylene	16.8	9.6	10.3 octylene
3.67 limonene			3.4 limonene
17.60 octylene	28.4	16.1	17.3 octylene
5.69 limonene			5.8 limonene

As already stated, a solution containing octylene and limonene, upon treatment with sulfuric acid under the specific conditions given, results in a distillate containing the equivalent of 7 per cent of the limonene and 89 per cent of the octylene added. The olefin content, D , in terms of octylene is then

$$D = 0.89 E + (0.07 \times 1.92) L \quad (5)$$

By the simultaneous solution of Equations 4 and 5, the values of E and L are obtained.

$$L = 0.56 M - 0.63 D \quad (6)$$

$$E = M - 1.92 L \quad (7)$$

Mixtures 1, 2, and 3, Table V, were analyzed with satisfactory results, shown in Table VIII.

The method can be applied to pinene and linalool, and probably to other terpenes and terpene alcohols. However, it is very limited in its scope as, for example, trimethyl ethylene is wholly polymerized and 3-methylcyclohexene is two-thirds polymerized.

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Approximate Determination of Olefin and Aromatic Hydrocarbons

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A METHOD has been described for the determination of olefin and aromatic hydrocarbons (2) in cracked gasolines involving the determination of the sum of the concentration of these hydrocarbons, the removal of the olefins by means of sulfur monochloride and distillation from the reaction products, and finally, the determination of the aromatic hydrocarbons in the olefin-free oil. Where the work is of such nature that an absolute error of 1 to 3 per cent is acceptable, the time may be shortened considerably by the use of the method described herein.

The sum of the olefins and aromatic hydrocarbons is determined in a manner in which the technic is modified slightly from that described in the previous article. The olefin concentration may then be calculated from the weight of residue remaining after distillation of the oil obtained upon treatment with 91 per cent sulfuric acid by the use of empirical formulas developed in this work.

Obviously, the aromatic hydrocarbon content constitutes the difference between the total volume per cent of olefin and aromatic hydrocarbons and the olefin concentration.

All values of concentration in this work are expressed in terms of volume per cent.

DETERMINATION OF TOTAL OLEFIN-AROMATIC HYDROCARBON CONTENT

The oil (100 cc.), measured in a weighed graduate, is shaken with 3 volumes of 91 per cent sulfuric acid for 30 minutes in a 500-cc. separatory funnel. The mixture is allowed to settle for 30 minutes, the acid layer withdrawn, and the oil permitted to stand 30 minutes longer, any sludge accumulating being withdrawn in the meantime. The stopcock and stem of the separatory funnel are also freed from sludge. The oil is transferred directly into a weighed 200-cc. short-neck round-bottom flask, from which the oil is distilled to a temperature 5° above the end point of the original oil, as previously determined in a similar manner. The flask is provided with a small uninsulated Hempel column (effective size 3 by 0.5 inches). The weighed graduate is used as a receiver.

The distillation loss may be determined from the weight loss and the density. If the distillation is carried out with

ice in the condenser and with the receiver in an ice-water bath, the loss may be assumed to be 1 cc., which is the average loss sustained in the many distillations made in this work. The distillate is transferred to the same funnel used for the 91 per cent sulfuric acid treatment, and treated with 3 volumes of 98 per cent sulfuric acid in the manner described above. The treated oil is measured and weighed in the graduate used heretofore, and its specific gravity calculated. The total volume per cent of olefins and aromatic hydrocarbons is calculated according to the formula

$$S = V_1 - (V_2 + l) \quad (1)$$

where V_1 is the volume of the original oil, V_2 the volume of oil remaining after the second acid treatment, and l the average distillation loss. The following equations showing the relationship between the weight of the distillation residue and olefin content were developed empirically:

A: For gasolines with a $\frac{P}{D}$ factor of 10 to 25 (15 to 35 per cent olefin content)

$$U = 1.3 \frac{P}{D} \quad (2)$$

or
$$U = \frac{P}{D} + 6 \quad (3)$$

B: For gasolines with a $\frac{P}{D}$ factor of 25 to 35 (35 to 50 per cent olefin content)

$$U = 1.4 \frac{P}{D} \quad (4)$$

or
$$U = \frac{P}{D} + 13 \quad (5)$$

C: For gasolines with a $\frac{P}{D}$ factor of 35 to 40 (50 to 60 per cent olefin content)

$$U = 1.5 \frac{P}{D} \quad (6)$$

or
$$U = \frac{P}{D} + L + 15 \quad (7)$$

where P is the weight of the distillation residue, L the loss in volume per cent sustained on the treatment with 98 per cent sulfuric acid subsequent to distillation, and D the density of the oil remaining after the 98 per cent acid treatment.

As applied to the present work, Group A corresponds roughly to gasolines produced by cracking processes operating at temperatures of 400–480° C., Group B at temperatures of 480–510° C., and Group C at temperatures of 510–570° C. The temperature relationship may be highly limited, as the time-temperature factor is controlling in this respect.

For use of Formula 7, the volume of distillate at room temperature must be known in order to determine L . Otherwise, even this reading need not be considered. The volume of oil, V_T , at room temperature, T , may be calculated from the observed volume, V , and the observed temperature of the distillate, t , according to the formula

$$V_T = V \left(1 + \frac{T - t}{1000} \right) \quad (8)$$

Several cracked distillates were analyzed using the more accurate method previously referred to (sulfur monochloride), and the results were compared with those determined by the present method using Equations 2 to 7, inclusive. These results are shown in Tables I, II, and III.

TABLE I. ANALYSIS OF DISTILLATES ACCORDING TO GROUP A

ANALYSIS	CRACKED DISTILLATE	OLEFIN CONTENT		
		Observed (S ₂ Cl ₂ method)	Calculated Eq. 2	Calculated Eq. 3
		%	%	%
1	California	21.4	22	22
2	Panhandle	32.8	34	32
3	Seminole	29.1	26	26
4	Pennsylvania	25.5	25	25
5	Venezuela	20.6	20	22
6	West Texas (Pecos)	32.8	32	30
7	Mexican (Panuco)	27.3	28	27
8	Smackover	31.1	32	30
9	Pennsylvania	28.0	27	26
10	Pennsylvania	28.7	29	28
11	Midcontinent	30.9	28	27
12	Midcontinent	29.8	27	26

An overhead distillate, boiling range 210° to 258° C., from a Midcontinent pressure distillate was analyzed. It contained 16.2 per cent olefins according to the sulfur chloride method, and gave 17 and 19 per cent, respectively, for the olefin content, according to Equations 2 and 3.

TABLE II. ANALYSIS OF DISTILLATES ACCORDING TO GROUP B

ANALYSIS	CRACKED DISTILLATE	OLEFIN CONTENT		
		Observed (S ₂ Cl ₂ method)	Calculated Eq. 4	Calculated Eq. 5
		%	%	%
1	Midcontinent kerosene	44.4	45	45
2	Pennsylvania kerosene	48.3	52	50
3	Pennsylvania fuel oil	47.9	45	45

A preliminary test indicates that oil obtained by polymerizing ethylene falls in Group B.

TABLE III. ANALYSIS OF DISTILLATES ACCORDING TO GROUP C

ANALYSIS	METHOD	OLEFIN CONTENT		
		Observed (S ₂ Cl ₂ method)	Calculated Eq. 6	Calculated Eq. 7
		%	%	%
1	Laboratory experimental	60.1	59	61
2	Semi-commercial experimental	59.1	58	59
3	Commercial A	60.6	62	61
4	Commercial B	61.4	65	61

Equation 7 gives better results than Equation 6.

DISCUSSION

It should be stressed that the formulas given for the calculation of the olefin content are purely empirical. Whereas the olefin-residue ratio for Group A gasolines shown in Table I is about 1.3, that of octylene in the presence of aromatic hydrocarbons is only 1.0. This is probably due

to a portion of the latter appearing as condensation products with octylene, balancing the portion of octylene dissolved in the acid. On the other hand, the ratio for amylenes is very high, 2.5, indicating great solubility of the olefin in the acid. This value decreases to 1.4 when aromatic hydrocarbons are also present.

It is interesting to note that olefin-residue ratios may vary with the boiling range of gasoline. For a Group A gasoline, the fractions boiling within the ranges 64° to 95°, 95° to 125°, 125° to 150°, and 150° to 180° C., the ratios are 1.4, 1.2, 0.93, and 0.94, respectively. For the fractions of a Group C gasoline boiling between 60° to 95°, 95° to 125°, 125° to 150°, 150° to 175°, 175° to 200°, and 200° C. to the end point, the ratios were 1.4, 1.2, 1.2, 1.6, and 2.0. Removal of a part of the olefins, as may be done by treatment with 80 per cent sulfuric acid, changes the ratio from 1.3 to 1.1. This result clearly shows the effect of the absence of the olefins that are readily soluble in the acid.

OLEFIN-RESIDUE RATIO

As has been stated in the literature (1), several types of reaction take place between sulfuric acid and olefins—namely, esterification, alcohol formation, oxidation, polymerization, and condensation with aromatic hydrocarbons when the latter are present. Another complex reaction takes place in which the products are saturated hydrocarbons (3, 4, 5). To what extent each of these types of reaction occurs depends chiefly upon the concentration of acid used and the nature of the olefin. Therefore, when an oil is treated with 91 per cent sulfuric acid, the concentration of products remaining in the oil and appearing as residue upon distillation—i. e., the polymerized products—is a function of the type of olefins.

Examination of the analyses has shown that the ratio between the olefin content of a gasoline obtained from a cracked distillate and the distillation residue in these analyses is fairly constant. This shows that regardless of the source and composition of the charging stock, the mixture of the olefins formed upon cracking consisted of the same types in the same relative proportions. The calculation showed, therefore, that for Group A three-quarters of the olefins originally present in the gasoline are found in the residue as reaction products. The constancy of the olefin-residue ratio (U to P/D) seems to hold for distillates obtained from various charging stocks and methods of processing, and depends principally on the operating conditions, particularly the time-temperature history, of the cracking operation. Other factors being equal, increase in cracking temperatures produces gasolines with increased olefin-residue ratios. Hence, not only is the total olefin content greatly increased, but the ratio of acid soluble to total olefins is also increased. This increased solubility is an indication of the presence of the more reactive olefins, and thus of the gum-forming constituents. In some types of gasoline the olefin-residue ratio may also bear a relationship to the antiknock properties of the gasoline which increase with this ratio. As a consequence, the antiknock value and gum content should increase at a greater rate than the olefin content.

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Automatic Apparatus for Intermittent Washing

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THE device here described was developed for washing experimental photographic emulsions, but it may be of value in other cases where the interchange between the solvent and the product is slow and the solvent must be utilized efficiently.

A photographic emulsion is normally prepared by precipitation of the silver halide in the presence of gelatin; after digestion to "ripen" the product, the emulsion is chilled until the gelatin sets to a firm jelly, then cut into shreds or "noodles" and washed to remove the by-products of the reaction and the soluble bromide which is invariably present in excess. For mechanical reasons, the shreds must be at least a few millimeters thick, so that the diffusion of soluble salts out into the wash water takes much longer than from the thin layer of emulsion on a finished plate or film.

In commercial practice emulsions are washed in running tap water, preferably from deep wells for uniformity, and prefer-

ably containing some hardness to reduce swelling of the gelatin. For certain experimental work the use of distilled water, plus a small amount of magnesium sulfate, became desirable for reproducibility. As the batches of emulsion had an initial volume of 1.0 to 1.2 liters, from which 10 grams of ammonium bromide plus other salts were to be removed quite completely, the expenditure of distilled water would be at best very considerable.

The apparatus now in use is shown in vertical section in Figure 1, and the wiring diagram for the clock control is indicated in Figure 2. The emulsion is held in a nickel wire-screen basket in the tank *A* (made by cutting the bottom off a 3-gallon bottle). The wash water enters and leaves through a two-way stopcock, *B*, of 4-mm. bore, connected to the bottle neck. The amount of water supplied for each change by siphon from a tank is regulated by the float valve *C*, which is of the general design suggested by Othmer (1), but with a glass needle to close the inlet hole in a rubber stopper. The valve and float assembly may be slid up and down in the float chamber to regulate the height of water in *A*. The distinctive feature of the apparatus is the use of the stock two-way cock, turned by a small motor which can be controlled directly by clock contacts. The motor, *D* ($\frac{1}{100}$ h. p., 110 volt, 60 cycle, a. c. series wound), drives the stopcock through a worm gear and belt. On the driven shaft, between the driven pulley and the clamp attached to the stopcock key, there are three slip rings. Brushes supported by the same cross strut as the shaft bearings make contact on these as indicated in the wiring diagram, Figure 2. One ring is split in half; each segment is connected with one of the other rings. The clock contacts are alternately connected to the other two rings. When contact is made at the clock, the motor is energized and rotates the shaft 180 degrees. The brush on the split ring is allowed to bridge the gap so that as soon as contact with one half is broken, the circuit is ready to be completed through the other half and the corresponding clock contact.

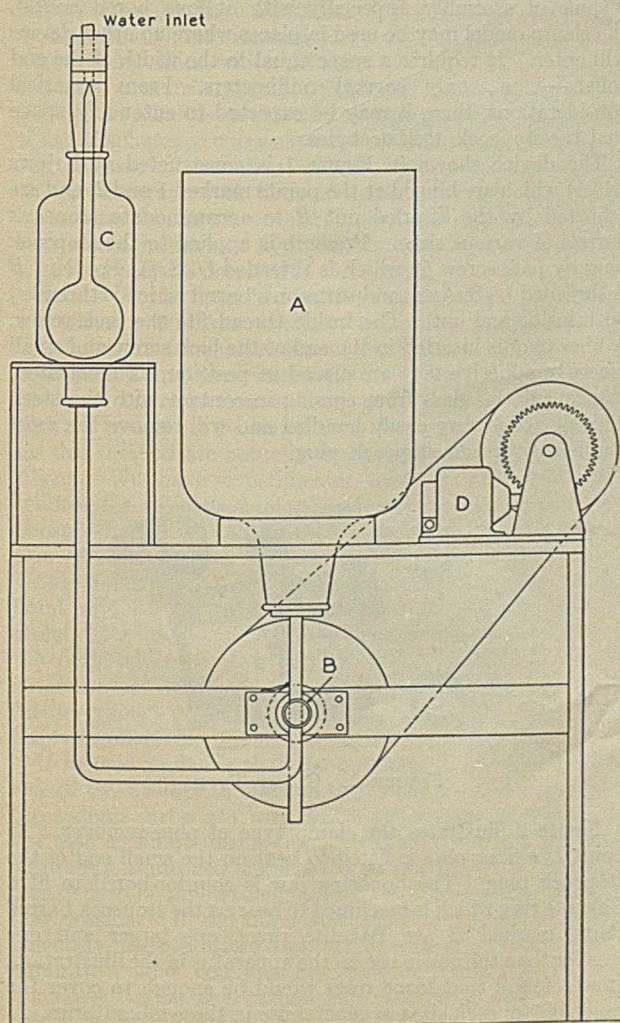


FIGURE 1. AUTOMATIC WASHING DEVICE FOR PHOTOGRAPHIC EMULSION

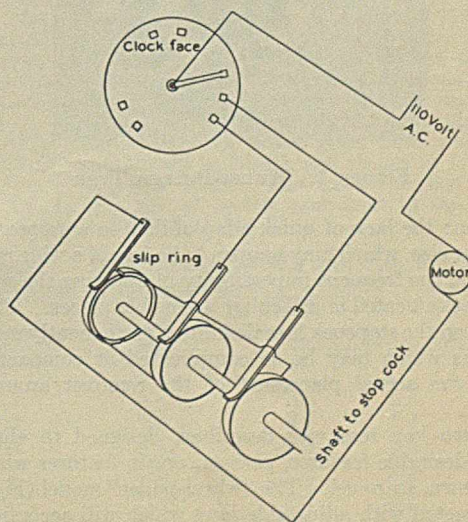


FIGURE 2. WIRING DIAGRAM FOR EMULSION-WASHING DEVICE

The shop work involved in construction of the apparatus was no greater than would be required for construction of solenoid valves, and no relays or heavy currents are necessary. The apparatus now runs on a 20-minute cycle, allowing 3 minutes for draining, but it may obviously be adopted to any other timing where the intervals are not too short. Batches of emulsion of 1.2 liters initial volume can be washed to a bromide-ion concentration of $1 \times 10^{-4} N$ with an expenditure of 60 to 75 liters of water (6 to 7 hours at 5° to 10° C.).

The water is used more efficiently than by an intermittent

siphon device, since the emulsion is completely covered within a minute after the cock is turned to the inlet position. Provision might obviously be made for stirring the material in the tank; it has been omitted for these relatively small batches of emulsion because the jelly is easily broken up by handling.

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RECEIVED March 1, 1932. Published by permission of the Director, Bureau of Standards.

Device for Removing "Frozen" Plugs from Stopcocks

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THE successful removal of a "frozen" stopcock plug has frequently resulted in saving valuable apparatus and time. The gain accruing from this simple operation has tempted many chemists to delve somewhat into this, and almost every laboratory has constructed at least one stopcock key remover. At present, several forms are commercially available from apparatus companies. Although some of these efforts are ingenious and to a degree successful, they possess as a group one distinct disadvantage and one severe

limitation; the lack of quick adaptability to a stopcock of a particular size, which may happen to be any of a wide range of sizes; and the frequent impossibility of applying the remover to stopcocks located in difficultly accessible places. This will occur when the stopcock is sealed into a permanently mounted apparatus which may be so complicated or compact as to prevent the actual placement of the remover around the stopcock.

The device shown in Figure 1 is constructed with jaws (A-A) which are hinged at the points marked 1 and 2, and are adjusted by the knurled nut B to accommodate stopcock barrels of various sizes. Pressure is applied to the stopcock plug by jack screw C, which is threaded $\frac{3}{8}$ S. A. E. Nut B is threaded $\frac{5}{8}$ S. A. E. and turns on a barrel which is threaded both inside and out. The inside thread fits the jack screw. A fiber plug is inserted in the end of the jack screw and small pieces of adhesive tape are placed in position, as illustrated, to prevent the glass from coming in contact with the steel. This device is very easily handled and will remove the most stubbornly frozen stopcock plug.

be used in all cases where the stopcock is accessible, and in addition will serve in places not easily reached in a mounted apparatus where the stopcock is placed with the longitudinal axis of the barrel perpendicular to the plane of the apparatus front. The clamp type (Figure 2) is designed specifically to overcome the limitation of inaccessibility, and is particularly applicable when the remover must be brought to the stopcock. When the cock is sealed into a mounted apparatus so that the longitudinal axis is parallel to the apparatus front (a preferable technic of assembly, especially with oblique bored cocks), the clamp model may be used in places where no other device will enter. It requires a space equal to the width of the end collars—i. e., only several millimeters. From practical considerations, then, it may be expected to enter any space that the stopcock itself occupies.

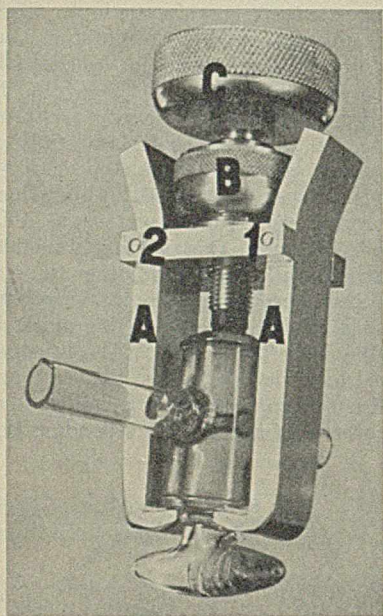


FIGURE 1. WHEEL-PULLER TYPE

The two key removers described, designed to eliminate these undesirable features, possess certain features which, so far as known, are novel. The "wheel-puller" model (Figure 1) is constructed with adjustable jaws which will accommodate stopcocks of any size without recourse to one of a set of fixed spacers, receptacles, or collars. It is quickly adaptable, may

be used in all cases where the stopcock is accessible, and in addition will serve in places not easily reached in a mounted apparatus where the stopcock is placed with the longitudinal axis of the barrel perpendicular to the plane of the apparatus front. The clamp type (Figure 2) is designed specifically to overcome the limitation of inaccessibility, and is particularly applicable when the remover must be brought to the stopcock. When the cock is sealed into a mounted apparatus so that the longitudinal axis is parallel to the apparatus front (a preferable technic of assembly, especially with oblique bored cocks), the clamp model may be used in places where no other device will enter. It requires a space equal to the width of the end collars—i. e., only several millimeters. From practical considerations, then, it may be expected to enter any space that the stopcock itself occupies.

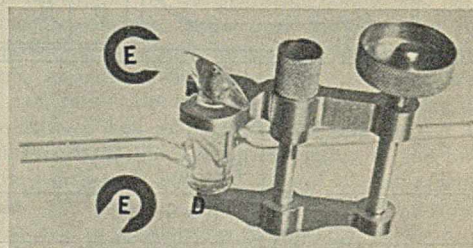


FIGURE 2. CLAMP TYPE

Figure 2 illustrates the clamp type of plug remover. At point D a fiber plug is fitted to bear on the small end of the stopcock plug. The opposing jaw is counter-bored to fit a Bakelite ring which is machined to bear on the stopcock barrel. Parts marked E are Bakelite rings, one larger and one smaller than the one in use on the apparatus in the illustration. It was found that three rings would be enough to cover the range of stopcock sizes in general use in these laboratories.

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Impurities in White Sugars

V. Determination of Phosphorus and Silica

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FURTHER work with the adaptation to white sugars of the Briggs-Bell-Doisey method for determining phosphorus (1) revealed the fact that the method for total or organic phosphates gives consistent results only on duplicate determinations which are carried out simultaneously. A short time after the publication of this method, Pincussen et al. (5) described a very similar one for the determination of small quantities of silica after phosphates have been precipitated from the solution as ammonium magnesium phosphate. Oberhauser and Schormüller (4) have described a ceruleomolybdate method for determining silica which differs from the authors' and from Pincussen's in that the color is developed in alkaline solution by sodium stannite. They state that phosphates and arsenates interfere in this method by giving the same color as the silicates. They point out, however, that in accurate work there is no danger of error in identity, since, after the silica has been removed completely by dehydration with concentrated hydrochloric acid, the phosphates and arsenates may be detected in the filtrate.

