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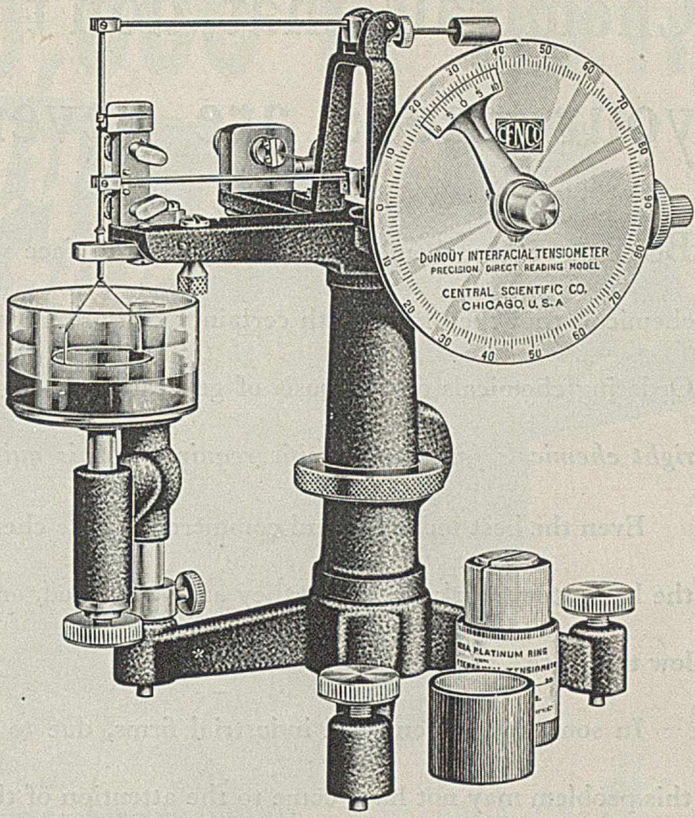
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