Isaacs (3) has described another ceruleomolybdate technic for silica which was critically examined by Foulger (2). The latter, in concluding his report, states: "The fact that both silicon and phosphorus can be estimated by the color produced on reduction of their molybdates would suggest that the results for the phosphorus content of tissues obtained by this method are actually estimations of phosphorus plus silicon. We have experimental evidence that some procedures for estimation of phosphorus by reduction of the phosphomolybdate can be used equally well for the estimation of silicon. This question is worthy of a separate investigation. We are undertaking further research on this point and on the whole mechanism of the reduction of molybdates." So far as the authors are aware, this is the only reference to a ceruleomolybdate method for the determination of silica and of phosphorus together, and no further report of the investigation mentioned by Foulger has been made.

It seemed probable that the difficulty in our method was caused by incomplete reaction of the silica in the sugar with the sodium carbonate with which the sample is ashed. In the case of simultaneous duplicates, each receives the most accurately controlled duplication of conditions of temperature, length of time of incineration, and details of manipulation possible. If the duplicates are not carried on simultaneously, the conditions and technic cannot be so accurately duplicated, and consequently varying quantities of the silica react with the carbonate. A critical study of the procedure has confirmed this supposition and has led to the development of the method so that it is possible to determine both the silica and the phosphorus. The only other known

Irregularities in the results obtained by the authors' method for determining phosphorus in white sugars have been found to be due to the interference of silica. The ceruleomolybdate method, by means of a definite technic, may be used to determine total phosphates plus silica. After removal of the silica by dehydration with nitric acid, the total phosphates may be determined colorimetrically in the filtrate. The difference of the values found in the two determinations represents the silica. Inorganic phosphates may be determined directly on solutions of the sugar. The silica present in white sugars is in a combination which does not react in the ceruleomolybdate method until after the ash has been fused with alkali carbonates.

interference is the possible presence of arsenic in the sugars. Although this seemed hardly probable, it could not be completely ignored in view of the wide occurrence of small amounts of arsenic in manufactured products. The ash from 20-gram portions of sugar was prepared and fused by the method given below and tested for arsenic by the Gutzeit procedure. No arsenic in excess of the quantity present in the reagents was detected. If arsenic should be present in the sugar, it would render the values for P_2O_5 inaccurate, but would not affect those for silica.

REAGENTS

MOLYBDATE SOLUTION. Twenty-five grams of ammonium molybdate are dissolved in 300 cc. of water and to this are added 200 cc. of water containing 75 cc. of concentrated sulfuric acid.

HYDROQUINONE SOLUTION. Half a gram of hydroquinone is dissolved in 100 cc. of water to which a drop of sulfuric acid has been added to retard oxidation.

SULFITE SOLUTION. Twenty grams of sodium sulfite are dissolved in 100 cc. of water. The solution should be freshly prepared.

MIXED ANHYDROUS CARBONATES. Equal parts of pure anhydrous sodium and potassium carbonates are intimately mixed and kept stoppered as a stock reagent.

CONCENTRATED NITRIC ACID. Sp. gr. 1.42.

ACETIC ACID SOLUTION. Twenty per cent by volume.

STANDARD PHOSPHATE SOLUTION. A sample of potassium dihydrogen phosphate weighing 0.4394 gram is dissolved in water and diluted to 1 liter. Twenty-five cubic centimeters of this solution are then diluted to 200 cc. This gives a solution which contains 0.0287 mg. of P_2O_5 per cc.

STANDARD SILICATE SOLUTION. The percentage of SiO_2 in a solution of water glass is determined gravimetrically. A portion of the water glass solution sufficient to contain 0.725 gram of SiO_2 is weighed out and diluted with distilled water to 1 liter. Five cubic centimeters of this solution are diluted to 100 cc. with distilled water. Both of these silica solutions must be made fresh on the day they are to be used, since on standing the silicate hydrolyzes to silicic acid, which becomes colloidal and nonreactive. The solution of water glass from which these solutions are made should be limpid, and should be taken from a previously unopened bottle. The dilute solution contains 0.0363 mg. of SiO_2 per cc. and is equivalent to the standard phosphate solution (Tables I and II).

TABLE I. EQUIVALENCY OF SiO_2 AND P_2O_5 SOLUTIONS
(1 cc. of SiO_2 solution contains 0.0363 mg. of SiO_2 ; 1 cc. of P_2O_5 contains 0.0287 mg. of P_2O_5)

SiO_2 SOLN. TAKEN	P_2O_5 SOLN. TAKEN	EQUIVALENT TO P_2O_5 SOLN.		
Cc.	Cc.	Cc.	Cc.	Cc.
0.0	0.0	0.0	0.0	
0.5	0.0	0.5	0.5	
1.0	0.0	1.0	1.1	1.0
1.5	0.0	1.5	1.5	
2.0	0.0	2.0	2.1	1.9
2.5	0.0	2.9	2.5	
3.0	0.0	3.2	2.9	2.9
3.5	0.0	3.5	3.4	
4.0	0.0	3.7	3.5	
0.5	0.5	1.0		
1.0	1.0	2.0		
1.5	1.5	3.1		
2.0	2.0	4.0		

TABLE II. RECOVERY OF SiO_2 AND P_2O_5

SiO_2 SOLN. TAKEN Cc.	P_2O_5 SOLN. TAKEN Cc.	SiO_2^a STD. SOLN. FOUND		P_2O_5 STD. SOLN. FOUND	
		Cc.	Cc.	Cc.	Cc.
A. NO SUGAR USED					
0.0	0.5	0.6	0.4
0.0	1.0	1.2	0.8
0.0	1.5	1.6	1.4
0.0	2.0	2.2	2.0
0.5	0.0	0.6	0.5
1.0	0.0	1.2	1.0
1.5	0.0	1.5	1.6
2.0	0.0	1.9	2.0
B. ADDED TO SUGAR "A"					
0.0	1.0	-0.1		1.0	
0.0	2.0	0.0		2.0	
0.0	3.0	0.0		3.0	
1.0	0.0	0.9		0.0	
1.0	1.0	1.1		0.9	
1.0	2.0	1.1	1.2	1.9	1.9
1.0	3.0	1.0		2.9	
2.0	0.0	1.9	1.8	0.1	0.1
2.0	1.0	2.0		1.0	
2.0	2.0	1.9		2.0	
3.0	0.0	2.8		0.0	
3.0	1.0	2.8		1.0	

^a Measured against P_2O_5 standards.

PREPARATION OF COLORIMETRIC STANDARDS. The standards for the colorimetric comparison are developed simultaneously with the unknowns. Since the silica standard is equivalent to the phosphate standard, only the latter need be used in analyses, which obviates the uncertainty liable to be encountered concerning possible deterioration of the silica standard and also saves time and expense. Measured volumes ranging from 0.1 to 4.0 cc. of the standard phosphate solution are placed in 100-cc. Nessler tubes. To each are added, in the order given, 5 cc. of the molybdate solution, 1 cc. of the sulfite solution, 1 cc. of the hydroquinone solution, and enough distilled water to make a final volume of 100 cc. The solutions are mixed and allowed to stand for 30 minutes. Standard solutions made up with and without the addition of pure sucrose showed no difference in hue or depth of the colors developed.

PROCEDURE

P_2O_5 PLUS SiO_2 . Five grams of sugar were mixed with 0.2 gram of the anhydrous mixed carbonates in a platinum dish which just previously had been thoroughly cleaned by fusion of a considerable quantity of the carbonates. When the mixture had been reduced to a white ash by careful charring followed by incineration at 550°C . in an electric muffle, the residue was fused over a free flame to a clear liquid melt. After the melt had cooled it was dissolved in about 15 cc. of cold distilled water, acidified with 1 cc. of the dilute acetic acid (which just neutralizes the carbonates), and transferred without filtering to a 100-cc. Nessler tube. The color was developed by the addition of the molybdate, sulfite, and hydroquinone solutions as described above, and after 30 minutes was compared colorimetrically with standards which were developed simultaneously from the standard phosphate solution. Iron in the sugars causes a yellowish tinge, which is conveniently equalized by viewing both the standards and the unknown through a yellow Wratten light filter (K-3 No. 9). The result was recorded as the number of cubic centimeters of the standard solution which matches the unknown and was corrected for the amount of P_2O_5 plus SiO_2 found in the reagents in a blank determination.

TOTAL P_2O_5 . Five grams of the sugar were ashed with 0.2 gram of the mixed carbonates as in the preceding determination, but the ash was not fused. After it had cooled it was dissolved in a little water and acidified with concentrated nitric acid. The silica was rendered insoluble by evaporating the solution to dryness on the steam bath, moistening the residue thoroughly with concentrated nitric acid, again evaporating to dryness, and taking up in a little water (β). The solution was immediately filtered to remove the separated silica, and the filtrate and washings were collected together in a 100-cc. Nessler tube. The color was developed and measured as before, similarly recorded, and corrected for the

total P_2O_5 found in the reagents in a determination made on them alone. A series of experiments involving various modifications of technic showed that this method of removing the silica was both simple and sufficiently accurate for this work (Table II).

INORGANIC P_2O_5 . Ten grams of the sugar were dissolved in a little water in a Nessler tube. To this the molybdate, sulfite, and hydroquinone solutions were added, the colors developed, measured, and corrected for inorganic P_2O_5 in the reagents, and the results recorded as described above.

CALCULATION OF RESULTS

SiO_2 . The value obtained in the determination of total P_2O_5 was subtracted from that obtained in the determination of SiO_2 plus P_2O_5 and the result multiplied by 0.0363. This gave the weight of SiO_2 in milligrams, from which the parts per million were obtained by multiplying by 200.

ORGANIC P_2O_5 . One-half the value obtained for the inorganic P_2O_5 was subtracted from that obtained for the total P_2O_5 and the result multiplied by 0.0287. This product multiplied by 200 gave the parts per million.

INORGANIC P_2O_5 . The corrected value found for inorganic P_2O_5 was multiplied by 0.0287 and again by 100 to obtain the parts per million.

DISCUSSION

This ceruleomolybdate procedure for silica is much more sensitive to changes in hydrogen-ion concentration than the one for phosphates. If the solution in which the determination of silica is to be made is strongly acid, the color develops very slowly, and only very pale shades are obtained. If, however, the original solution is alkaline, the color develops very rapidly and becomes very intense. Attempts to neutralize the fused carbonates with nitric acid showed that the establishment of neutrality with this acid was not practicable, since the least excess caused irregularities probably due not only to a lowering of the pH, but also to some extent to a partial transformation of the silicate ions into complex polysilicate ions whereby some of the SiO_2 is rendered inactive. Acetic acid, however, added in the stoichiometric amount necessary for neutralization (0.2 gram per 0.2 gram of mixed carbonates) gives a buffered solution of lower hydrogen-ion concentration in which the blue color due to silica develops at such a rate that at the end of 30 minutes it is comparable to that due to the phosphates when the technic described in the preceding paragraphs is adhered to. Any divergence from this technic requires the determination and use of a different equivalent value for SiO_2 in relation to P_2O_5 .

Because of the depth of the color produced, it is almost impossible to make accurate comparisons with the naked eye (or with the color filter) if the solutions contain more P_2O_5 plus SiO_2 (or either) than is equivalent to a total of 4 cc. of the standard phosphate solution. If larger amounts are encountered, the determination may be repeated on a smaller sample of the sugar, or suitable aliquots of the darker solution may be diluted to 100 cc. before the comparison is made.

The method is subject to errors of 0.1 and 0.2 cc. of standard solution in the determinations of phosphates and of silica, respectively, as is shown by the results which are recorded in Table II-B and which were obtained by adding known volumes of the standard solutions of phosphate or silica, or both, to sugar "A" and carrying out the procedures described. Calculated on the basis of 5 grams as the weight of the samples taken, these errors are 0.57 and 1.5 parts per million for P_2O_5 and SiO_2 , respectively. By using larger samples of the sugar for the ashing, the errors calculated to

parts per million may be proportionately decreased. However, the use of a larger original sample for the P_2O_5 plus SiO_2 is not feasible, since in most cases it would make the quantity of SiO_2 greater than that which may be measured accurately by this technic. If only the total P_2O_5 is to be determined, this limitation does not hold, and in general weights of sample up to 15 grams may be used.

TABLE III. SiO_2 AND P_2O_5 IN WHITE SUGARS

SAMPLE	SiO_2	ORGANIC P_2O_5	INORGANIC P_2O_5
	P. p. m.	P. p. m.	P. p. m.
a	8.7	0.0	0.0
b	29.0	0.8	0.3
c	21.8	1.1	Trace
d	45.1	1.1	Trace
e	38.5	0.5	0.1
f	9.4	0.6	Trace
g	8.0	0.6	Trace
h	53.0	0.3	0.3
i	29.0	1.1	Trace
j	52.3	1.1	0.0

The values for organic P_2O_5 recorded in the previous article (1) are incorrect in that they include a part of the SiO_2 as well as the actual organic phosphorus. Unfortunately the samples of the sugars on which those analyses were made have been exhausted, and therefore the correct values cannot be given. Table III gives the values found in more recent sugar samples representing both refined and direct-consumption cane sugars, as well as beet sugars. It is to be noted that the quantity of SiO_2 greatly exceeds that of the organic phosphates.

The results indicate that the silica in the sugars is in a nonreactive form, since it does not give the reaction until after it has been made soluble by carbonate fusion, as shown in those cases which contain silica but which give no test for inorganic phosphates. The extreme ease with which

the silicate ions pass into nonreactive complexes is shown by the impossibility of preserving the standard silicate solutions and by the following experiment which was performed in triplicate: A solution of water glass containing 0.109 mg. of reactive silica was added to 10 grams of sugar "A" and heated in a vacuum oven at 70° C. for 24 hours. After the lumps had been broken up, the sugar was allowed to stand in the open air for 7 days. A determination by the procedure for inorganic phosphates showed no more color than that developed in the blank on the reagents. Since by this simple treatment the silica was rendered nonreactive, there is no reason to suppose that silica in the juices will remain in the active form throughout the more vigorous treatments used in the processes of manufacturing white sugar.

ACKNOWLEDGMENT

The tests for arsenic were made by C. R. Gross of the Insecticide Division, Bureau of Chemistry and Soils, Department of Agriculture, to whom the authors extend their thanks and appreciation.

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RECEIVED February 25, 1932. Presented before the Division of Sugar Chemistry at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932. Contribution 122, Carbohydrate Division, Bureau of Chemistry and Soils.

A Convenient Feed Cup for Rats

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THE feed cup described by McCollum (1) is a useful device for feed conservation in nutrition studies. Frequently, however, the materials available locally for its construction are of such proportions that the cup occupies considerable space within the cage and requires an excessive amount of feed to fill it. Large amounts of feed are consequently lost during periodic renewal of the ration.

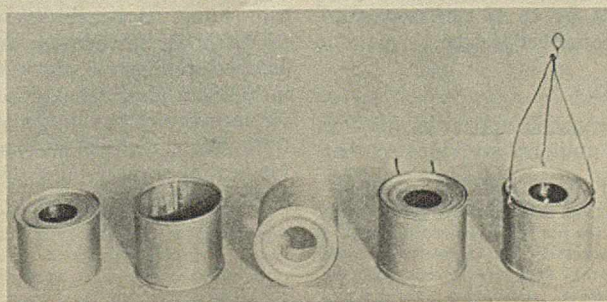
A feed cup constructed entirely from tin cans has been devised for use in this laboratory. Its construction is quite simple, as the accompanying photograph indicates. Two cans of closely similar diameters are chosen so that one will readily fit within the other without binding. The cans are cut to approximately the same height on a lathe or by means of tin shears. A round hole is then made in the end of the inner can by a lathe or round tinner's punch. The hole should be of sufficient size to permit easy entrance of the animal's head. Diameters of 1, 1.125, and 1.25 inches have been found to be the most useful sizes.

When the larger can is

filled with feed and the smaller forced down into position, the rat must reach through the hole in order to consume the ration. The cup appearing in the photograph was constructed from cans of 2¹¹/₁₆ and 2⁸/₁₆ inches in diameter. The hole in the end of the inner can is 1 inch in diameter.

The cup may be suspended from the top of the cage by wires or permanently attached to the side. In the latter case it will be found that, by fastening the cup to the cage at a decided angle, the possibility of excreta lodging in the cup as a result of the animal perching upon it will be greatly reduced.

The device is compact and easily manipulated and cleaned. Many standard can sizes are available, making possible the construction of a number of different sized feed containers.



COMPONENT PARTS SHOWING METHOD OF ASSEMBLY AND SUSPENSION

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RECEIVED February 15, 1932.

Effect of Inerts on Coking Properties of Pittsburgh Bed Coal

Determination by Small-Scale Carbonization Test

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IN A previous publication (2) the effect of inerts on the coking power of Pittsburgh coal was studied. The Marshall-Bird method for determining agglutinating power was used to measure the effect, and it was found by this method of investigation that the addition of fine inert material, such as fusain, pyrites, and sand in moderate amounts, tended to increase the strength of the cokes obtained above that made from the clean coal. The results, however, varied considerably with the diluting agent used in the agglutinating-power or coking-power tests, and were not entirely conclusive. Accordingly, for the present investigation, a test method was devised which dispensed entirely with the use of a diluent other than the inert material whose effect it was desired to test.

In industrial by-product oven practice, stability of the coke in handling is usually determined by the standard tumbler test of the American Society for Testing Materials (1), or some modification of it. For the work now to be described, the coals and mixtures of coals with various inert materials were coked at coke-oven temperatures in 4-pound charges, and the cokes were tested for comparative size stability and hardness by the tumbler method.

The results of the work are in accord with the previous ones where the agglutinating-power test was used. That is, the addition of fine inert materials commonly contributing to coal ash up to 10 per cent of the charge tends to increase the hardness¹ of the coke as measured by the tumbler test. Pyrites is an exception. It cannot be said that the addition of inert in any case increased the size stability¹ of the coke appreciably. On the other hand, a deleterious effect was not pronounced when inerts in amounts up to 10 per cent were present, except in the case of coarse washery refuse.

APPARATUS

The main requirement in carbonizing apparatus for this work was that it yield cokes of uniform structure so that

¹ The hardness and stability factors of coke are defined by the tumbler test procedure as standardized by the American Society for Testing Materials (1). The stability factor is the cumulative per cent coke remaining on a 1.050-inch (nominal value, 1-inch) square-mesh sieve after treatment in the tumbler machine. The hardness factor is the cumulative per cent remaining on a 0.263-inch (nominal value, 0.25-inch) sieve. Although it is not so stated in the test procedure, stability may be taken as an approximate measure of the tendency of a coke to cross fracture and the hardness factor as an approximate measure of abrasability.

A modified tumbler-test method for the preparation of small samples of coke and for testing their quality is described. When compared with the standard Bureau of Mines 85-pound scale test method, it gave results closely approximating those by the larger scale as regards yield and quality of coke. The method was applied in testing the effect of inerts (washery refuse, gypsum, calcite, pyrites, fusain, and moisture) on the quality of coke made from a Pittsburgh bed coal, with the following results:

1. Mineral inerts tend to increase hardness.
2. Except with gypsum, they lower the stability factor, but not excessively, until as much as 1 part inert to 10 parts coal is added.
3. Washery refuse behaves similarly to other inerts when fine but when coarse it greatly decreases stability.
4. Excessive moisture (25.5 per cent) does not seriously affect pore size, but weakens the coke because of the formation of cross-fracture lines.

reproducible results could be obtained in testing their quality. Another requirement was that the scale of test be as small as practical so that the expense of making the large number of tests required would not be prohibitive. Accordingly, the minimum charge that could be used with this coal was determined by trial. It was found to be approximately 4 pounds (1.8 kg.) with the cylindrical type of retort used, the dimensions of which were 5 inches (12.7 cm.) in diameter by 8 inches (20.32 cm.) high. When a retort of smaller diameter was used, the coke obtained was not uniform, there being excessive amounts of soft, dark coke with large pores at the center of the charge. If a charge of less depth was used, it was difficult to secure sufficient packing of the coal.

The carbonizing apparatus adopted was a small replica of the outfit described by Fieldner, Davis, et al. (3), and used by the Bureau of Mines for the determination of gas and of coke-making properties of American coals. Figures 1, 2, and 3 show the furnace, retort, and complete set-up, respectively. The furnace consisted of a molded fire-clay tube 7 inches (17.78 cm.) internal diameter by 16 inches (40.64 cm.) high mounted on insulating brick, as shown, and provided with a 16-inch (40.64-cm.) steel casing, with heads of transite, containing Sil-O-Cel insulation. The heating element, which was made of No. 3 nickel-chromium wire, was wound in spiral form on a steel mandrel and then placed in the clay tube, where it was protected from contact with the steel retort by a coating of alundum cement. The retort was made from an 8-inch (20.32-cm.) length of standard 5-inch (12.7-cm.) black iron pipe closed top and bottom with sheet steel disks by welding. A 1-inch (2.54-cm.) nipple, welded through the top as shown, served as an outlet for the distillation products. The set-up, Figure 3, shows the retort in place in the furnace, including a glass reflux condenser and Cottrell precipitator² for recovery of the liquor and tar. The gas was measured by a wet test meter of a capacity of 80 feet per hour. Current for heating was supplied by a 7.5-kilowatt regulating trans-

² The writers have been asked repeatedly for details of a simple satisfactory precipitator of this type. The construction will be clear from the figure. Two important points, however, are to be kept in mind: (1) The inner wire electrode must be accurately centered in the bore of the tube. (2) Where a glass tube is interposed between the electrodes, as in this case, a higher voltage than with an iron tube is required. This precipitator tube was supplied by an induction coil capable of giving a 6-cm. spark between needle-point electrodes in the secondary circuit.

former at from 2 to 50 volts in 31 steps, depending on the heating rate desired. A Brown thermoelectric temperature controller, not shown, keeps the temperature constant at the point desired. The tumbler for testing the cokes made in the above apparatus is shown in Figure 4, from which its construction will be sufficiently clear. The drum was mounted horizontally on the shaft of a standard laboratory reducing gear and driven at 22 r. p. m. by a 1/8-h. p. electric motor.

PROCEDURE

For making a test, the retort is filled with coal through the off-take pipe with gentle jolting so that the top level of the coal is 0.75 inch (1.9 cm.) from the top. Some coals swell more than others while the charge is plastic, and coals might be encountered where more free space above the charge would be required to prevent stoppage of the off-take. However, the allowance is ample for Pittsburgh gas coal, which has considerable tendency to swell. The furnace is first heated to a temperature of 950°C., and then the retort charged with 1750

For the two largest sizes, square holes cut in 1/16-inch (0.15-cm.) steel plate are used, and all the large pieces of coke are tested by hand to find if they will pass the holes in any position. The 0.5-inch (1.27-cm.) and 4-mesh sizes are separated on square mesh sieves.

The cumulative per cent on 1 inch (2.54 cm.) is taken as indicating the relative stability, and the cumulative per cent on 4 mesh is taken as indicating the hardness of the coke.

The gas obtained is calculated to cubic feet of gas saturated with water vapor at 60° F. and 30 inches of water vapor, per ton of charge. The tar recovered in the precipitator is added to that in the distillation-flask receiver and weighed therein together with the distillation water. The water is distilled off and separated from the light oil which comes over with it. This light oil is now returned to the flask, which is again weighed. Both tar and liquor are reported in per cent by weight of the charge.

COMPARISON OF RESULTS, 85-POUND AND 4-POUND SCALE OF TEST

The yield of by-products and the quality of the coke obtained by this apparatus were compared with those from the 85-pound standard carbonizing apparatus (3), which in turn had been standardized against coke ovens and other types of industrial carbonizing equipment. For the purpose of this investigation, it was not essential that the yield of by-products agree precisely with those obtained in industrial practice, but it was required that they be of the same order, since otherwise their quality would be quite different from and not comparable with that of industrial carbonization products. The quality of the coke is, of course, the main point of interest in this work.

Table I shows to what extent the yields of coke, tar, gas, and liquor are reproducible in the 4-pound retort, and Table II shows how the average of these results agrees with results for the same coals obtained in the standard 85-pound retort. Reproducibility of yields in the 4-pound retort is clearly close enough for the present purpose and agreement with results obtained on the 85-pound scale is fairly good. The tar for the 4-pound charge is slightly low, but it is known that the tar yield from the 85-pound retort at 900° C. carbonizing temperature is slightly high as compared with coke-oven practice. The differences in gas yield are somewhat larger than would be desirable in an assay test, and reproducibility of gas yields in the case of coal 1 is hardly as good as would be desirable. No doubt the method could be considerably improved in this regard by further comparative work. At least this has been the experience with the standard 85-pound scale test method.

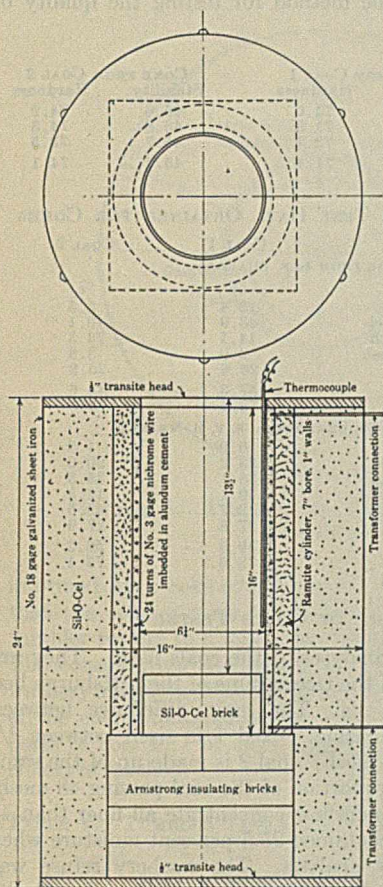


FIGURE 1. FURNACE FOR PRODUCING SMALL QUANTITIES OF COKE

grams of coal, crushed to pass 0.25 inch (0.63 cm.), is lowered into place and quickly connected with the tar recovery train. Charging the furnace with the cold retort causes the temperature of the former to drop quickly to 900° C., at which point the controller is now set. The controller keeps the temperature constant at 900° during the run. As soon as the meter registers 0.3 cubic foot, the precipitator current is turned on and the gas leaving the meter is passed through a large Bunsen burner and burned. The test is continued till the gas flow drops below 0.03 cubic foot per minute, the total time required being approximately 1.75 hours. At the end of the test the retort is removed from the furnace, capped, and allowed to cool, after which it is opened by sawing off the bottom. The coke is then removed, weighed, and sized for testing on the tumbler for which a 1-kilogram charge is used. This charge, which will all pass a 2-inch (5.08-cm.) square opening and remain on one 1.5-inch (3.81-cm.) square, is now placed in the tumbler and rotated at 22 r. p. m. for 1.5 hours, after which it is subjected to the following size analysis:

Through 1.5 inch, on 1 inch.....	—	%
Through 1 inch, on 0.5 inch.....	—	
Through 0.5 inch, on 4 mesh.....	—	
Through 4 mesh.....	—	

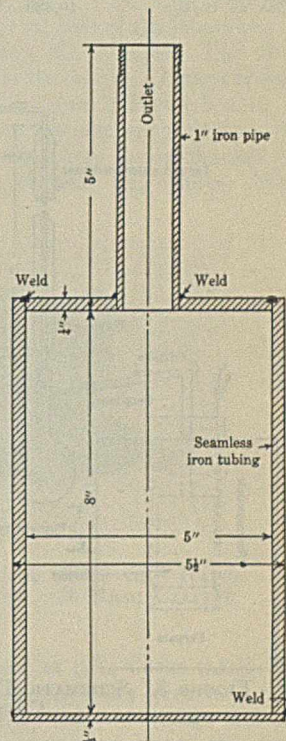


FIGURE 2. RETORT FOR MAKING SMALL QUANTITIES OF COKE

TABLE I. YIELDS OBTAINED WITH QUANTITIES OF 4 POUNDS

COAL	TEST	COKE %	TAR %	LIQUOR %	GAS Cu. ft./ton
1	1	68.3	6.6	4.7	10,010
	2	67.4	6.7	5.1	10,080
	3	68.2	6.8	4.9	10,280
	4	67.9	6.9	4.6	10,120
	5	68.2	7.1	4.9	10,310
	6	68.4	7.0	4.8	10,210
	7	67.6	7.0	5.0	10,190
	Av.	68.0	6.9	4.9	10,170
2	1	64.5	7.7	6.5	10,430
	2	64.3	7.6	6.4	10,470
	3	63.5	7.5	6.6	10,455
	4	64.1	7.6	6.5	10,400
	Av.	64.1	7.6	6.5	10,440

TABLE II. COMPARATIVE YIELDS BY CARBONIZING 85- AND 4-POUND CHARGES OF COAL

	COAL 1		COAL 2	
	85-pound charge	4-pound charge	85-pound charge	4-pound charge
Coke, %	69.2	68.6	64.3	64.1
Tar, %	7.4	6.9	8.0	7.6
Liquor, %	4.7	4.9	6.3	6.5
Gas, cu. ft./ton	10,389	10,170	10,022	10,440

ing as closely reproducible results as the standard one of larger scale; this is usually the case with highly empirical test methods of this sort. It does seem surprising that the two tumbler-test methods give figures for hardness and stability of so nearly the same magnitude. The following triplicate hardness and stability results for two different coals and for three separate charges in each case indicate the order of reproducibility of the method for testing the quality of coke:

TEST	COKE FROM COAL 1		COKE FROM COAL 2	
	Stability	Hardness	Stability	Hardness
1	58.0	71.0	45.6	74.2
2	55.6	71.3	45.8	74.3
3	57.2	72.1	45.7	73.5
	Av. 56.9	71.4	45.7	74.1

TABLE III. TUMBLER TEST DATA OBTAINED FOR COKES

	COAL 1	COAL 2
	MADE FROM 4-LB. CHARGES	MADE FROM 85-LB. CHARGES, A. S. T. M. METHOD
On 1.5 inch	13.4	5.5
On 1.5 inch to 1 inch	43.9	40.1
On 1 inch to 0.5 inch	14.1	23.8
On 0.5 inch to 4 mesh	2.0	3.8
On 4 mesh	26.6	25.8
Stability factor	57.3	45.6
Hardness factor	73.4	73.3
On 2 inch	0.0	1.0
On 2 inch to 1.5 inch	23.2	20.0
On 1.5 inch to 1 inch	36.1	35.3
On 1 inch to 0.5 inch	10.1	12.3
On 0.5 to 0.25 inch	2.7	3.5
Through 0.25 inch	27.5	27.9
Stability factor	59.3	56.3
Hardness factor	72.5	72.1

ANALYSES OF COALS TESTED

Table IV gives the analyses of the coals used. They are all washery products of the Ocean mine of the Pittsburgh bed in Allegheny County, Pa. The main difference between these coals lies in the sizing. Coal 1 is sized between $\frac{3}{8}$ inch (0.96 cm.) and 48 mesh; coal 2 is made up of the same cut but with a large proportion of the coal passing 48 mesh; and coal 3 is a Dorr underflow concentrate all finer than 48 mesh. The last coal contained 25.5 per cent moisture when received, as shown by analysis. The washery refuse was mostly bone and slate, all passing $\frac{3}{8}$ inch (0.96 cm.). Coal 1 was used as the clean coal for mixing with the inert materials, washery refuse, gypsum, pyrites, calcite, and fusain in testing their effect on the properties of coke.

RESULTS OF TESTS WITH INERTS

Table V gives results showing the effect on tumbler-test values of adding the inert washery refuse, gypsum, pyrites, calcite, and fusain to coal 1 in the proportions given, before coking. The test of the washery refuse is perhaps the most informative of the series from a practical viewpoint, since the refuse contained all the inert ash minerals in approximately the proportion found in the coal as mined. The writers were

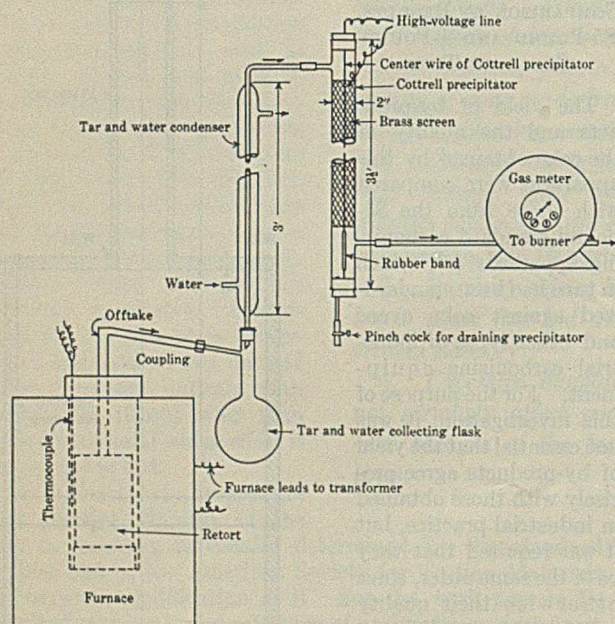


FIGURE 3. SCHEMATIC DIAGRAM SHOWING APPARATUS CONNECTIONS

The behavior of cokes from the 4-pound and 85-pound charges in the small-scale and in the A. S. T. M. standard tumbler tests, respectively, are compared in Table III. It will be noted that the small-scale tumbler test shows a greater difference in the stability factors for the two coals than the A. S. T. M. test, and a somewhat higher hardness factor. Doubtless the small-scale test is not capable of giving

TABLE IV. DESCRIPTION AND ANALYSIS OF PITTSBURGH COALS

COAL No.	DESCRIPTION	LABORATORY No.	BASIS ^a	PROXIMATE ANALYSIS			ULTIMATE ANALYSIS						CALORIFIC VALUE B. t. u./lb.
				Moisture	Volatile matter	Fixed carbon	Ash	Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur	
				%	%	%	%	%	%	%	%	%	
1	Partially cleaned coal from Champion No. 4 washery	A66879	A	0.8	34.5	77.3	7.4	5.1	77.7	1.5	7.2	1.1	13,930
			B	..	34.8	57.7	7.5	5.1	78.2	1.5	6.6	1.1	14,040
			C	..	37.6	62.4	..	5.5	84.6	1.7	7.0	1.2	15,170
2	Clean coal containing large proportion of clean -48-mesh coal from Champion No. 1 washery	A66881	A	2.2	36.7	54.0	7.1	5.2	75.0	1.4	8.7	2.6	13,520
			B	..	37.5	55.2	7.3	5.1	76.7	1.4	6.9	2.6	13,830
			C	..	40.5	59.5	..	5.5	82.7	1.5	7.5	2.8	14,910
3	Clean Dorr underflow concentrate made by froth flotation	A70792	A	25.5	22.4	47.2	4.9	10,840
			B	..	30.1	63.5	6.4	14,240
			C	..	32.2	67.8	15,210
4	Washery refuse from Champion No. 4 washery	A77705	A	1.0	15.4	14.3	69.3	1.0	3,520
			B	..	15.6	14.4	70.0	1.1	3,560

^a A, sample as received; B, moisture-free; C, moisture- and ash-free.

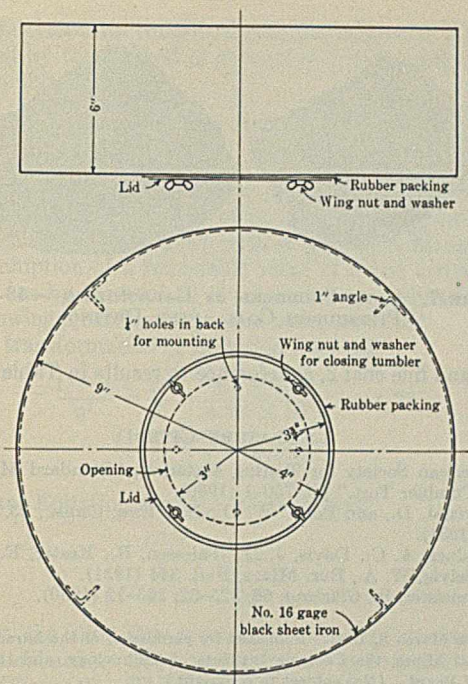


FIGURE 4. TUMBLER FOR TESTING 1-KG. COKE CHARGE

informed by a coke-oven operator using coal from this bed that the coarser sizes of ash-forming minerals affected the tumbler results to a much greater extent than the fine sizes. The comparative test results on $-3/8$ inch and -50 mesh washery refuse bear out this contention, although the effect of the coarse material is not pronounced until a ratio of 10 parts of coal to 1 of inert (approximately 9 per cent of the latter) is reached.

TABLE V. TUMBLER TEST DATA SHOWING EFFECTS OF INERTS

RATIO OF COAL TO INERT	ON 1.5 INCH		1 TO 0.5 INCH		THROUGH 4 MESH	STABILITY FACTOR	HARDNESS FACTOR
	%	%	%	%			
Pure coal	13.4	43.9	14.1	2.0	26.6	57.3	73.4
Washery refuse, $-3/8$ inch							
100 to 1	6.9	49.9	19.1	1.2	22.9	56.8	77.1
40 to 1	9.5	44.5	20.2	2.2	23.2	54.0	76.8
20 to 1	5.3	49.8	16.5	2.9	25.5	55.1	74.5
15 to 1	6.5	44.7	18.3	2.0	28.5	51.2	71.5
10 to 1	..	33.5	27.0	8.8	31.3	33.5	69.7
Washery refuse, -50 mesh							
100 to 1	11.9	45.1	18.2	1.6	23.2	57.0	76.8
40 to 1	8.3	47.9	16.7	3.5	23.6	56.2	76.4
20 to 1	5.4	49.4	19.5	1.5	24.3	54.8	75.7
15 to 1	7.1	48.3	18.1	1.1	25.4	55.4	74.6
10 to 1	6.0	48.2	16.9	2.0	26.9	54.2	73.1
Gypsum, -50 mesh							
100 to 1	8.5	47.9	19.8	1.1	22.7	56.4	77.3
40 to 1	12.2	43.2	20.3	1.3	23.0	55.4	77.0
20 to 1	14.5	42.4	17.2	2.4	23.5	56.9	76.5
15 to 1	9.4	48.4	16.3	1.0	24.9	57.8	75.1
10 to 1	13.5	44.7	15.2	1.3	25.3	58.2	74.7
Pyrites, -50 mesh							
100 to 1	10.7	43.7	18.4	1.0	26.2	54.4	73.8
20 to 1	7.2	46.5	16.8	2.2	27.3	53.7	72.7
10 to 1	13.0	41.4	13.5	2.2	29.9	52.2	70.1
6 to 1	3.2	49.5	11.5	1.7	34.1	52.7	65.9
Calcite, -50 mesh							
100 to 1	12.5	43.6	17.5	1.6	24.8	56.1	75.2
20 to 1	8.4	44.5	21.3	2.3	23.5	52.9	76.5
10 to 1	9.0	43.5	22.6	2.7	22.2	52.5	77.8
Fusain, -50 mesh							
10 to 1	12.8	42.8	14.1	1.7	28.6	55.6	71.4
6 to 1	13.9	35.5	12.3	3.2	32.1	52.4	67.9
4 to 1	3.0	21.5	19.0	4.9	51.6	24.5	48.4

Strangely enough the tendency of all the inerts is to produce harder cokes than the pure coal, as measured by the modified

tumbler test. It will be recalled that Davis and Pohle (2) found that addition of these same inerts to coal from the same bed increased the resistance of the coke to crushing, as measured by the agglutinating-power test.

Only in one case (that with gypsum as inert) does the stability of the coke as measured by this method show a definite tendency to increase over this testing range. The comparative effect of the various inerts at the 10 to 1 testing ratio arranged in the order of decreasing stability is as follows:

Gypsum.....	58.2
Clean coal.....	57.3
Fusain.....	55.6
Washery refuse.....	54.2
Calcite.....	52.5
Pyrites.....	52.2
Washery refuse ($-3/8$ inch).....	33.5

All these cokes were dry-quenched—that is, the hot retorts containing them were capped and allowed to cool in air, or the capped retort was cooled with water which did not have access to the coke. Cokes made from 10 to 1 mixtures, however, were allowed to stand in the atmosphere of the laboratory to find if such exposure would affect the stability. The effect was noticeable only in the case of the calcite. Lumps of coke containing this inert crumbled, as shown in Figure 5, after 10 days' exposure. Deterioration in this case was very probably caused by slaking of the lime formed from the calcite, and the observation is no doubt of practical importance. Wet-

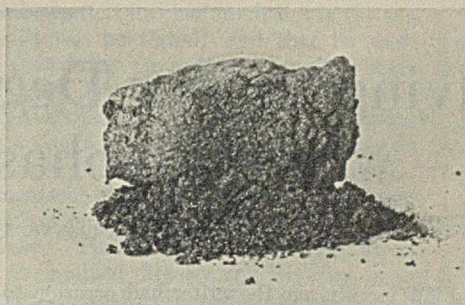


FIGURE 5. COKE PRODUCED BY 10 TO 1 RATIO OF PITTSBURGH COAL TO -50 -MESH CALCITE, AFTER STANDING 10 DAYS

quenching as ordinarily practiced at coke works would certainly slake the lime present, and even if dry-quenching were adopted, the lime would gradually slake in storage and the coke would deteriorate. It appears important, therefore, that manufactured cokes be low in lime.

TABLE VI. AVERAGE RESULTS OF CARBONIZING -48 -MESH CLEAN PITTSBURGH COAL

	CARBONIZED AS RECEIVED	CARBONIZED AFTER DRYING
Tar, %	4.28	5.69
Liquor, %	28.17	3.42
Coke, %	33.40	69.90
Gas, cu. ft./ton	7310	10010
TUMBLER-TEST RESULTS		
On 1.5 inch, %		Coke of 0.0
On 1.5 inch to 1 inch, %		too poor 49.4
On 1 inch to 0.5 inch, %		quality 22.0
On 0.5 inch to 4 mesh, %		to test 0.7
Through 4 mesh, %		27.9
Stability factor		49.4
Hardness factor		72.1

Excess moisture may be looked upon as an inert, since it contributes no valuable carbonization product and absorbs heat in vaporization. Hofmeister (4) has shown that moisture greatly affects the pressure of a charge of coal during coking. Therefore, it must have some effect on the quality of the coke. Results of tests on coal 3 (Table IV) indicate that this is so. This fine coal was first tested in the "as re-

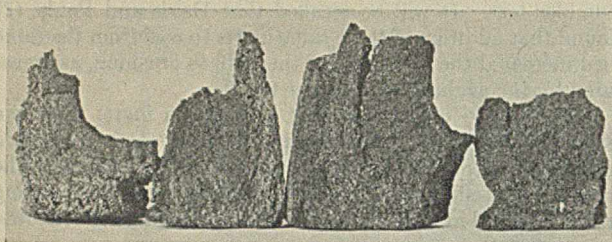


FIGURE 6. COKE PARTICLES PRODUCED BY CARBONIZING -48-MESH PITTSBURGH COAL CONTAINING 25 PER CENT MOISTURE

ceived" condition (25.5 per cent of moisture) as it came from the concentrator, because it was desired to know its carbonizing properties without further treatment. It was then dried at 110° C. without admitting air to a moisture content of approximately 1 per cent, and was tested again. Table VI gives the comparative results of the tests, and Figures 6 and 7 show the appearance of the cokes. The pore size of the coke made from the wet coal is not more variable than of that from the dried coal. However, the former was excessively ringed with cracks normal to the direction of heat penetration so that it easily fell apart in small pieces not of sufficient size to test. Coke made from the dried coal was somewhat inferior to that made from coarse coal 1 and the mixture of

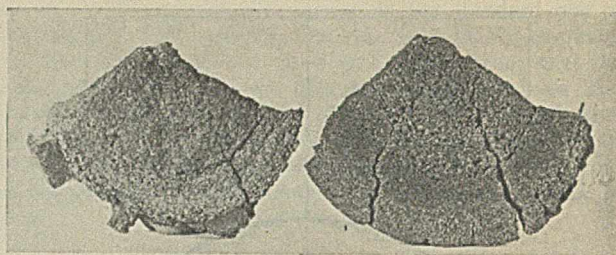


FIGURE 7. COKE PRODUCED BY CARBONIZING -48-MESH PITTSBURGH COAL AFTER DRYING

coarse and fine coal 2, as reference to results in Table III will show.

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Solving Higher Degree Equilibrium Equations with Polyphase Duplex Slide Rule

MILTON J. POLISSAR, University of California, Berkeley, Calif.

A FEW months ago the writer had occasion to solve a fifth-degree equilibrium equation of a type that could not be readily solved by the method of successive approximations. He then devised a procedure whereby the unknown was found in a very short time and without much effort. Since then, this procedure has been used in the solution of many other equations, and its use has been accompanied by a saving in time and in mental effort.

The principle involved is simple, and it is probable that a large number of individuals are using it, but the writer has not found this method mentioned in any of the several slide rule manuals examined recently.

Many equilibrium equations can be reduced to the form:

$$(x + a)^m \cdot (x + b)^n = K \quad (1)$$

in which m and n are small integers, positive or negative. In applying the present method, the first step consists of replacing Equation 1 by a set of two equations containing monomials instead of binomials:

$$U^m \cdot V^n = K \quad (2)$$

$$U - V = a - b \quad (3)$$

$$(x = U - a = V - b) \quad (4)$$

In certain cases it is possible to set the slide of a slide rule in such a way as to obtain all the pairs of solution of Equation 2. It remains only to pick out that pair which will also satisfy Equation 3, and the problem is solved. In other cases it is necessary to manipulate Equation 2 and possibly invert or reverse the slide before a setting is obtained from which the pairs of solutions can be obtained by reading the proper scales.

APPLICATION OF METHOD

Let us now consider a few equations and apply the procedure outlined above for their solution.

$$I. (x + 7) \cdot (x + 3) = 35$$

This equation can be developed into a quadratic and solved by means of the standard formula. However, even in this case the solution can be obtained much more rapidly by finding two numbers, U and V , such that their product is equal to 35 and their difference is equal to 4. Figure 1 shows the slide setting that gives directly all the pairs of numbers whose product is equal to 35. U is read on the D scale, and V is read on the (reciprocal) CI scale. By sliding the hairline along the rule, we find, after testing a small number of pairs, that 8.25 and 4.25 are the two numbers whose product is 35 and whose difference is 4.00. Hence, x is equal to 1.25.

$$II. (x + a)^2 / (x + b) = K$$

As an illustration we shall find the degree of hydrolysis of a 0.08-formal solution of chlorine at 25° C. The equilibrium constant is $K = 4.84 \cdot 10^{-4}$.

Let the degree of hydrolysis be equal to x . The following equilibrium equation must be satisfied:

$$\frac{x^2 c^2}{(1 - x)} = K \quad (5)$$

where c is the formality of the chlorine. For very small values of c , the value of x is given quite accurately by the formula:

$$1 - x = c^2 / K$$

For intermediate concentrations, the value of $1 - x$ can be obtained by the method of successive approximations, using the formula:

$$1 - x = x^2 c^2 / K$$

and starting with the assumption that the hydrolysis is practically complete, and that x^2 is practically equal to unity. For a 0.08-formal solution of chlorine such an assumption would lead to an impossible value of x . One could start with the assumption of a reasonable value of x and arrive at the correct one by the method of successive approximations, but the following procedure is speedier and more direct.

By a transformation of Equation 5 we get:

$$\frac{1 - x}{x^3} = \frac{c^2}{K} = \frac{64 \times 10^{-4}}{4.84 \times 10^{-4}} = 13.23$$

$$\frac{(1 - x)^{1/3}}{x} = 2.361 \tag{6}$$

Replace Equation 6 by the following pair:

$$\frac{U^{1/3}}{V} = 2.361 \tag{7}$$

$$U + V = 1.00 \tag{8}$$

Invert the slide (by rotating it 180 degrees around its longitudinal axis). Set 1 on the C scale against 2.361 on the D scale (Figure 2). This setting gives all the pairs of numbers, U (to be read on the K scale) and V (to be read on the C scale), which satisfy Equation 7. Moving the hairline along the rule we find that the pair of numbers $U = 0.636$, $V = 0.364$ also satisfy Equation 8. Hence, $x = V = 0.364$, and we find that the hydrolysis is 36.4 per cent complete.

$$\text{III. } \frac{(x + a)^3}{(x + b)^2} = K$$

This equation can be transformed as follows:

$$\frac{(x + b)^{2/3}}{(x + a)} = C \tag{9}$$

$$\frac{U^{2/3}}{V} = C \tag{10}$$

$$U - V = b - a \tag{11}$$

$$(x = U - b = V - a)$$

Set 1 on the B scale against C on the A scale. The two scales are now coupled in such a way as to give all the pairs of numbers whose ratio is equal to C . Figure 3 is self-explanatory and shows that U should be read on the K scale, and V on the B scale. It remains to select the pair whose difference is equal to $b - a$.

$$\text{IV. } (x + a)^3(x + b)^2 = K$$

Transforming this equation, we get:

$$(x + b)^{2/3}(x + a) = C$$

$$U^{2/3}V = C$$

Reverse the slide (by rotating it 180 degrees in its own plane). Set 1 on the B scale against C on the A scale. Note that B now functions as a reciprocal scale. It is coupled with the A scale in such a way that the *product* of the pairs of numbers is equal to C . It will be seen from Figure 4 that U and V should be taken from the K and the B scales, respectively. Again, that pair should be selected whose difference is $b - a$.

CONCLUSIONS

It should be pointed out that this is essentially a trial and error method; that its chief merit lies in the ease with which the guesses can be tested; and that its usefulness is the greater, the smaller the number of guesses before the correct one is made. Just as one can waste a great deal of time weighing a sample if one does not proceed systematically, so one can spend a great deal of time arriving at the correct solution, unless a systematic procedure is used. The following arrangement was tried and found satisfactory.

The values of U and V are recorded in two parallel horizontal rows. Their sum (or difference, as the case may require) is obtained directly and recorded in the third row. The first guess usually gives a decidedly low or high value for the third quantity. It will be found generally that the

Fig. 1. Solutions of the equation: $U \times V = 35$

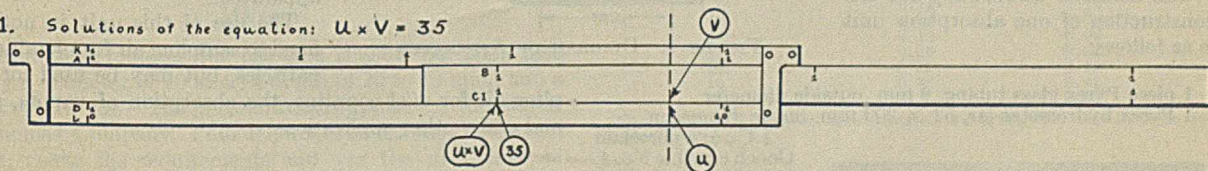


Fig. 2. Solutions of the equation: $U^{1/3} : V = 2.361$

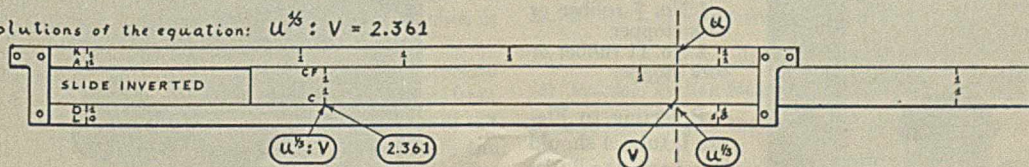


Fig. 3. Solutions of the equation: $U^{2/3} : V = C$

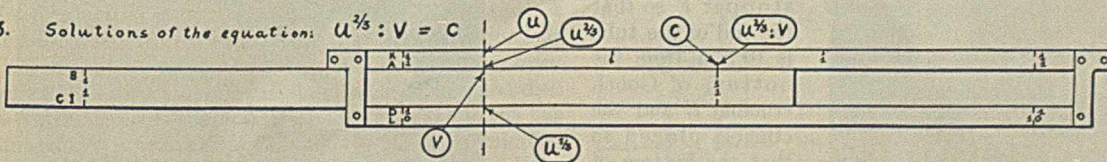
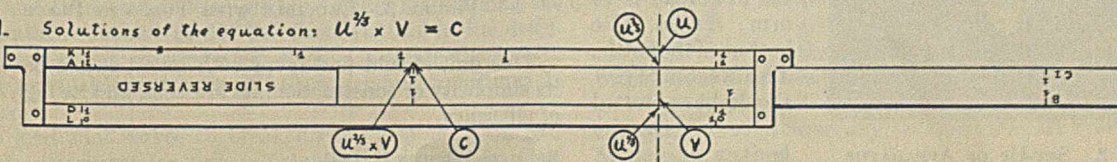


Fig. 4. Solutions of the equation: $U^{2/3} \times V = C$



scales from which the first two quantities were taken have different number densities. The scale with the larger number density will determine the direction in which the hairline should be moved to give the desired sum (or difference). After this

it takes three or four more guesses, and the solution is obtained with slide rule accuracy.

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Improved Unit for Removal of Solid Particles from Gas Streams

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IN A recent study of metallic fumes and particles in air, it was necessary to use an apparatus for the absorption of the particles in a suitable dissolving acid when the rate of flow of the air varied between 0.2 and 1.0 liter per minute.

Several types of gas-washing units were tried, such as the ordinary type of gas-washing bottle, a bottle having a glass spiral, a porous, fritted plate bubbler, and a bottle provided with an impinger unit so arranged that the gas or air stream struck the bottom of the bottle at a relatively high velocity. None of these absorption units proved entirely satisfactory. After considerable experimentation the apparatus shown in Figures 1, 2, and 3 was developed and gave surprisingly efficient and uniform results.

The material necessary for the construction of one absorption unit is as follows:

- 1 piece Pyrex glass tubing, 9 mm. outside diameter
- 1 Pyrex hydrometer jar, 52 × 200 mm. inside dimension
- 1 Coors porcelain Gooch crucible No. 4, glazed
- 1 No. 7 rubber or cork stopper
- 1 No. 11 rubber or cork stopper

Referring to Figure 1, tube *A* should be inserted in stopper *F* so that the end of the tube is 10 mm. from the bottom of Gooch crucible *E* and the crucible placed so that the bottom of the crucible is 10 mm. from the bottom of the bottle. The assembly *A* should be so located as to be in the center of jar *D*.

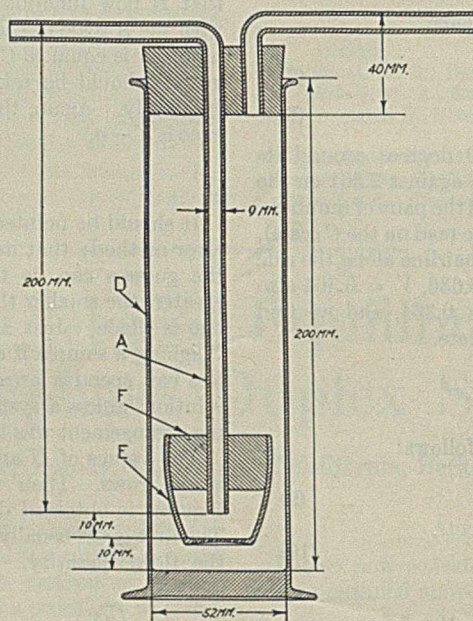


FIGURE 1. DIAGRAM OF APPARATUS

Figures 2 and 3 show the unit which was used in this laboratory.

The air to be sampled is drawn through tube *A* against the bottom of crucible *E*, where the air or gas stream is broken up and allowed to pass through the holes of the crucible into the washing solution in a series of small bubbles, after striking against the bottom of bottle. As the bubbles rise through the solution their progress is somewhat retarded between the sides of the Gooch crucible and the jar, thereby giving a slight scrubbing action. The effects just mentioned tend to give surprisingly good quantitative results in the removal of foreign materials from the gas stream.

It was found that 150 cc. of washing solution were satisfactory for general purposes when using this apparatus.

The use of this unit is not confined to sampling air for metallic dust particles, but may be used for sampling air for dust counting, the absorption of vapors, gases, and many other applications.

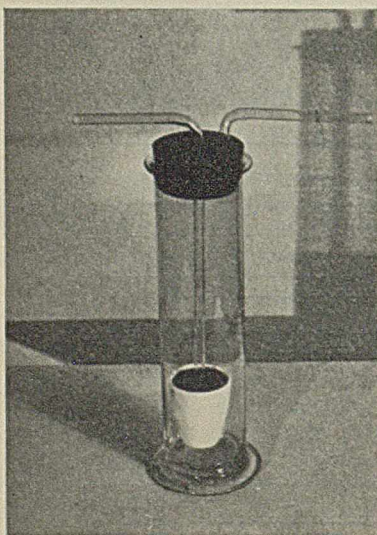


FIGURE 2. SET-UP OF APPARATUS

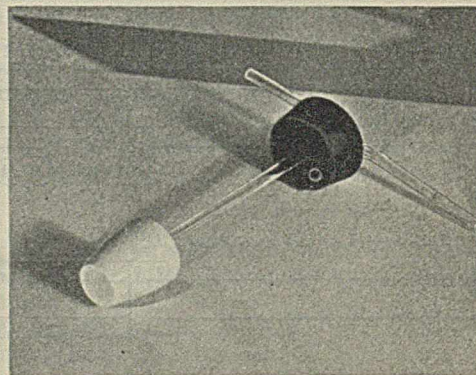


FIGURE 3. CRUCIBLE WITH TUBES IN PLACE

This unit should find favor with investigators because of its simplicity of construction, its low cost, and its high degree of efficiency.

RECEIVED February 29, 1932.

Simple Evaporation Tests for Mineral Oils

J. J. SHANK, The Wayne Laboratories, Waynesboro, Pa.

DURING the course of some work undertaken at this laboratory for the purpose of assisting clients to obtain information relative to various desirable properties of petroleum oils for use in a manufacturing process, the necessity of making comparative determinations of the volatility of different oil samples became apparent.

It has been found useful to impregnate certain varieties of crushed rock granules with oil when these granules are to be used as a surfacing on asphalt felt roofing. This treatment is given in order to eliminate to some extent certain conditions which arise when the surfacing is applied to the felt, among which are blistering and staining of the granules.

The volatility tests now in use do not give results which indicate what may be expected when mineral oils are exposed to evaporation (and oxidation) under such conditions. It is felt that under such conditions there is an accelerated evaporation and oxidation which is entirely different from the volatilization observed when conducting a test under A. S. T. M. designation D 6-30 (1). Since the result desired was to be an expression of the rate of volatilization and oxidation for a given sample when spread out upon a relatively large and uneven surface, and it was desired to compare various samples of oil to obtain a sample which was most constant under such conditions, it was felt that a method could be devised which would give this information with more certainty than the procedure outlined under D 6-30.

The following method has been found very satisfactory when used for comparing the changes obtained with various petroleum oils when subjected to the conditions of the test. The procedure is designed to simulate as closely as possible actual exposure conditions on the roof in regards to area and surface exposed. The results obtained agree very closely, and it has been found possible to reproduce them at will.

METHOD

The method requires the use of a shallow porcelain dish having a diameter of 70 mm., a depth of 10 to 12 mm., and a capacity of 45 ml. The porcelain dish supplied by the Arthur H. Thomas Company, Philadelphia, Pa., Catalog No. 4484, Size 1, meets the requirements and was the dish used in these experiments. In addition, there will be required a quantity of ordinary lead shot, Size 6. This lead shot is carefully dried and stored in a desiccator until used.

Place 44 grams of lead shot (= 1 shot) in the porcelain dish and weigh the dish and shot accurately. Add from a weighing bottle fitted with a dropping pipet 0.3 gram of the oil to be tested. This should preferably be done while the dish is on the balance pan, since this will eliminate the necessity of weighing the oil and the weighing bottle. This amount of shot and oil has been worked out so that there is a sufficient quantity of shot to present a large oil surface to the oven atmosphere when a 0.3-gram sample is used. Place the dish and its contents in an ordinary electric drying oven which has been brought to a temperature of 60° C. Allow 15 minutes for the dish and contents to attain the temperature of the oven, and then heat the sample for 5 hours maintaining the temperature constant at 60° C. Remove, cool in the desiccator, and weigh rapidly when cold. Calculate the loss in weight as volatile matter at 60° C. under test conditions as outlined.

The lead shot serves to break up the sample of oil and present a large area for a given volume in the form of a film.

No comparison has been made between this method and the standard A. S. T. M. method of test, D 6-30. It is quite possible that there will be little if any agreement. It is felt, however, that the method as outlined is a good indication of the relative volatility of the various petroleum oils which we are called upon to test. This is more particularly true since, under the conditions of use, the oil will be spread over a large surface, thus presenting a large area for evaporation. Comparisons with samples of oil of equivalent weight but tested without the addition of lead shot show that the results are higher when the shot is used. This was expected, since it was felt that the addition of lead shot would in a sense produce an accelerated volatilization. The increase was practically proportional when the results on various samples were compared by both methods. A small amount of additional work seems to indicate that so long as the size of the sample is kept reasonably small there is little or no difference in results, whether they are determined on catch weights or on exactly 0.3-gram samples. The main point seems to be that only enough oil should be taken so that it is evenly distributed over the shot without covering it completely, thus insuring a large surface for evaporation.

RESULTS

The following figures of actual tests performed in duplicate are indicative of the results obtained by this method:

OIL	LOSS WITH SAMPLE 1	LOSS WITH SAMPLE 2
	%	%
1	0.12	0.12
2	0.26	0.20
3	0.22	0.23
4	0.48	0.49
5	0.57	0.60
6	0.22	0.18
7	0.14	0.12
8	0.25	0.25
9	0.14	0.12
10	0.09	0.09
11	0.12	0.09
12	0.06	0.06
13	0.12	0.18
14	0.37	0.41
15	0.27	0.31

NOTE. Catch weights of approximately 0.3 gram were used in these determinations.

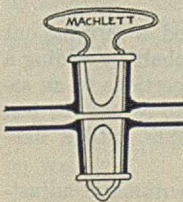
The possibility of oxidation of oil has not been overlooked, but no work has been done on this feature.

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New Hollow Glass Stopcock



A hollow stopcock plug, devised by R. R. Machlett, 50 William St., Long Island City, N. Y., is built from a single piece of glass with the bore drilled through it in exactly the same manner as for a solid plug. This procedure gives plugs made by the new method all the advantages of the old hollow plugs with none of their disadvantages—leakage, tendency to freeze, and high cost. All the customary styles of stopcocks—straight, two-way, three-way, oblique, etc.—are available built by the new method.

Rinnmann's Green Test for Zinc

A. A. BENEDETTI-PICHLER, Washington Square College, New York University, New York, N. Y.

THE formation of Rinnmann's green is generally recognized as one of the best methods of confirming the presence of zinc, and the test is recommended by all of the outstanding textbooks on qualitative analysis (2, 7, 8). Up to the present, however, there has been no perfectly satisfactory way of carrying out the test. This can be easily understood from a discussion of the reactions involved.

According to Hedvall (6), the so-called Rinnmann's green consists of mixed crystals of zinc oxide and cobaltous oxide.

The mixed crystals are obtained by heating the oxides to about 800° C. On heating for a long time at 1100° C., the crystals will be obtained as hexagonal plates, needles, and pyramids of about 2 to 3 mm. in length.

Owing to the limited solubility of cobaltous oxide in zinc oxide, it is found, after ignition, that more than 1 part of cobaltous oxide to about 10 parts of zinc oxide produces reddish brown crystals of cobaltous oxide in addition to the green mixed crystals. With a further increase in the amount of cobaltous oxide present, it finally becomes impossible to confirm the presence of green mixed crystals. Furthermore, though the cobaltic oxide, Co_2O_3 , is not stable above 900° C., oxidation of the cobaltous oxide present in the mixed crystals may take place in the temperature range from 900° to about 300° C. when the preparation cools to room temperature. The cobaltic oxide formed then gives a solid solution with the cobaltous oxide, and the color of the preparation changes to brown or black.

Therefore, in order to obtain a good Rinnmann's green test the following requirements must be fulfilled:

1. Zinc and cobalt must be used in the form of oxides or compounds which are easily transformed to oxides on ignition (nitrates, carbonates).

2. Zinc and cobalt must be present in certain proportions. Especially must an excess of cobalt be avoided. An excess of zinc oxide is by far less dangerous because it acts more or less as a colorless solvent. In the presence of not too large an excess of zinc the green color becomes paler but can be perceived.

3. While hot (below 900° C.) the preparation must be protected against oxidation (presence of a reducing agent—e. g., charcoal or filter paper as carrier of the test—or imbedding in an inert slag), or it must be cooled rapidly through the dangerous temperature range.

Accordingly, aside from the special method of carrying out the test, it is usual to avoid an excess of cobalt by adding a very dilute solution of the latter in small portions to an assumed excess of the zinc preparation, and to repeat the test with increased quantities of cobaltous nitrate until a definitely green residue is obtained.

Emich (3) was the first to attempt an automatic adjustment of the zinc-cobalt ratio. He allowed a droplet of the unknown solution and a 1 per cent cobaltous nitrate solution to diffuse toward each other in a narrow strip of filter paper which was then dried and ignited. It was expected that the

Rinnmann's green test for zinc can be carried out in a very simple way by placing a drop of the test solution on a piece of filter paper impregnated previously with potassium cobalticyanide, drying, and ashing the paper; 0.0006 mg. of zinc still produces a disk of green ash on the spot where the solution had been added. The test is best carried out with a solution obtained by dissolving the zinc sulfide precipitated in the course of a separation in nitric acid. Some of the limit proportions for the presence of other metals are given. The reasons for the reliability of the technic employed may be seen from the discussion of the reactions involved.

correct ratio zinc-cobalt would finally prevail in some zone of the strip, but this method occasionally failed.

Later Emich thought that if a compound containing the cobalt and the zinc in the proper ratio is first prepared, chance could no longer influence the result. He also pointed out that zinc cobalticyanide, which can easily be obtained by precipitation with potassium cobalticyanide from an acid solution, seems to possess the desirable properties.

The zinc cobalticyanide of approximately the formula

$\text{Zn}_3(\text{CoCy}_6)_2$ ¹ resembles the corresponding ferricyanide very closely with respect to crystal form and solubility. It forms a white finely crystalline precipitate which is very difficultly soluble even in acid solutions. On ignition it gives zinc oxide and cobalt oxide in the ratio 3 to 2. Therefore, not all of the cobaltous oxide formed can be dissolved by the zinc oxide. As a result of the ignition we may expect a mixture of mixed crystals and crystals of cobaltous oxide. In fact, the Rinnmann's green obtained in this way exhibits a brownish hue.

It was shown that it is possible to confirm the presence of very small amounts of zinc by precipitating a droplet of the unknown solution on a narrow slide with potassium cobalticyanide, washing the precipitate with dilute nitric acid, drying, and igniting on the slide. Even with a little less than 10^{-4} mg. of zinc it was possible to identify the Rinnmann's green formed under the microscope by its color and shape (pseudomorphic crystals showing the square-shaped outlines of the former zinc cobalticyanide crystals, 1). The properties of the zinc cobalticyanide and of the Rinnmann's green can be investigated in succession even with a single crystal of the former compound.

It is obvious that the reliability and sensitivity of this procedure cannot be surpassed. It has only one disadvantage. In carrying out the ignition on the slide, the slightest overheating causes complete oxidation of the small quantities of Rinnmann's green and, therefore, the ignition must be carried out in a current of inert gas (carbon dioxide). This, of course, renders the procedure complicated and will cause many to refrain from using it.

For the student's use in qualitative analysis the author has always recommended the old practice of soaking a piece of filter paper in a solution containing zinc and cobaltous nitrate, drying, and ashing. Under these conditions failure due to oxidation of the Rinnmann's green already formed never results. This may be due to the protective action of the gaseous products formed by the burning paper, or to the rapid cooling of the small quantity of ash. The ash of the paper may also have an effect. Of course, the test is often spoiled by adding too much of the cobaltous nitrate solution.

The next step was obviously to try the precipitation of the zinc cobalticyanide in filter paper followed by ashing of the paper. This method, using the automatic adjustment of the

¹ Cy = Cn.

zinc-cobalt ratio and a carrier for the test which prevents oxidation during the ignition, appears to be satisfactory in every respect. It combines reliability with sensitivity and outstanding simplicity.

PROCEDURE

According to the technic involved, the test described may be classified as a spot test (5).

The necessary reagent paper is prepared by soaking "ash-free" filter paper in a solution of 4 grams of potassium cobalticyanide and 1 gram of potassium chlorate in 100 cc. of water and drying at room temperature or at 100° C.² When slightly heated, this paper bursts into flame and leaves a perfectly black ash consisting mainly of cobaltous oxide.

For carrying out the test, two ways may be suggested, depending upon the quantity of zinc available.

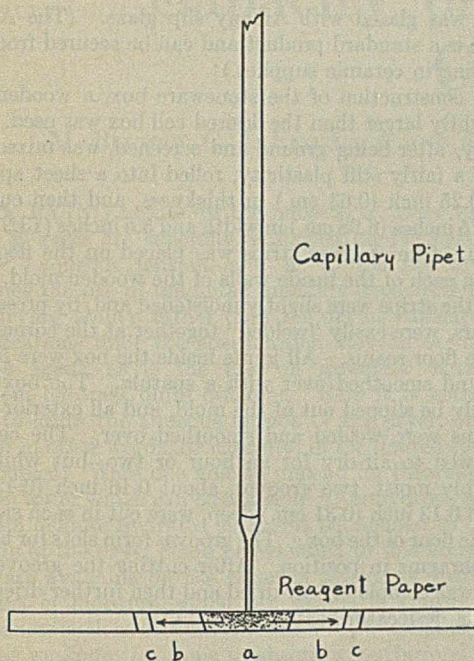


FIGURE 1

MACROTECHNIC. By means of a glass rod transfer one drop of the test solution to the center of a piece of cobalticyanide paper about 1 inch (2 cm.) square, which is held horizontal by means of a forceps. When the drop is completely absorbed, dry by holding the piece of paper high above a small Bunsen flame. A yellow line will appear first along the outline of the drop. Continue drying until the center turns brown. Then light the paper. Place the ash on a clean porcelain dish or plate for inspection. In case zinc is present, a disk of green ash will be visible on the spot where the drop of solution had been added. The green disk is always surrounded by a circular zone containing very little ash. Sometimes it is connected with the surrounding sheet of black ash only by a delicate network of black fibers. This phenomenon is more pronounced when using the second procedure.

MICROTECHNIC. The size of the cobalticyanide paper may be decreased to less than one fourth of the aforementioned. First take the test solution up into a micropipet, a glass capillary of 0.5- to 1-mm. bore with a finely drawn out point of about 0.1-mm. bore at the opening. Touching the center of the reagent paper with the point of the capillary pipet, the solution is sucked into the paper and is spread out in all directions. The arrows in Figure 1 indicate the direction of the flow of the liquid.

It is self evident that the zone around the point where the solution enters the paper, *a*, will finally contain the zinc cobalticyanide precipitate and probably (and favorably) also some zinc nitrate in excess, because toward the end the potassium cobalticyanide originally present will already be used up. Zone *b* finally will

contain only a small amount of salts, the potassium cobalticyanide originally present being rinsed out by the liquid coming from zone *a*. In zone *c* the salt concentration becomes increased. When the paper is dried and ashed as already described, the Rinnmann's green will appear in the center zone, *a*, and zone *b* will form the ring zone containing little ash. The final appearance of the test depends, of course, not only upon the absolute amount of zinc present, but also on the concentration (and volume) of the zinc solution, etc. It is obvious that the study of ash pictures obtained in similar experiments might offer a means for the investigation of diffusion and adsorption phenomena.

Of course, a very small amount of zinc cannot form a disk of green ash. In this case only a small thread or a delicate network of green fibers will be found, but the green color can be distinctly observed under the microscope using a low-power objective and reflected light. Daylight illumination is, of course, most convenient for the inspection of colored objects.

SENSITIVITY OF TEST

The zinc solution used for the test should be acid. The sensitivity of the test was determined using solutions containing about 5 per cent free nitric acid. The following limits (4) were found:

Macrotechnic:	
Limit concentration,	1 mg. zinc/cc.
Limit of identification, about	0.05 mg. zinc
Microtechnic:	
Limit concentration,	0.4 mg. zinc/cc.
Limit of identification, about	0.0006 mg. zinc
(Droplets of 1 to 4 cu. m. volume used)	

But it must be pointed out that the Rinnmann's green test is to be used only after separation of the zinc from most of the other elements. Tin and antimony can also give a green ash. A drop of 1 per cent titanium solution causes an intense blue color of the ash. More dilute (0.2 per cent) titanium solutions give a gray ash. The presence of larger amounts of other metals, such as manganese, iron, cobalt, nickel, or cadmium, interfere with the test, because they also give precipitates with potassium cobalticyanide and dark residues on ashing. The following limit proportions (4) may be mentioned: Zn : Cd = 1 : 5; Zn : Mn = 10 : 1; Zn : Co = 2 : 1; Zn : Ni = 1 : 1; Zn : Ti = 1 : 1; Zn : Al = 1 : 2 (aluminum gives a light blue ash).

It will be seen that it is especially necessary to remove the manganese completely.

Dark-colored zinc sulfide obtained in the course of a separation is best redissolved after washing. The solution is treated with sodium hydroxide and sodium peroxide in order to remove nickel, cobalt, manganese, and iron. From the filtrate the zinc is again precipitated as sulfide, which is finally dissolved in a small volume of 2 *N* nitric acid, and this solution used for the Rinnmann's green test. It is not necessary to adjust the acidity of the solution very carefully, as the test works also with strongly acid solutions (30 per cent nitric acid).

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² Addition of potassium chlorate is not essential. The "cobalticyanide paper" may also be ordered from Microchemical Service, 30 Van Zandt Ave., Douglaston, N. Y.

A New Type of Electrolytic Cell

GEORGE I. WHITLATCH AND ROBERT D. BLUE, Indiana University, Bloomington, Ind.

PORCELAIN cells are used extensively as diaphragms in electrochemical processes, both organic and inorganic, and the conventional, round, white cell is a familiar sight to all workers in this field of chemistry. Commercial cells used for some types of electrochemical work are unsatisfactory, however, in that they do not seem sufficiently porous. Further, difficulty is experienced in that the commercial cells, after 36 to 100 hours of service, begin to disintegrate, and pieces of the outer surface of the cell "spall off" into the electrolytic bath.

The purpose of this paper is to describe a new type of electrolytic cell devised for inorganic electrochemistry. The length of service derived from this new type of cell is in striking contrast to the service obtained from the commercial round cell. One of these new cells has been in use for over a year and as yet has shown no serious deterioration. The porosity of the cell is also considerably greater than that of the usual commercial cell.

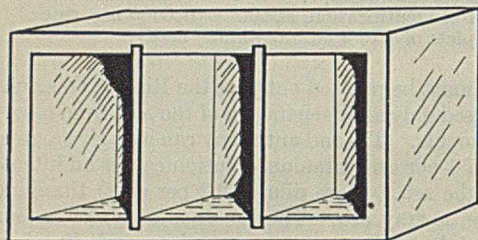


FIGURE 1. DIAGRAM OF MULTIPLE-CELL BOX

Although it is possible to make the ordinary round type of commercial cell by the casting process, the writers found it more convenient to make thin plate-like diaphragms which were used as partition diaphragms between the cells of a multiple electrolytic cell box. The multiple-cell box in which the diaphragms were used was of stoneware, consisting of three cells, made especially for the diaphragms.

THE DIAPHRAGMS

The mixture used in casting the diaphragms, expressed in parts by weight, was as follows:

French flint.....	1 part
Kentucky ball clay.....	2 parts
English china clay.....	2 parts

The three ingredients were first sifted through a 100-mesh screen and then mixed with a sufficient quantity of water to produce a slip of fairly low viscosity. This clay-flint-water mixture is generally known as a "casting slip."

In preparation for the casting of the diaphragms, a shallow tray with sides at least 1.5 inches (3.81 cm.) in height and a plaster of Paris floor 1 inch (2.54 cm.) in thickness was constructed. The tray measured approximately 1 foot (.304 meter) square. The casting slip was poured into this tray until it covered the plaster floor to a depth of about 0.16 inch (0.42 cm.). A slight jarring of the tray during the pouring of the mixture spread the slip uniformly over the floor of the tray.

The plaster floor of the tray absorbed the excess water from the slip rather rapidly, and in less than an hour the casting had "set," although it was still moist and comparatively soft. At this stage the casting was divided into 3-inch

(7.62-cm.) squares with the aid of a spatula. The squares were then allowed to dry thoroughly in air.

THE MULTIPLE-CELL BOX

The stoneware multiple-cell box and the method of fitting the diaphragms into it are shown in Figure 1.

The cell box was approximately 5 by 2.5 by 2.25 inches (12.7 by 6.35 by 5.71 cm.) outside dimensions, and was built by hand from an Indiana underclay (fire clay) having a refractoriness of Cone 10 (standard pyrometric cone scale). The box was glazed with Albany slip glaze. (The Albany slip glaze is a standard product and can be secured from any firm dealing in ceramic supplies.)

In the construction of the stoneware box, a wooden box-mold slightly larger than the desired cell box was used. The underclay, after being ground and screened, was mixed with water to a fairly stiff plasticity, rolled into a sheet approximately 0.25 inch (0.63 cm.) in thickness, and then cut into strips 2.75 inches (6.98 cm.) in width and 5.5 inches (13.97 cm.) in length. One of these strips was placed on the floor and one along each of the inside walls of the wooden mold. The edges of the strips were slightly moistened and, by pressure of the fingers, were easily "welded" together at the corners and along the floor seams. All joints inside the box were further welded and smoothed over with a spatula. The box could now safely be slipped out of the mold, and all exterior joints and seams were welded and smoothed over. The cell box was allowed to air-dry for an hour or two, but while still appreciably moist, two grooves, about 0.16 inch (0.42 cm.) wide and 0.13 inch (0.31 cm.) deep, were cut in each side and across the floor of the box. The grooves form slots for holding the diaphragms in position. After cutting the grooves, the cell box was completely air-dried and then further dried for 8 hours in a desiccator heated to 100° C.

FINISHING CELL BOX

On removal of the cell box from the desiccator, the diaphragms were trimmed to fit the prepared slots in the cell box and were slid into position. Care was exercised to see that the diaphragms fit snugly into the slots. With the diaphragm in place, the entire cell box was dipped into a thin slip of Albany glaze. The glaze was allowed to air-dry before the cell box was again sent to the desiccator where it was given a second drying of 4 hours at 100° C.

On removal from the desiccator this second time, the raw glaze was thoroughly scraped off the diaphragms to within 0.25 inch (0.63 cm.) of their margins. The cell box was fired in a muffle kiln until the glaze "matured."

The type of glaze used on the cell box matures about Cone 4, and experimentation has demonstrated that this temperature is sufficient to produce the desired porosity of the diaphragms as well as burn the body of the cell box to a well-fused condition. The porosity produced at this heat in a diaphragm composed of the mixture used by the writers is considerably higher than the porosity of the commercial cell and has proved satisfactory for the type of research for which the diaphragms have been used.

CONCLUSIONS

The cell-box described above has several points of merit. In the first place, the multiple-cell feature of the box is

desirable as it gives a very compact unit containing two cells for the electrodes and a central supply cell. Further, the stoneware box and its cells are glazed with a material that is resistant to most acids and bases, and therefore is well adapted to chemical work. The diaphragms are sealed into place by the glaze and danger of leakage around them is impossible as long as the glaze remains intact. Sealing of the diaphragms into position by the glaze also allows the use of the cell box for heated and strongly alkaline solutions; this would not be possible if a wax seal were used.

The composition of the mixture used in the diaphragms is similar to that used in the manufacture of commercial cells.

The writers do not claim any originality for that feature, but the casting method of making these diaphragms is felt to be an improvement over the commercial cell made by dry-press methods. Casting of the diaphragms has resulted in a more uniformly porous product free of spalling, and it is believed that this method of making diaphragms has a practical value. It is entirely possible to make the electrolytic cells in the usual round shape by casting methods, and the writers are of the opinion that the present commercial cell can be improved by manufacturing such cells by the casting process instead of by the present dry-press methods.

RECEIVED March 21, 1932.

Capacity of Drying Agents for Gas Masks

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DRYING agents for the removal of water vapor from gases are generally employed on the basis of their aqueous tension, and as a rule the investigator assumes the use of unlimited amounts depending merely on the drying ability rather than the drying capacity. When specifications limit the space which may be occupied by a drying agent, as is the case in gas-mask canisters, the problem becomes quite different. Here it is necessary not only to know the aqueous tension of the dryer, but also its life, or in other words, its capacity, in the limited space which it occupies. Were one able to depend on theoretical values for the water which can be taken up by anhydrous substances to form definite hydrates, he might be inclined to think that the life of the dryer could be extended to this limit. Where data are available on the aqueous tension of hydrates, the amount of moisture which can escape is known. Certain substances such as calcium chloride and phosphorus pentoxide will, as we know, continue to absorb water beyond the point where definite hydrates have formed. Here we are not only confronted with a tendency toward increasing aqueous tension, but also with the further tendency of the dryer to become pasty or even liquid. For units such as the canisters in gas masks, pasty and liquid dryers cannot be used.

In the investigation undertaken, a catalyst for the conversion of carbon monoxide to carbon dioxide was employed at room temperature, with the gas stream at 50 per cent humidity, and with a rapid flow of gas. The use of various adsorbents, reactants, and dryers necessarily limits the space which the drying agent may occupy in a unit which shall be of a convenient size for safety and rescue work. With this in mind, the life of the drying agent was based on its ability to insure complete conversion of the carbon monoxide to carbon dioxide, with the particular catalyst concerned, in low-temperature conversion.

A catalyst sufficiently active to oxidize completely the carbon monoxide present in the gas at temperatures as low as 0° C. was found to be very sensitive to water vapor. The activity of this catalyst was decreased by 5 per cent when 1 per cent of its weight of water was adsorbed, and it became completely inactive when it had adsorbed 2.5 per cent of its weight of water. The above characteristics of the catalyst suggested its use for the determination of the capacity of drying agents.

The catalyst was intended for use in a carbon monoxide

gas-mask canister whose volume is limited by practical considerations, such as weight and breathing resistance. The space occupied by the drying agent was 150 cc. One tenth of this volume was used in the following tests.

A drying agent had to satisfy two requirements before its capacity was determined: it has to be granular in form in order to have low resistance to gas flow; also no noxious gases should be eliminated when water was adsorbed.

As has been intimated, the above requirements eliminate all liquid drying agents commonly used, as sulfuric or phosphoric acids, as well as materials which react with water with the subsequent evolution of a gas or vapor—i. e., a calcium carbide. Phosphorus pentoxide cannot be used, as it has a high initial resistance to gas flow which rapidly increases with the absorption of water vapor.

METHOD OF TESTING

The method used in testing the capacity of the drying agents was as follows: 15 cc. of the drying agent of 12–14 mesh were placed in an upright glass tube, 3 cm. in diameter, and the catalyst placed above it, a wire screen disk separating the two materials. Air 50 per cent saturated with water vapor at 20° C., containing 1 per cent of carbon monoxide by volume, was passed through the tube at 200 liters per hour. A carbon monoxide indicator sensitive to 0.01 per cent of carbon monoxide was used to determine the presence of carbon monoxide in the effluent gas. Twenty cubic centimeters of catalyst granules of 12–14 mesh were used in all tests. The capacity of the drying agent was measured by the time required to decrease the activity of the catalyst from 100 to 95 per cent. This 5 per cent decrease in activity meant that the dryer had permitted 0.17 gram of water vapor, which is 1 per cent of the catalyst weight, to escape and be adsorbed by the catalyst.

The relative humidity of the gas was controlled by passing it through two bottles of dilute sulfuric acid placed in series, the vapor pressure of water vapor over the acid being 13.2 mm. of mercury at 20° C.

At 200 liters per hour, the barometric pressure being 746.0 mm. of mercury, the volume of water vapor in the gas is 3.54 liters per hour, which is equivalent to 3.2 liters per hour at standard conditions, or 0.043 gram of water per minute. Since 4 minutes are required to deliver 0.17 gram of water, the

time when the dryer failed, as determined by experimentation, was reduced by 4 minutes, thus giving the actual life of the drying agent.

All drying agents tested were dehydrated at 400° C. under a total pressure of 20 mm. of mercury, with the exception of aluminum oxide and magnesium perchlorate. Aluminum oxide was dehydrated by heating to 1000° C. for 6 hours, magnesium perchlorate by gradually heating to 200° C. under a total pressure of 5 mm. of mercury.

TABLE I. CAPACITY OF DRYING AGENTS

DRYING AGENT	LIFE Minutes	WT. OF	WT. OF MATE-	WATER
		WATER ABSORBED	RIAL OCCUPY- ING 15 CC.	
		Grams	Grams	%
Al ₂ O ₃	71	3.04	11.2	27.2
Mg(ClO ₄) ₂	56	2.40	7.5	32.0
CaCl ₂	56	2.40	11.0	21.8
BaO	26	1.11	30.0	3.7
CaCl ₂ , soda lime (50% each)	20	0.86	9.5	9.05
BaO ₂	16	0.69	27.0	2.6
Al ₂ (SO ₄) ₃	13	0.56	7.4	7.6
NaOH pellets	6	0.258	15.2	1.7
Na ₂ SO ₄	4	0.172	11.6	1.5
MgCl ₂	2	0.086	7.8	1.1
MgSO ₄	1	0.043	8.3	0.52
CaO	1	0.043	21.2	0.21

COMPARATIVE CAPACITIES OF VARIOUS DRYING AGENTS

Of the twelve drying agents tested in the above manner, only three were able to protect the catalyst for a minimum of 1 hour. Some of the drying agents permitted a small amount

of water vapor to escape from the start, the amount increasing as the material became hydrated. Calcium chloride, calcium oxide, and sodium hydroxide belong to this class. Others completely absorbed the water vapor up to a certain point, and then broke sharply, causing a rapid decrease in the activity of the catalyst. Magnesium perchlorate, aluminum oxide, sodium sulfate, barium oxide, and barium peroxide belong to this group.

Table I contains the experimental data, 15 cc. of drying agent and 20 cc. of catalyst being used in each test.

The significant value in this table is the weight of water absorbed by a definite volume of drying agent. Aluminum oxide absorbed the most water; next were calcium chloride and magnesium perchlorate. The others had relatively poor capacity.

It is of interest to observe that calcium chloride and magnesium perchlorate have the same capacity for water, although calcium chloride has a higher vapor pressure than magnesium perchlorate. The important difference in their behavior is that calcium chloride permits a small but measurable amount of water vapor to escape from the start, whereas magnesium perchlorate completely dries the gas until its capacity is reached.

RECEIVED March 4, 1932. Presented before the Division of Gas and Fuel Chemistry at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932. Contribution 229 from the Department of Chemistry, University of Pittsburgh.

Direct Gravimetric Determination of Sodium in Commercial Aluminum

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THE magnesium uranyl acetate method for sodium is capable of giving satisfactory quantitative results when minute quantities of the element are present (1), and aluminum does not interfere with the determination (3). Since sodium is sometimes present as an impurity in aluminum, it was thought desirable to ascertain whether or not this method could be applied directly for estimating the percentage of this impurity in the commercial metal, and thus avoid difficulties inherent in any method based upon the preliminary separation of the sodium from the aluminum and other components of this material.

The samples for the experiments were furnished through the courtesy of the Research Laboratories of the Aluminum Company of America.

As the result of certain preliminary trials, the procedure followed was first to dissolve the weighed sample of drillings in the minimum possible amount of dilute hydrochloric acid, using a silica dish for this purpose. After dilution with water, the solution was filtered and the filtrate was concentrated to the smallest possible volume in a Pyrex flask, usually until hydrated aluminum chloride just started to separate. Then 100 cc. of magnesium uranyl acetate reagent were added and the determination completed as detailed elsewhere (2, 3). Apparently the various other impurities in the particular samples examined caused no interference. Precipitates were examined for silica with a view to applying a correction, but the amount present was always found to be insignificant. There was no reason to suspect that metallic impurities would cause error, and no evidence was found that they did.

With a sample of comparatively high sodium content the method proved quite satisfactory. As the results in Table I

show, the individual determinations checked well with each other and with the value for the sodium content of this particular material as determined in the laboratories of the Aluminum Company of America by their procedures. With a sample of somewhat lower sodium content, however, considerable difficulty was experienced in reducing the solution volume of the necessarily larger sample down to the point required for obtaining correct values by this method. The irregular results obtained in the second group of determinations reflect this difficulty. Even the use of a more concentrated reagent and the addition of this to larger volumes of solution, in this case 10 to 12 cc., as recommended in a recent paper (1), failed to produce entirely acceptable results. The last three values in the table were obtained in this manner.

TABLE I. DIRECT DETERMINATION OF SODIUM IN COMMERCIAL ALUMINUM

SAMPLE	WT. OF SAMPLE TAKEN Grams	WT. OF PPT. FOUND Gram	SODIUM FOUND		STATED VALUE %
			To 3rd decimal %	To 2nd decimal %	
A	0.750	0.0183	0.037	0.04	0.04
	1.000	0.0230	0.035	0.04	
	1.500	0.0367	0.037	0.04	
			Av. 0.036	0.04	
B	2.000	0.0114	0.009	0.01	0.009
	2.000	0.0204	0.016	0.02	
	2.000	0.0171	0.013	0.01	
	2.000	0.0185	0.014	0.01	
	2.000	0.0095	0.007	0.01	
	2.000	0.0190	0.015	0.02	
			Av. 0.012	0.01	
B	2.000	0.0115	0.009	0.01	0.009
	2.000	0.0107	0.008	0.01	
	2.000	0.0173	0.013	0.01	
			Av. 0.010	0.01	

In general, it was apparent from the experiments that the amount of sodium in sample B represented the lowest possible percentage that could be estimated by this procedure, and that even in this case the results were not very satisfactory. It is recommended, therefore, that this method be applied only to the determination of sodium in metallic aluminum when the percentage of this impurity is greater than 0.01 per cent.

When this is the case, the above simple procedure is capable of yielding good results.

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RECEIVED February 27, 1932.

Construction of Accurate Air Separator

PAUL S. ROLLER, U. S. Bureau of Mines, New Brunswick, N. J.

THE author has previously described (1) a new type of air separator holding a charge of 600 cc. of powder and capable of effecting a particle-size separation into successive fractions beginning with 0-3 or 0-5 microns. Operations with this apparatus were at the time confined chiefly to Portland cement and pulverized anhydrite.

Recently there has been occasion to fractionate a gypsum powder that had been ground very fine in a pebble mill. In making a 0-5 micron cut on this material the rate of separation was found to be unusually low compared to the corresponding anhydrite fraction, even when allowing for the smaller rate of air flow due to the lower density of gypsum (2.32 as against 2.98). With the anhydrite the rate at which 0-5 micron particles collected in the felt filter bag, averaged over the first hour and a half, was 27 grams per hour; with the gypsum, however, the rate was only 3.3 grams per hour.

The difference was attributed to suspension and adherence of the soft fine gypsum particles in the lower conical portion of the 60.8-cm. (24-inch) settling chamber used. To counteract this condition, it was decided to tap the conical portion automatically. When this was done the 0-5 micron gypsum fraction separated out much more rapidly; the rate, averaged over the first hour and a half, being 16 grams per hour as against 3.3 grams per hour without tapping—i. e., the increase in rate was fivefold.

Besides greatly augmenting the rate of separation, the automatic tapper also increases the homogeneity of a given fraction. To understand how this comes about, it is recalled that in a given fractionation the particles that are blown over progressively increase in size with time. At the end point, corresponding to a definite rate of separation, which depends upon air flow and particle size and may be as high as 10 or 12 grams per hour, the particle sizes are in the boundary between the given fraction and the next succeeding fraction. If the fractionation is prolonged beyond the end point, the particle sizes will increase to a maximum value 1.41 times the theoretical maximum given by Stokes' law. This is because the maximum velocity at the center of the vertical chamber is by Poiseuille's law twice the mean velocity. Automatic tapping of the settling chamber renders the succession of particle sizes blown over more uniform, so that at the end point the number of particles which are greater or smaller than the theoretical maximum in size are reduced to a minimum. This result is particularly important at the higher rates of air flow.

Because of the pronounced increase in rate of separation and greater homogeneity of the fractions, not only for gypsum but also as observed for all other powders, the automatic tapper is now used as a standard adjunct to the air separator previously described (1).

The construction and method of mounting the automatic tapper, *I*, are shown in Figure 1. The oscillations of the U-tube, *C*, about bearing *B* impart the required motion to the tapper. The latter consists of three leaves, clipped to-

gether, of 0.8-mm. ($\frac{1}{32}$ -inch) spring steel about 4.5 cm. (1.75 inches) wide and 30.5 cm. (12 inches) high. At the upper end is a wooden hammer head weighted with lead so as to give an optimum blow. At the lower end the tapper is clamped in cantilever fashion to an L-shaped bracket which moves along a slotted horizontal plate. The latter is rigidly attached to the U-bend by means of uprights. The

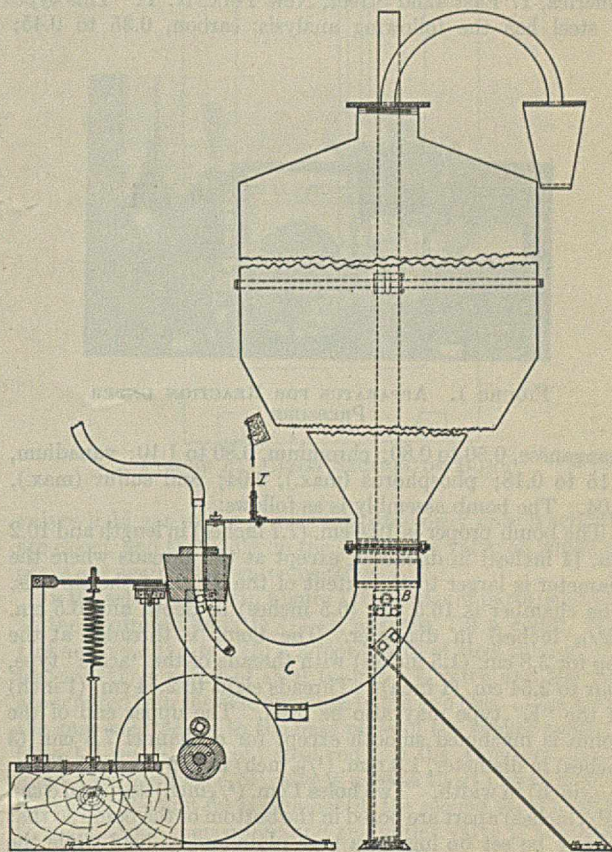


FIGURE 1. AIR SEPARATOR, VERTICAL SECTION

tapper is brought into position for maximum impact by moving it along the two slots in the horizontal plate, and is fastened in place on the horizontal plate by means of washers and wing nuts that screw onto bracket studs projecting through the slots.

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RECEIVED February 23, 1932. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures

HOMER ADKINS, University of Wisconsin, Madison, Wis.

AN APPARATUS considered most satisfactory for laboratory use in carrying out reactions involving the agitation of a liquid and solid in the presence of a gas at temperatures and pressures above the normal (1) is pictured in Figure 1. It is convenient to describe this equipment under five heads—i. e., bomb, liner, gas inlet, heater, and shaker assemblies.

BOMB ASSEMBLY

A photograph of the bomb assembly and its parts is reproduced in Figure 2, and a cross-sectional diagram shown in Figure 3. All parts were made from a special steel S. A. E. No. 6140, obtained from the Crucible Steel Company of America, 17 East 42nd Street, New York, N. Y. This type of steel has the following analysis: carbon, 0.35 to 0.45;

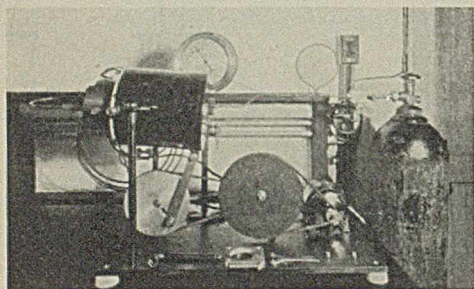


FIGURE 1. APPARATUS FOR REACTION UNDER PRESSURE

manganese, 0.50 to 0.80; chromium, 0.80 to 1.10; vanadium, 0.15 to 0.18; phosphorus (max.), 0.04; and sulfur (max.), 0.04. The bomb assembly is as follows:

The bomb proper is 19.6 cm. (7.7 inches) in length and 10.2 cm. (4 inches) in diameter, except at the threads where the diameter is larger to the extent of the depth of the threads. The chamber is 16.5 cm. (6.5 inches) in depth and 6.5 cm. ($2\frac{9}{16}$ inches) in diameter. The bomb is threaded at the top for 3.8 cm. (1.5 inches) with threads of the "acme" type, four to 2.54 cm. (1 inch). Threads eight to 2.54 cm. (1 inch) of the "E" type may also be used. The upper end of the bomb is machined smooth except for a channel 7.6 cm. (3 inches) in diameter, 1.3 mm. ($\frac{1}{20}$ inch) in depth, and 1.3 mm. ($\frac{1}{20}$ inch) in width. Two holes 1 cm. ($\frac{3}{8}$ inch) deep and 8 cm. ($3\frac{1}{3}$ inches) apart are bored in the bottom of the bomb so that it may be set on lugs in a base plate and so held while the cap screws in the bomb-head cover are tightened.

The bomb head is 10.2 cm. (4 inches) in diameter and 1.4 cm. ($\frac{9}{16}$ inch) thick. The boss is 3.2 cm. (1.25 inches) in height, and 5.4 cm. ($2\frac{1}{8}$ inches) in diameter. The thermocouple well is bored out of a steel rod 12.8 cm. (5 inches) in length and 1 cm. ($\frac{3}{8}$ inch) in diameter. Thermocouple wells are also readily made from 1.4 by 0.47 cm. ($\frac{9}{16}$ by $\frac{3}{16}$ inch) high-pressure tubing welded at one end. It is screwed into the bomb head to a depth 1.6 cm. ($\frac{5}{8}$ inch) against a copper gasket. The chamber in the thermocouple well and the corresponding opening in the bomb head is 4.7 mm. ($\frac{3}{16}$ inch) in diameter. If a thermometer is to be used, the diameter of the well should be increased to 16 by 8 mm. ($\frac{5}{8}$ by $\frac{5}{16}$ inch).

The thermocouple well is set 8 mm. ($\frac{5}{16}$ inch) off center. The inlet for the gas line is the standard one for use with 6.4 by 3.2 mm. ($\frac{1}{4}$ by $\frac{1}{8}$ inch) tubing. The opening from the chamber through the bomb head to the connection for the gas line is 3.2 mm. ($\frac{1}{8}$ inch) in diameter. The lower surface of the bomb head is machined smooth except for a groove similar to that on the top of the bomb and for a recess 0.8 mm. ($\frac{1}{32}$ inch) in depth and 6.4 mm. (0.25 inch) in width which holds the copper gasket. The bomb head is protected from the cap screws in the bomb-head cover by interposing a brass or steel plate 6.4 mm. (0.25 inch) in thickness and 9.9 cm. ($3\frac{7}{8}$ inches) in diameter with a circular opening in the center for the boss of the bomb head. The copper gasket is made from a copper sheet 3.2 mm. ($\frac{1}{8}$ inch) in thickness. It is 8.3 cm. (3.26 inches) outside diameter and 7 cm. (2.75 inches) inside diameter, and is therefore 6.4 mm. (0.25 inch) in width and fits into the recess provided for it in the bomb head. Lead gaskets from 3.2 mm. ($\frac{1}{8}$ inch) sheet lead and cut with an outside diameter of 9.9 cm. ($3\frac{7}{8}$ inches) and an inside diameter of 6 cm. ($2\frac{3}{8}$ inches) may ordinarily be used in place of copper.

The bomb-head cover is 12.7 cm. (5 inches) in diameter and 8.6 cm. ($3\frac{3}{8}$ inches) in height. The thread recess is 6.3 cm. (2.5 inches) deep. The opening in the bomb-head cover for the boss of the bomb head is just over 5.4 cm. ($2\frac{1}{8}$ inches) in diameter. The bomb-head cover carries eight square-headed cap screws 12.7 mm. (0.5 inch) in diameter, 3.8 cm. (1.5 inches) in length, thirteen threads to 2.54 cm. (1 inch). These are equally spaced on a circle 8 cm. ($3\frac{1}{8}$ inches) in diameter. Three holes 12.7 mm. (0.5 inch) in diameter and depth are bored at equal intervals in the side near the top of the bomb-head cover.

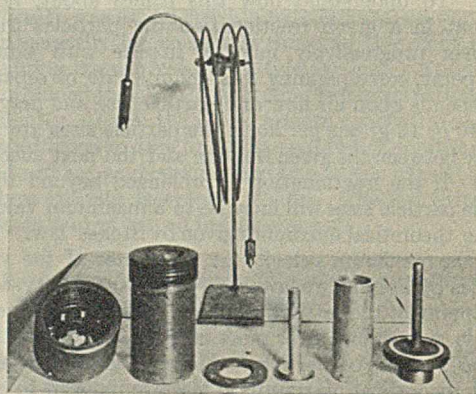


FIGURE 2. STEEL SPIRAL AND PARTS OF BOMB AND LINER

A bomb having about five times the capacity of the one described above but having essentially the same construction was made for us by the American Instrument Company, 774 Girard Street, Washington, D. C. This bomb is 12.5 cm. ($4\frac{1}{16}$ inches) in diameter, 37.5 cm. (14.75 inches) in length, and the chamber is 8.4 by 33.7 cm. (3.3 by 13.25 inches). The bomb head is 10.5 cm. ($4\frac{1}{8}$ inches) in diameter, 1.4 cm. (0.5 inch) thick, with a boss 5.1 cm. (2 inches) in diameter

and 5.5 cm. ($2\frac{1}{8}$ inches) high. The bomb-head cover is 15.2 cm. (6 inches) in diameter and 10.5 cm. ($4\frac{1}{8}$ inches) high. The bomb and bomb-head cover are threaded for 6.4 cm. (2.5 inches) with "E" type threads, eight to 2.54 cm. (1 inch). There is an offset 11 by 19 mm. ($\frac{1}{25}$ by $\frac{3}{4}$ inch) just above the threads in the cover. The twelve 32 by 12.7 mm. (1.25 by 0.5 inch) cap screws extend through steel for 16 mm. ($\frac{5}{8}$ inch) to press against the steel thrust plate, which in turn is forced against the bomb head. The copper gasket is 9.6 cm. (3.77 inches) outside and 9.2 cm. (3.62 inches) inside diameter, and 1.6 mm. ($\frac{1}{16}$ inch) thick.

LINER OR REACTION CONTAINER

This is made of standard brass tubing having a wall thickness of approximately 1.6 mm. ($\frac{1}{16}$ inch). A reproduction of a photograph of one of these liners is shown in Figure 2 and a cross-sectional diagram in Figure 4. (The closure of the liner pictured in Figure 2 is somewhat different from that recommended and shown in Figure 4.) For the smaller bomb described above, the liner is made from brass tubing 6.4 cm. (2.5 inches) outside diameter, and for the larger bomb from 8.3-cm. (3.25-inch) tubing. The over-all length of the liner complete should be approximately 6.4 mm. (0.25 inch) less than the depth of the chamber in the bomb. The bottom of the liner is a brass plate 3.2 mm. ($\frac{1}{8}$ inch) thick, silver-soldered into place. The top of the liner is a brass plate 9.6 mm. ($\frac{3}{8}$ inch) thick, which carries a well for the thermocouple well of the bomb head. The top plate is screwed down against a lead gasket. A piece of brass of the shape indicated in the drawing is placed inside the larger brass tube and attached to it with silver solder. The ledge for the gasket is 6.4 mm. (0.25 inch) wide and grooved as described for the bomb and bomb head. The threads are eighteen to 2.54 cm. (1 inch). A 1.6-mm. ($\frac{1}{16}$ -inch) hole is located in the side half way from the top to the bottom of the liner, through which gas may enter the reaction space. The well in the liner is of brass tubing 0.8 mm. ($\frac{1}{32}$ inch) in wall thickness, and is closed at the bottom. It is screwed into and soldered to the top of the liner so that it is 8 mm. ($\frac{5}{16}$ inch) off center. The tubing may be either 19 mm. (0.75 inch) or 12.7 mm. (0.5 inch) inside diameter, depending upon the diameter of the well in the bomb head. Two holes 6.3 mm. (0.25 inch) deep and 4.8 mm. ($\frac{3}{16}$ inch) in diameter are located in the head of the liner to permit the insertion of the lugs of a wrench to be used in opening and closing the liner. The capacity of the liner for the smaller bomb is approximately 150 ml., whereas the larger accommodates 750 ml.

GAS INLET ASSEMBLY

The essential parts of this assembly are a spiral of steel tubing, a gage, two valves, and such nipples and connections as are necessary for attaching these to the hydrogen tank, to the bomb, and to each other. Drawn molybdenum steel tubing 6.4 mm. (0.25 inch) outside diameter by 3.2 mm. ($\frac{1}{8}$ inch) inside diameter is used for the spiral and nipples. A suitable arrangement of the spiral is shown in Figure 2. A piece 2.3 meters (7 feet) or more in length may be made into a spiral by wrapping it around a gas tank 15 cm. (6 inches) in diameter. The spiral will then spring out to a diameter of approximately 23 cm. (9 inches). The spiral is washed out with hydrochloric acid and then with acetone before it is put into use. This washing is to remove scale, etc., loosened during the bending process and which may later accumulate at one point and close the opening.

The dimensions and type of connection will necessarily depend upon the valves, etc., which are to be used. The standard connection for 6.4 by 3.2 mm. ($\frac{1}{4}$ by $\frac{1}{8}$ inch) tubing has been described (2). All other connections should be made gas-tight with the aid of lead or copper gaskets.

The gage is of the hydraulic type, 15.2-cm. (6-inch) iron case, with 12.7-mm. (0.5-inch) straight pipe thread connection, purchased from the United States Gauge Company. It is calibrated for pressures up to 340 atmospheres (5000 pounds per square inch). The valves supplied by the American Instrument Company are perhaps the most satisfactory, although the much cheaper Hoke valves have given excellent service. If these latter are used, care must be taken to insert them in the system so that the arrows on them are pointing away from the bomb system. This is necessary because these cheaper

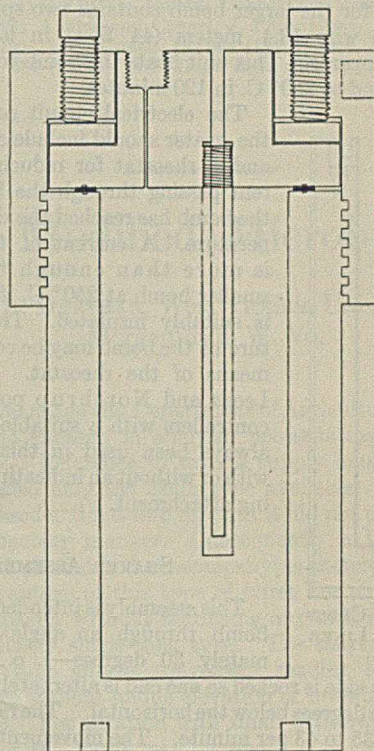


FIGURE 3. CROSS SECTION OF BOMB

valves hold gas under pressure satisfactorily only when they are closed, and then only on the side of the valve on which the gas is not against the valve packing.

In the set-up shown in Figure 1, the order of parts beginning at the hydrogen tank is (1) an adapter, (2) a collar, (3) a Hoke valve, (4) a tee, (5) a 2-foot length of steel tubing, (6) a tee, and (7) a spiral of steel tubing. A valve and the gage are screwed into the side openings in the two tees. The tee for the gage is attached to the base plate of the shaker assembly by a 1.9-cm. (0.75-inch) steel rod. If the American Instrument Company type of valve is used, a short nipple replaces the collar, the first tee is eliminated, the second tee is changed to a four-way connection, and the outlet valve is connected to it by a short nipple.

HEATER ASSEMBLY

The heating unit is made of two spirals of No. 18 nichrome wire connected in parallel and each carrying approximately 3.5 amperes on a 110-volt current. These spirals are made by winding a 22.9-meter (75-foot) length of the nichrome wire on a 1-cm. ($\frac{3}{8}$ -inch) steel rod which is rotated in a lathe. The spiral is then removed from the rod and pulled out to a length of about 1.5 meters. A hollow cylinder of 0.8-mm. ($\frac{1}{32}$ -inch) sheet iron is then made of such a diameter as to slip over the bomb as far as the bomb-head cover. The sheet iron is covered with a layer of asbestos paper and the spirals of

nichrome wire wound over it. The spirals are kept separate from each other by interposing asbestos between them. The terminals of the spirals are fastened to binding posts on a circular piece of transite attached to one end of the sheet-iron cylinder. The spirals are covered with two layers of asbestos paper and a second sheet-iron cylinder slipped over the covered spirals. Such heating units have been in almost daily use for 2 or 3 years and have given entire satisfaction. When carrying the maximum of 7 amperes, the unit will heat the smaller bomb referred to above to 100° C. in 30 minutes, to 200° C. in 60 minutes, and to 250° C. in 80 minutes. The heating unit for the larger bomb contains two spirals of No. 18 nichrome wire 13.4 meters (44 feet) in length, each carrying 6 amperes. This unit heats the bomb to 200° C. in 87 minutes and to 250° C. in 120 minutes.

The electrical circuit connected to the heater should include an ammeter and a rheostat for reducing the current passing through the heater after the bomb has reached the desired temperature. A current of 4.5 amperes is more than enough to keep the smaller bomb at 250° C. if the heater is suitably insulated. The temperature of the bomb may be controlled by means of the rheostat. However, Leeds and Northrup potentiometer controllers with a suitable relay have always been used in this laboratory with or without an indicating or recording attachment.

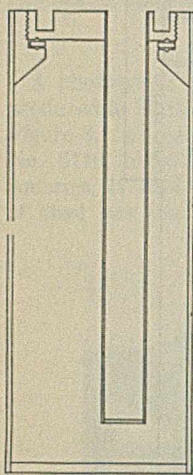


FIGURE 4. CROSS SECTION OF LINER

SHAKER ASSEMBLY

This assembly is intended to rock the bomb through an angle of approximately 30 degrees—i. e., the bomb placed on its side is rocked so one end is alternately 15 degrees above and 15 degrees below the horizontal. The rate of oscillation is from 35 to 43 per minute. The movement is obtained from a 0.05 h. p. electric motor having a speed of 1725 revolutions per minute and bearing a pulley 2.2 cm. ($\frac{7}{8}$ inch) in diameter. A belt from this pulley passes to a free running pulley 22.7 cm. (9 inches) in diameter, which has a pulley 2.2 cm. ($\frac{7}{8}$ inch) in diameter attached to it. A second belt passes from this smaller pulley to a 17.2-cm. (6.75-inch) slotted pulley. This slotted pulley is attached by a driving arm to the receptacle which holds the bomb heater, which in turn holds the bomb. The slot in the pulley makes it possible to adjust the stroke of the driving arm and hence to control to a certain extent the violence of the agitation of the reactants. This may be further modified by changes in the size of the pulley on the motor shaft.

It seems unnecessary to describe in any considerable detail the construction of the shaker, since it may be modified in so many ways. The heater receptacle should be so constructed as to minimize heat losses. The one illustrated has a layer of insulating material approximately 25 mm. (1 inch) thick about the heater. All parts of the shaker shown in Figure 1 are mounted on a 12.7-mm. (0.5-inch) steel base plate. It also carries two lugs for holding the bomb in position while it is being opened and closed, as well as a device for holding the liner while its head is being screwed down or loosened. The bearings for the pulleys and the shaker are mounted on five 1.9-cm. (0.75-inch) steel rods screwed into the base plate. The bearings are attached to the upright rods by means of the larger size muffs ordinarily used on ring stands. If, with the bomb in place and the spiral attached, the shaker is not well balanced, then a weight should be so added that the shaker

moves up and down with the expenditure of the minimum of effort.

OPERATION OF EQUIPMENT

The catalyst and reactant(s) with or without a solvent are placed in the liner and the head tightened down snugly. The liner is then placed in the bomb while the latter is resting on the lugs provided in the base plate. Care must be taken to note the location with respect to the bomb of the hole in the side of the liner. The bomb head (with the copper gasket in the recess provided for it) is placed in position with the thermocouple well extending down into the well in the liner. (The wells were made "off center" so that the liner cannot turn in the bomb after the bomb is closed.) The thrust plate is then placed on the bomb head and the bomb-head cover screwed down (to within a fraction of a turn) as far as it will go. The cap screws are then turned down. Each screw should be turned down only a little at a time, the order of tightening being in general

		3		
	5		8	
1				2
	7		6	
		4		

The bomb is placed in the shaker, care being taken that the hole in the side of the liner is uppermost. The gas line is screwed in and tightened, the bomb being held from turning by a rod inserted into one of the holes in the side of the bomb-head cover. Gas is allowed to flow into the bomb from the tank slowly until a little more than the desired pressure is registered by the gage. The valve between the tank and the bomb is then closed and the shaker started. There will be a slow drop in pressure for a few minutes, but after 5 minutes there should be no further drop. If there is a further drop in pressure, all connections (valve stems, etc.) should be tested with a soap solution. If the leak is at the gasket, then the cap screws may be further tightened. If the leak persists, there is probably a defect in the gasket. This may sometimes be remedied by simply opening and closing the bomb. If this is not effective, a new gasket should be used. When no drop in pressure has been noted on the gage for an interval of 5 or 10 minutes, the heater may be turned on. Shortly before the temperature of the bomb reaches the desired value, the current passing through the heater should be reduced to such a value as will not permit the bomb to go much higher in temperature.

As the bomb is heated, the pressure as indicated by the gage will rise approximately in accord with the temperature expressed on the absolute scale, the amount of the deviation being mainly a function of the compounds in the liner. The deviations will become considerable as the critical temperature of any compound is reached (190° to 200° C. for ether, 245° to 250° C. for ethanol). In general, however, the discrepancy between the calculated and observed pressure is due to the absorption of hydrogen. Thus a comparison of the calculated and observed pressures at various temperatures will indicate the point at which hydrogenation begins.

The relationship between the drop in pressure, indicated by the gage and the amount of hydrogen absorbed should be determined by hydrogenating some compound such as acetone which is smoothly and quantitatively hydrogenated to a single product. For a smaller bomb described with 100 ml. of liquid in the liner, the pressure drop for one mole of hydrogen will approximate 1250 pounds persquare inch (85 atmospheres) measured at 22° C., or 1740 pounds (119 atmospheres) measured at 150° C. For the larger bomb with 500 ml. of liquid in the liner, the pressure drop per mole of hydrogen will

approximate 275 pounds per square inch (19 atmospheres) measured at 22° C. The drop in pressure per mole of hydrogen is a linear function of the amount of liquid in the bomb, the slope of the line being dependent upon the space for gas in the bomb.

The extent of hydrogenation may be approximated by observing the drop in pressure at the temperature of hydrogenation. However, such a value is in general much less accurate than that based upon a comparison made at room temperature between the pressure before the bomb was heated up with that observed after the contents of the bomb have cooled to the original temperature.

When the desired reaction is complete, the bomb may be pulled partially out of the heater in order to facilitate its cooling. Often it is advantageous then to place a water jacket around the bomb so that it may be more rapidly cooled to room temperature.

When the bomb has cooled to room temperature, the pressure is *slowly* released by allowing the gas to escape through the outlet valve. The gas inlet is disconnected from the bomb, the latter removed from the heater, the cap screws loosened, and the bomb-head cover unscrewed. The head should then be gently loosened by tapping and attempting to rotate it. (If an attempt is made to lift it directly from the bomb, the gasket will probably be ruined.) The liner is then removed, opened, and the catalyst removed by filtering through a sintered glass filter. The bomb and liner may be washed out with a suitable solvent and this solution added to the reaction mixture. In many cases it is advantageous to centrifuge the mixture before attempting to filter off the catalyst.

PRECAUTIONS

The smaller bomb described above is intended for use at pressures up to 175 atmospheres and temperatures up to 250° C., although the factor of safety under these conditions is several hundred per cent. The larger bomb is intended for use at pressures up to 400 atmospheres. The pressure of the hydrogen in the usual type of commercial cylinders is approximately 135 atmospheres, so that the maximum pressure obtainable (without the use of special equipment for compressing the gas) would be approximately 240 atmospheres at 250 C. A gage should only be used over the lower 60 per cent of its range, so that 200 atmospheres is approximately the maximum pressure that should be used with the equipment suggested. The gage is the weakest point in the system, and it is well to replace the glass in it with celluloid and to have it so located that it is not faced directly but is read by means of a mirror. The temperature of hydrogenation should be carefully watched, and if the reaction is proceeding too rapidly, the shaker should be stopped for a time.

ACKNOWLEDGMENT

The author's experience with the apparatus and technic for carrying out the reaction of organic compounds at temperatures up to 400° C. and pressures of several hundred atmospheres began in 1927 with apparatus purchased from the American Instrument Company. This equipment is still in use and it has never developed any fundamental defects. Since that time the bomb design, gaskets, etc., described in this paper have been developed as being more convenient and cheaper, and in general more satisfactory. The author is particularly indebted to W. H. Reynolds and Leopold Freedman of the American Instrument Company, and to Messrs. Hanson, Brockman, and Henke of the shops of the University of Wisconsin. The American Instrument Company have on the market an outfit for catalytic hydrogenation which includes the essential features of the unit described in

this paper. The Burgess-Parr Company of Moline, Ill., also have for sale an outfit patterned after the unit herein described.

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- (2) Ernst, *IND. ENG. CHEM.*, 18, 664 (1926); Am. Instrument Co., *Bull.* 405 (1927); U. S. Dept. Agr., *Circ.* 61 (1929).

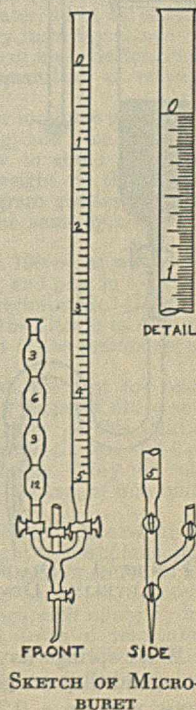
RECEIVED March 19, 1932.

A Modified Microburet

R. B. DUSTMAN, West Virginia University
Morgantown, W. Va.

SOME years ago the Department of Agricultural Chemistry became engaged in analyses necessitating the use of a microburet. Reference to several supply house catalogs at hand revealed only the Folin type available. One of these was purchased and put into use, but it did not meet the needs in a satisfactory manner. Consequently a buret was designed as illustrated in the accompanying sketch.

The advantage of this type of buret lies chiefly in its increased capacity without sacrificing any of the conveniences of the ordinary single-tube type. The short length of the graduated tube affords convenient reading throughout its entire range without undue elevation or lowering of the level of the eyes. For titration with small withdrawals of liquid, this part of the buret may be used exclusively if desired. When titrating from the graduated tube, the bulb side furnishes a convenient outlet for excess solution run into the buret from the stock bottle and adjusted to the zero graduation. However, when considerable quantities of solution are required, the bulbed tube is more suitable. When titrating from the bulb side, the titration is completed by manipulation of the lowest stopcock, the stopcock on the left remaining open. After the titration is finished, the stopcock on the right is opened and the liquid in the partially emptied bulb allowed to rise to the nearest graduation mark above. It may be noted that the zero graduation on the top bulb stands slightly below the level of the 3-ml. graduation on the uniform-bore tube. This permits the refilling of any one of the four bulbs on the left hand side with liquid drawn from the main tube on the right. The total quantity is then read off by adding to the volume of the emptied bulbs from the gradu-



ated tube. All titrations are best controlled by the use of the lowest stopcock.

This buret delivers approximately 26 drops per ml. and is suitable for work with blood and urine in addition to the more general analytical procedures. The graduation interval is 0.02 ml., but readings are easily possible to 0.01 ml. Because of the relatively small bore of the graduated tube, some time must be allowed for afterflow if the tube has been emptied rapidly and readings of greatest accuracy are desired. This seldom requires a total of more than 1.5 to 2 minutes, and ordinarily most of this drainage will have taken place during the time necessary for the withdrawal of the last few drops.

Two of these burets have been made at moderate cost by E. Machlett & Son of Long Island City, N. Y., the first of which has been in constant use over a period of 2 years. They are of rugged construction and excellent workmanship. The calibration is highly accurate, the volumes being adjusted well within the tolerances required by the U. S. Bureau

of Standards for measuring pipets. The approximate dimensions of the buret are as follows:

	Cm.
Total length.....	60
Length of graduated main tube from 0 to 5 ml.....	38
Height of side tube with bulbs.....	23
Distance from 5-ml. graduation to point of curved tip	15
Length of tip below stopcock.....	4
Diameter of graduated main tube (outside).....	0.8
Diameter of bulbs (outside).....	1.4
	Ml.
Total capacity.....	17
Capacity of graduated main tube.....	5
Capacity of single bulb.....	3
Subdivisions.....	0.02

These dimensions give a small unit convenient both for general laboratory use and for certain specialized procedures. Manipulation is rapid and easy, total capacity large, and accuracy adequate for exact measurements.

RECEIVED January 11, 1932. Published with the approval of the Director of the West Virginia Agricultural Experiment Station, as *Scientific Paper 106*.

Pressure Control with Automatic Liquid-Leveling Device

J. V. VAUGHEN, E. I. du Pont de Nemours & Co., Wilmington, Del.

THERE is often a need in the laboratory for a device which will automatically control liquid levels in the leveling bulbs of gasometers and combustion pipets and in mercury reservoirs in such a way as to give constant pressure or constant liquid flow.

Figure 1 represents a variation of the arrangement used by Stone (1) that has been used in this laboratory for maintaining a constant flow of mercury to displace liquids at a constant rate into a reaction vessel.

The mercury reservoir, *C*, is suspended by a suitable spring, *B*, which lifts the reservoir a distance equal to the fall in mercury level in the bulb when mercury flows out. The spring and reservoir are matched by measuring the elongation, *X*, of the spring with a load of 100 cc. of mercury. The appropriate diameter, *D*, of the reservoir is then calculated according to the formula

$$D = 2\sqrt{\frac{100}{X\pi}}$$

The reservoir is made of tubing of approximately this diameter, and further matching is accomplished by changing the length of the spring.

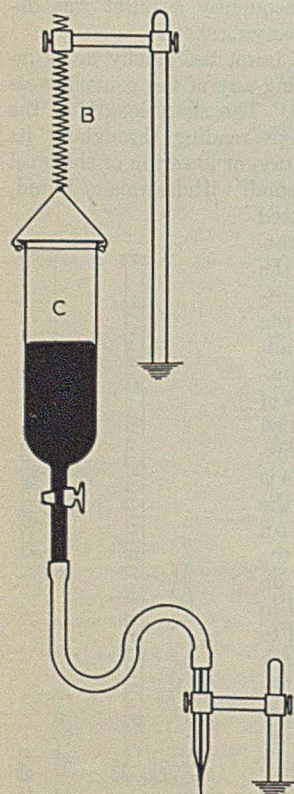


FIGURE 1. DIAGRAM OF LEVELING DEVICE

Brass springs have been found more suitable than steel ones, and they are generally made by winding No. 16 B. & S. brass wire on a 0.25-inch (0.62-cm.) mandrel. In one in-

stance two springs 27 cm. long were used together to support a mercury reservoir. Together these springs stretched 6.8 cm. for 100 cc. of mercury. The calculated diameter of the reservoir was 4.32 cm. The reservoir was made with a diameter of 4.5 cm. and further adjustment of the apparatus was accomplished by shortening the spring. A volume of 200 to 300 cc. of mercury could be emptied from the reservoir with a change in mercury level of less than 3 mm.

In applying this scheme to the maintenance of constant pressure in gasometers and combustion pipets with leveling bottles, the following equation gives the relationship between the radius, *r*, of the gasometer or combustion pipet, the radius, *R*, of the leveling bottle, and the elongation, *X*, of the spring, for a volume, *V*, of confining liquid:

$$X = \frac{V}{\pi r^2} + \frac{V}{\pi R^2}$$

In one instance a leveling bottle for a gas-combustion pipet was suspended by two springs 42 cm. long. They elongated 8.0 cm. with a load of 100 cc. of mercury. Since the diameter of the pipet was 4.8 cm., the leveling bulb should measure 7.2 cm.

LITERATURE CITED

(1) Stone, *Engineering*, 100, 554 (1915).

RECEIVED February 16, 1932. Contribution 91 from the Experimental Station, E. I. du Pont de Nemours & Company.

WORLD POTASH PRODUCTION. According to the estimate of the general director of the Kaliwerke Aschersleben, reported to the Department of Commerce by the trade commissioner at Berlin, potash salts representing 1,457,400 metric tons of potash were produced in the world in 1931. In 1930 world production of potash was 2,018,000 tons, and in 1929, 2,118,000 tons. Germany is first in volume of potash produced, with 964,000 tons; France (Alsace) second with 340,000 tons; the United States third with 60,000 tons; and then Poland, Spain, Russia, in the order named. A decline from over 1,300,000 tons in 1930 is shown in German production, and a drop of 16 per cent for the first five months of 1932 over the corresponding period in 1931, in sales of German potash.

Recommended Specifications for Analytical Reagent Chemicals

Benzene, Cupric Acetate Normal ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$), Cupric Nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Lead Subacetate, Phenolphthalein, Potassium Nitrate, Sodium Fluoride, Sodium Nitrite, Toluene, Xylene

W. D. COLLINS, H. V. FARR, J. V. FREEMAN, JOSEPH ROSIN, G. C. SPENCER, E. WICHERS, AND H. H. WILLARD
Committee on Analytical Reagents, American Chemical Society

THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (1-9) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (3). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

BENZENE

REQUIREMENTS

Boiling Range—79.5° to 81° C.

Solidification Temperature—Not below 5.2° C.

Nonvolatile Matter—Not more than 0.001 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Thiophene—To pass test.

Sulfur Compounds (S)—Not more than 0.005 per cent.

TESTS

Boiling Range—When 100 cc. are subjected to the distillation test described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the range indicated.

Solidification Temperature—When tested according to the method described in the U. S. Pharmacopeia, the temperature of solidification should not be below 5.2° C.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not exceed 0.0010 gram.

Substances Darkened by Sulfuric Acid—Shake 25 cc. with 15 cc. of sulfuric acid for 15 to 20 seconds and allow to separate. Neither the benzene nor the acid should be darkened.

Thiophene—Add a few milligrams of isatin to the mixture of benzene and sulfuric acid from the preceding test, shake well, and allow to stand for 1 hour. The acid layer should not acquire a blue or green color.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the benzene and alcohol

are evaporated. Add 50 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess of 1 cc. of the acid, and concentrate to about 50 cc. Filter, if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0020 gram.

CUPRIC ACETATE NORMAL ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$)

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.003 per cent.

Sulfate (SO_4)—Not more than 0.010 per cent.

Alkali Salts—Not more than 0.20 per cent.

Iron (Fe)—Not more than 0.010 per cent.

Ammonium Sulfide Metals (other than Fe)—To pass test (limit about 0.01 per cent Ni).

TESTS

Insoluble Matter—Dissolve 10 grams in 150 cc. of water containing 1 cc. of glacial acetic acid and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 N silver nitrate. Any turbidity should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of water containing the quantities of reagents used in the test.

Sulfate—To the filtrate from the test for insoluble matter add 5 cc. of glacial acetic acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Filter, wash, ignite, and weigh. The weight of the barium sulfate should not be more than 0.0025 gram greater than the weight obtained in a blank test with the same quantities of reagents and including filtration.

Alkali Salts—Dissolve 4 grams in about 190 cc. of water, add 2 cc. of sulfuric acid, heat to about 70° C., and pass in hydrogen sulfide until the copper is completely precipitated. Dilute to 200 cc. and filter. Evaporate 150 cc. of the filtrate to dryness, ignite, and weigh the residue. The weight of the residue should not exceed 0.0060 gram.

Iron—Warm the residue obtained from the test for alkali salts with 1 cc. of hydrochloric acid and 2 drops of nitric acid, and dilute to 15 cc. with water. Dilute 5 cc. of this solution with 15 cc. of water, and add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be greater than is produced by 0.1 mg. of iron under the same conditions.

Ammonium Sulfide Metals, Other than Iron—To the remaining 10 cc. of the solution of the residue add a slight excess of ammonia, boil for 1 minute, filter, and wash with a small quantity of hot water. Dilute the filtrate and washings to 25 cc. Exactly neutralize 5 cc. of the filtrate and washings with dilute hydrochloric acid and dilute to 20 cc. Add 2 drops of ammonium hydroxide and 1 cc. of hydrogen sulfide water. The solution should not be darker than a standard prepared in the same way and containing 0.04 mg. of nickel.

CUPRIC NITRATE ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.002 per cent.

Sulfate (SO_4)—Not more than 0.01 per cent.

Alkali Salts—Not more than 0.05 per cent.

Iron (Fe)—Not more than 0.010 per cent.

Ammonium Sulfide Metals (other than Fe)—To pass test (limit about 0.01 per cent Ni).

TESTS

Insoluble Matter—Dissolve 10 grams in 100 cc. of water containing 0.5 cc. of nitric acid, and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, and dry at 105° to 110° C. The weight of insoluble residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water and 1 cc. of nitric acid, filter if necessary, and add 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of water containing the quantities of reagents used in the test.

Sulfate—Dissolve 5 grams in 5 cc. of hot water, add 10 cc. of hydrochloric acid and evaporate to dryness on the steam bath, redissolve the residue in about 5 cc. of hot water, add 10 cc. of hydrochloric acid and reevaporate to dryness. Dissolve the residue in 100 cc. of water, add 1 cc. of hydrochloric acid, and filter. Heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. The weight of the precipitate should not be more than 0.0013 gram greater than the weight obtained in a blank test with the same quantities of reagents and including filtration.

Alkali Salts—Dissolve 4 grams in about 190 cc. of water, add 2 cc. of sulfuric acid, heat to about 70° C., and pass in hydrogen sulfide until the copper is completely precipitated. Dilute to 200 cc. and filter. Evaporate 150 cc. of the filtrate to dryness, and ignite and weigh the residue. The weight of the residue should not exceed 0.0015 gram.

Iron—Warm the residue obtained from the test for alkali salts with 1 cc. of hydrochloric acid and 2 drops of nitric acid, and dilute to 15 cc. with water. Dilute 5 cc. of this solution with 15 cc. of water. Add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be deeper than is produced by 0.1 mg. of iron under the same conditions.

Ammonium Sulfide Metals, Other than Iron—To the remaining 10 cc. of the solution of the residue add a slight excess of ammonia, boil for 1 minute, filter, and wash with a small quantity of hot water. Dilute the filtrate and washings to 25 cc. Exactly neutralize 5 cc. of the filtrate and washings with dilute hydrochloric acid and dilute to 20 cc. Add 2 drops of ammonium hydroxide and 1 cc. of hydrogen sulfide water. The solution should not be darker than a standard prepared in the same way and containing 0.04 mg. of nickel.

LEAD SUBACETATE

REQUIREMENTS

Assay of Lead (Pb)—70 to 73 per cent.

Insoluble in Acetic Acid—Not more than 0.05 per cent.

Chloride (Cl)—Not more than 0.005 per cent.

Nitrate (NO_3)—To pass test (limit about 0.003 per cent).

Substances Not Precipitated by Hydrogen Sulfide—Not more than 0.30 per cent.

Copper (Cu)—To pass test (limit about 0.005 per cent).

Iron (Fe)—Not more than 0.005 per cent.

TESTS

Assay of Lead—Weigh accurately about 1 gram in a porcelain crucible, add about 0.5 cc. of sulfuric acid, and ignite to drive off the excess of acid. The weight of lead sulfate should correspond to between 70 and 73 per cent of lead.

Insoluble in Acetic Acid—Dissolve 6 grams in 100 cc. of water and 5 cc. of glacial acetic acid, and warm if necessary. If an insoluble residue remains, filter and wash until the washings are no longer darkened by hydrogen sulfide. Dry at 105° to 110° C. The weight of the residue should not exceed 0.0030 gram.

Chloride—Dissolve 1 gram in 10 cc. of water and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Solution A—Dissolve 5 grams in 42 cc. of water and 3 cc. of glacial acetic acid, and add 5 cc. of sulfuric acid. After standing for about 10 minutes, filter the solution.

Nitrate—To 10 cc. of Solution A add 2 drops of indigo solution (1 in 1000) and 10 cc. of sulfuric acid. The blue color should not disappear in 5 minutes.

Substances Not Precipitated by Hydrogen Sulfide—Dilute 10 cc. of Solution A with water to 100 cc., pass hydrogen sulfide to precipitate all the lead, and filter. Evaporate 50 cc. of the filtrate to dryness and ignite gently. The weight of the residue should not exceed 0.0015 gram.

Copper—To 25 cc. of Solution A, add ammonium hydroxide until barely alkaline, heat on the steam bath for 10 minutes, and add 10 cc. of ammonium hydroxide. No blue color should be observed when the solution is compared with an equal volume of water in a Nessler tube.

Iron—Dissolve 2 grams in a few cc. of water, add 2 cc. of sulfuric acid, and heat to fumes of sulfuric acid. Allow to cool, dilute with water to 30 cc., and filter. To 15 cc. of the filtrate add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be deeper than is produced by 0.05 mg. of iron under the same conditions.

PHENOLPHTHALEIN

REQUIREMENTS

Nonvolatile Matter—Not more than 0.050 per cent.

Insoluble in Alcohol—To pass test.

Solution in Sodium Hydroxide—To pass test.

Sensitiveness—To pass test.

Melting Point—Not below 258° C.

TESTS

Nonvolatile Matter—Ignite 2 grams and weigh. The residue should not weigh more than 0.0010 gram.

Insoluble in Alcohol—Dissolve 1 gram in 15 cc. of alcohol. The solution should be clear, with no insoluble residue.

Solution in Sodium Hydroxide—One gram should dissolve completely in a mixture of 90 cc. of water and 10 cc. of *N* sodium hydroxide.

Sensitiveness—Dissolve 0.1 gram in 10 cc. of neutral alcohol. Add 0.10 cc. of this solution to 200 cc. of carbon dioxide-free water, and add 0.05 cc. of 0.1 *N* sodium hydroxide. The solution should show a pink color when compared with an equal volume of water.

Melting Point—Determine by the method described in the U. S. Pharmacopeia.

POTASSIUM NITRATE

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.

Neutrality—To pass test.

Chlorine, Total—Not more than 0.002 per cent.

Iodate, Nitrite—To pass test (limit about 0.0005 per cent IO₃; about 0.001 per cent NO₂).

Phosphate (PO_4)—Not more than 0.0005 per cent.

Sulfate (SO_4)—Not more than 0.003 per cent.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.010 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Iron (Fe)—Not more than 0.0003 per cent.

Sodium (Na)—To pass test (limit about 0.02 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Neutrality—Dissolve 5 grams in 50 cc. of water free from carbon dioxide, and add 3 drops of phenolphthalein. No pink color should be produced, but on the addition of 1 drop of 0.1 *N* sodium hydroxide a pink color should be produced.

Chlorine, Total—Ignite 1 gram, at first gently and then for a few minutes at a low red heat. Cool, dissolve in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion under the same conditions.

Iodate, Nitrite—Dissolve 1 gram in 10 cc. of water, add 2 drops of 10 per cent potassium iodide solution, 1 cc. of chloroform, and 2 cc. of 36 per cent acetic acid. Shake gently for a few minutes. The chloroform should not acquire a pink or violet color.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about

40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.025 mg. of phosphate (PO₄) is treated according to the above procedure.

Sulfate—Dissolve 12 grams in 20 cc. of water, add 25 cc. of hydrochloric acid, and evaporate to dryness. Treat the residue with 15 cc. of water and 15 cc. of hydrochloric acid, and again evaporate to dryness. Dissolve the residue in 75 cc. of water, add 1 cc. of *N* hydrochloric acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If any precipitate is formed, filter, wash, ignite, and weigh. The weight of the barium sulfate should not be more than 0.0010 gram greater than the weight obtained in a blank test with the same quantity of reagents and including filtration.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Dissolve 10 grams in 75 cc. of water, add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 15 cc. of ammonium hydroxide. Stir well and allow to stand overnight. If any precipitate forms, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not exceed 0.0010 gram.

Heavy Metals—Dissolve 2 grams in 20 cc. of water and add 10 cc. of hydrogen sulfide water. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals until it is alkaline. Any greenish color should not be greater than is produced by 0.006 mg. of iron in an alkaline sulfide solution.

Sodium—A 10 per cent solution tested with a platinum wire in the flame should give no distinct yellow color to the flame.

SODIUM FLUORIDE

REQUIREMENTS

Insoluble Matter—Not more than 0.050 per cent.

Chloride (Cl)—Not more than 0.01 per cent.

Free Acid (HF)—Not more than 0.2 per cent.

Free Alkali (as Na₂CO₃)—Not more than 0.25 per cent.

Sodium Fluosilicate (Na₂SiF₆)—Not more than 0.35 per cent.

Sulfate (SO₄)—Not more than 0.03 per cent.

Sulfite (SO₃)—Not more than 0.005 per cent.

Heavy Metals (as Pb)—Not more than 0.003 per cent.

Iron (Fe)—To pass test (limit about 0.003 per cent).

TESTS

Insoluble Matter—Dissolve 2 grams in 100 cc. of warm water in a platinum dish and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly with hot water, dry at 105° to 110° C., and weigh. The weight should not exceed 0.0010 gram.

Chloride—Dissolve 0.3 gram in 20 cc. of water. Add 0.2 gram of boric acid, 1 cc. of nitric acid, and 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Free Acid—Dissolve 2 grams in 40 cc. of water in a platinum dish, add 10 cc. of a saturated solution of potassium nitrate, and cool the solution to 0° C. Add 3 drops of phenolphthalein indicator. If no pink color is produced, titrate with 0.1 *N* sodium hydroxide until the pink color persists for 15 seconds while the temperature of the solution is near 0° C. Not more than 2 cc. of 0.1 *N* sodium hydroxide should be required.

Free Alkali—If a pink color is produced on the addition of the phenolphthalein in the test for free acid, add 0.1 *N* acid, stirring the liquid only gently, until the pink color is discharged. Not more than 0.5 cc. of the acid should be required.

Sodium Fluosilicate—Boil the solution from the preceding test and titrate while hot with 0.1 *N* alkali until a permanent pink color is obtained. Not more than 1.5 cc. of 0.1 *N* sodium hydroxide should be required.

Sulfate—Evaporate 0.5 gram in a platinum dish four or five times with 10 cc. of hydrochloric acid, evaporating the last time to dryness. Take up the residue in 20 cc. of water and 1 cc. of 0.1 *N* hydrochloric acid and filter if necessary. Add to the filtrate 2 cc. of 10 per cent barium chloride solution. Any turbidity produced in 10 minutes should not be greater than is produced by 0.15 mg. of SO₄ in a control made with the quantities of reagents used in the test.

Sulfite—Dissolve 6 grams in 150 cc. of water, add 2 cc. of hydrochloric acid and a few drops of starch solution, and titrate immediately with 0.1 *N* iodine. It should require not more than 0.1 cc. to produce a blue color.

Heavy Metals—Treat 2 grams in a platinum crucible with 10 cc. of hydrochloric acid and evaporate to dryness. Repeat with another 10 cc. of acid. Warm the residue with a few drops

of hydrochloric acid and dissolve in 40 cc. of hot water. Exactly neutralize 20 cc. with ammonium hydroxide, add 1 cc. of 0.1 *N* hydrochloric acid, and saturate with hydrogen sulfide. Any color produced should not be greater than is produced by 0.03 mg. of lead in an equal volume of water containing the quantities of reagents used in the test.

Iron—To the remaining 20 cc. from the test for heavy metals add 2 cc. of hydrochloric acid, filter if necessary, and add 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color produced should not be more than is produced in a control test made with the same quantities of reagents and containing 0.03 mg. of iron.

SODIUM NITRITE

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Assay—Not less than 97 per cent.

Chloride (Cl)—Not more than 0.01 per cent.

Sulfate (SO₄)—Not more than 0.020 per cent.

Calcium (Ca)—Not more than 0.010 per cent.

Heavy Metals (as Pb)—Not more than 0.002 per cent.

Iron (Fe)—Not more than 0.001 per cent.

Potassium (K)—Not more than 0.01 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in about 100 cc. of hot water and allow to stand on the steam bath for 1 hour, filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Solution A—Dissolve 10 grams in water and make to a volume of 100 cc.

Assay—Dilute 10 cc. of Solution A to 100 cc. Mix 300 cc. of water and 5 cc. of sulfuric acid and, while the mixture is still warm, add 0.1 *N* permanganate solution until a faint pink color is produced which persists for 2 minutes. Add 40 cc. of 0.1 *N* permanganate solution and mix gently. Run in slowly and with constant agitation 10 cc. of the sodium nitrite solution from a pipet, holding the tip of the pipet well under the surface of the liquid. Add 15 cc. of 0.1 *N* ferrous ammonium sulfate, and after allowing the solution to stand for 5 minutes, titrate the excess with 0.1 *N* permanganate. Each cc. of the permanganate consumed corresponds to 0.003450 gram of NaNO₂.

Chloride—To 10 cc. of Solution A add 10 cc. of water, and add slowly 2 cc. of glacial acetic acid. Warm gently until no more gas is evolved, cool, and dilute to 25 cc. Add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should correspond to not more than 0.1 mg. of chloride.

Sulfate—To 10 cc. of Solution A add slowly 2 cc. of hydrochloric acid and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of dilute hydrochloric acid (1 + 9) and dilute with water to 10 cc. Add 1 cc. of 10 per cent barium chloride solution. Any turbidity produced should not be greater than is produced by 0.2 mg. of SO₄ under the same conditions.

Calcium—To 10 cc. of Solution A add slowly 1 cc. of glacial acetic acid. Heat to expel oxides of nitrogen, cool, dilute to 10 cc., and add 2 cc. of 4 per cent ammonium oxalate solution. Any turbidity produced should not be greater than is produced by 0.1 mg. of calcium under the same conditions.

Heavy Metals—To 20 cc. of Solution A add slowly 3 cc. of hydrochloric acid and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of *N* hydrochloric acid, dilute to 10 cc., and add 2 cc. of hydrogen sulfide water. Any darkening should not be greater than is produced by 0.04 mg. of lead under the same conditions.

Iron—To 20 cc. of Solution A add 5 cc. of hydrochloric acid and evaporate on a steam bath almost to dryness. Take up the residue in 2 cc. of hydrochloric acid and 15 cc. of water; filter if necessary, and add to the solution 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color produced should not be greater than in a control test made with the same quantities of the reagent and containing 0.02 mg. of iron.

Potassium—Dissolve 2 grams in a mixture of 10 cc. of water and 5 cc. of hydrochloric acid, and evaporate to dryness on the steam bath, finally heating for 15 minutes to about 120° C. Dissolve the salt in 10 cc. of water, and add 10 cc. of sodium cobaltinitrite solution and 7 cc. of alcohol. Any turbidity should not be greater than that produced by a blank containing 10 cc. of water and 10 cc. of cobaltinitrite solution to which have been added 0.2 mg. of potassium and 7 cc. of alcohol. (The sodium cobaltinitrite solution is made by dissolving 25 grams of NaNO₂ in 50 cc. of water and adding 15 cc. of 6 *N* H₂C₂O₄ and 2.5 grams of Co(C₂H₃O₂)₂·4H₂O or an equivalent amount of nitrate or chloride. The solution is allowed to stand overnight, filtered, and diluted to 100 cc.)

TOLUENE

REQUIREMENTS

Boiling Range—110° to 111° C.

Nonvolatile Matter—Not more than 0.001 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Sulfur Compounds (as S)—Not more than 0.003 per cent.

Water—To pass test.

TESTS

Boiling Range—When 100 cc. are distilled by the method described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the temperature range indicated.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not be more than 0.0010 gram.

Substances Darkened by Sulfuric Acid—Shake 15 cc. with 5 cc. of sulfuric acid for 15 to 20 seconds and allow to stand 15 minutes. The toluene layer should be colorless and the color of the acid should not exceed that of a mixture of 2 volumes of water and 1 volume of a color standard containing 5 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 40 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 20 cc. of hydrochloric acid in a liter.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the toluene and alcohol are evaporated. Add 40 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess of 1 cc. of the acid, and concentrate to about 50 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0012 gram.

Water—Cool in crushed ice with the sample protected from moisture in the air. No cloudiness should be observed. Special care must be taken in handling the sample before as well as during this test to make sure that moisture has not been absorbed from the air.

XYLENE

REQUIREMENTS

Boiling Range—137° to 140° C.

Nonvolatile Matter—Not more than 0.002 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Sulfur Compounds (as S)—Not more than 0.003 per cent.

Water—To pass test.

TESTS

Boiling Range—When 100 cc. are distilled by the method described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the temperature range indicated.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not be more than 0.0020 gram.

Substances Darkened by Sulfuric Acid—Shake 15 cc. with 5 cc. of sulfuric acid for 15 to 20 seconds and allow to stand for 15 minutes. The xylene layer should be colorless, and the color of the acid should not exceed that of a mixture of 1 volume of water and 3 volumes of a color standard containing 5 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 40 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 20 cc. of hydrochloric acid in a liter.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the xylene and alcohol are evaporated. Add 50 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess

of 1 cc. of the acid, and concentrate to about 50 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0012 gram.

Water—Cool in crushed ice with the sample protected from moisture in the air. No cloudiness should be observed. Special care must be taken in handling the sample before as well as during this test to make sure that moisture has not been adsorbed from the air.

CORRECTIONS FOR PUBLISHED SPECIFICATIONS

Replace or modify requirements and tests previously printed as indicated below:

ACID MOLYBDIC ANHYDRIDE (4)

REQUIREMENT

Sulfate (SO_4)—Not more than 0.020 per cent.

TEST

Sulfate—Boil 1 gram with a mixture of 10 cc. of water and 5 cc. of nitric acid for 5 minutes. Cool thoroughly, dilute to 50 cc., mix well, and filter. Evaporate 10 cc. of the filtrate to dryness on the steam bath, warm the residue with 3 drops of hydrochloric acid and 10 cc. of water, filter if necessary, wash, make the filtrate to 50 cc., and add 1 cc. of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.04 mg. of sulfate ion in the same volume of solution containing the quantities of acid and barium chloride used in the test.

CUPRIC OXIDE, POWDERED AND GRANULAR (6)

REQUIREMENT

Chloride (Cl)—Not more than 0.005 per cent.

TEST

Chloride—Make comparison with 0.05 mg. of chloride ion.

POTASSIUM IODIDE (3)

TEST

Heavy Metals—Third sentence should begin "Add 1 cc. of 0.1 N hydrochloric acid. . . ." Run a blank involving the use of the quantities of sulfuric and hydrochloric acids and ammonium hydroxide used in the test.

SODIUM BICARBONATE (2)

REQUIREMENT

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.020 per cent.

TEST

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Use corrected test (8).

SPECIFICATIONS PREVIOUSLY PUBLISHED

- (1) Committee on Analytical Reagents, *IND. ENG. CHEM.*, 17, 756 (1925).
- (2) *Ibid.*, 18, 636, 759 (1926).
- (3) *Ibid.*, 19, 645 (1927).
- (4) *Ibid.*, 19, 1369 (1927).
- (5) *Ibid.*, 20, 979 (1928).
- (6) *Ibid.*, *Anal. Ed.*, 1, 171 (1929).
- (7) *Ibid.*, 2, 351 (1930).
- (8) *Ibid.*, 3, 221 (1931).
- (9) *Ibid.*, 4, 154 (1932).

RECEIVED May 16, 1932. Presented in connection with the report of the Committee on Analytical Reagents at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932.





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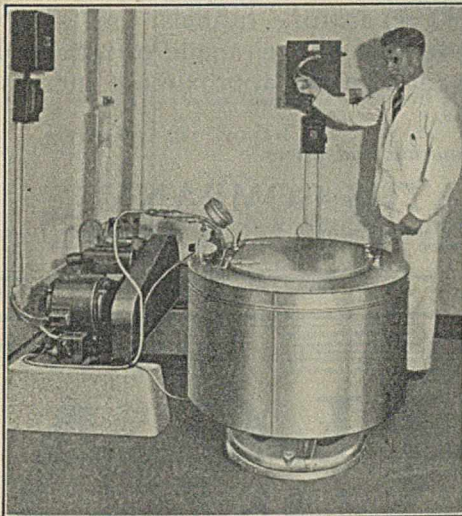


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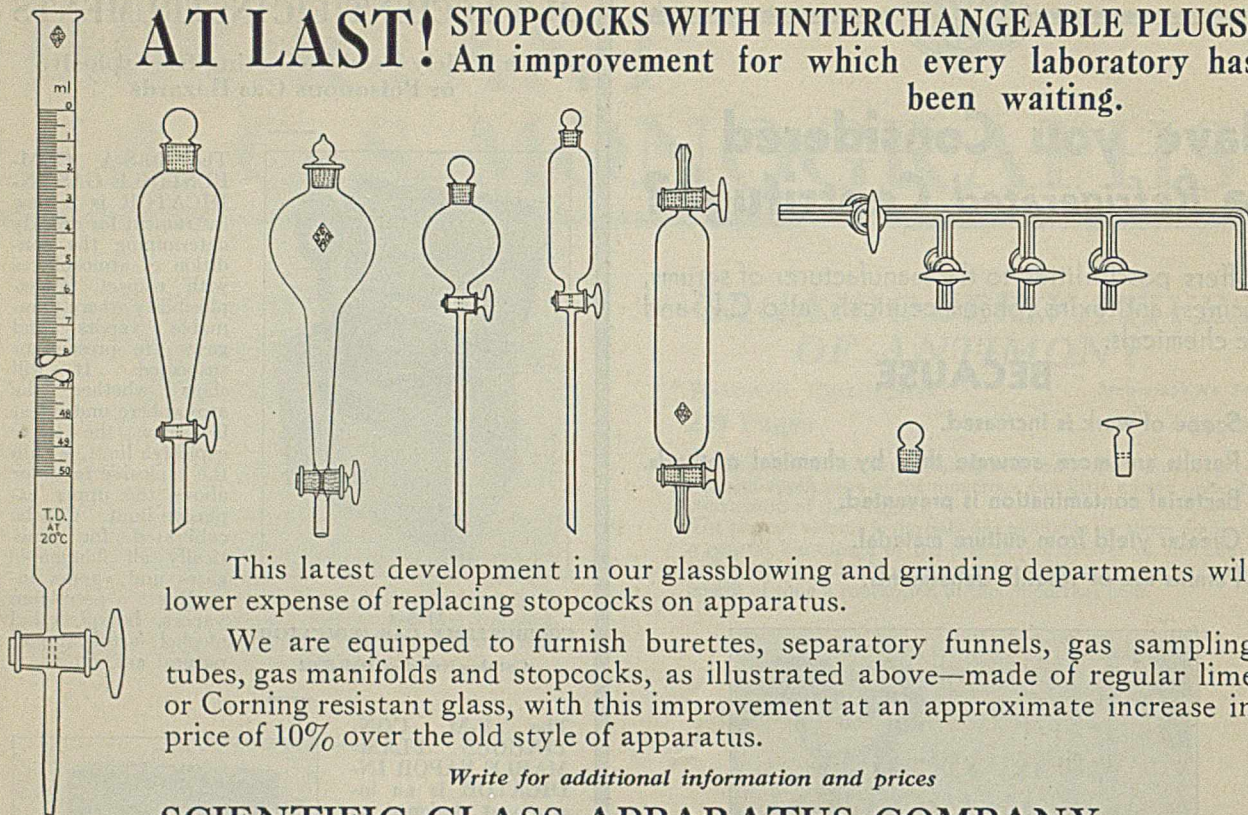
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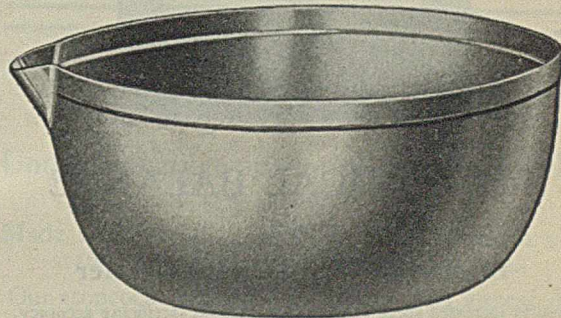
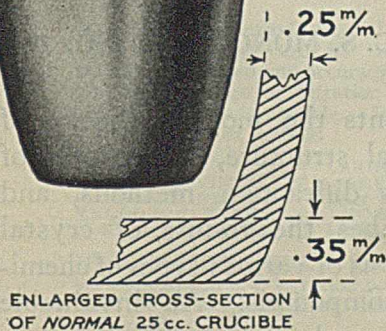
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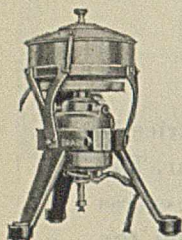
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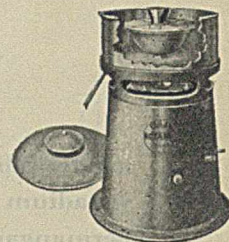
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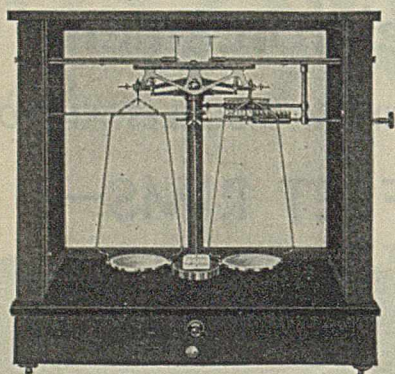
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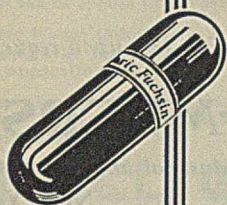
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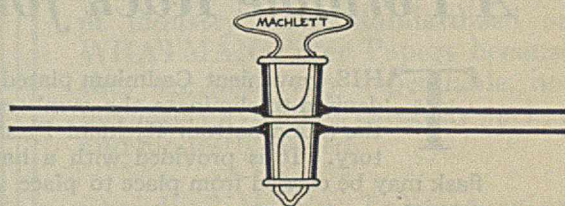
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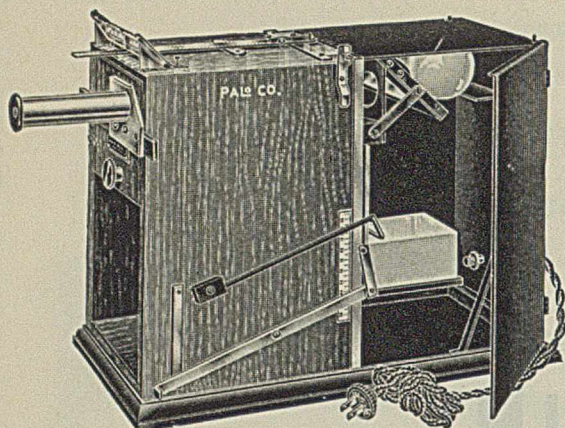
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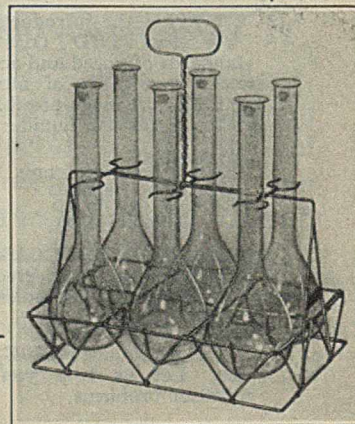
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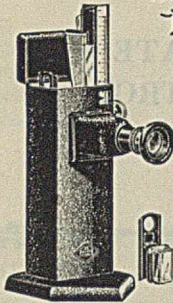
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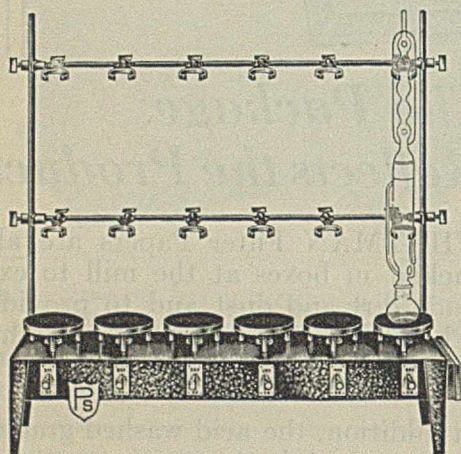
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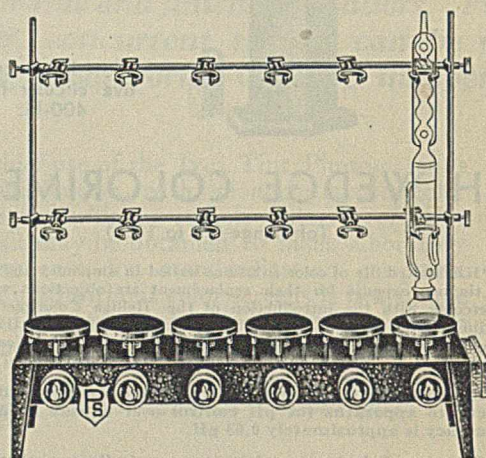


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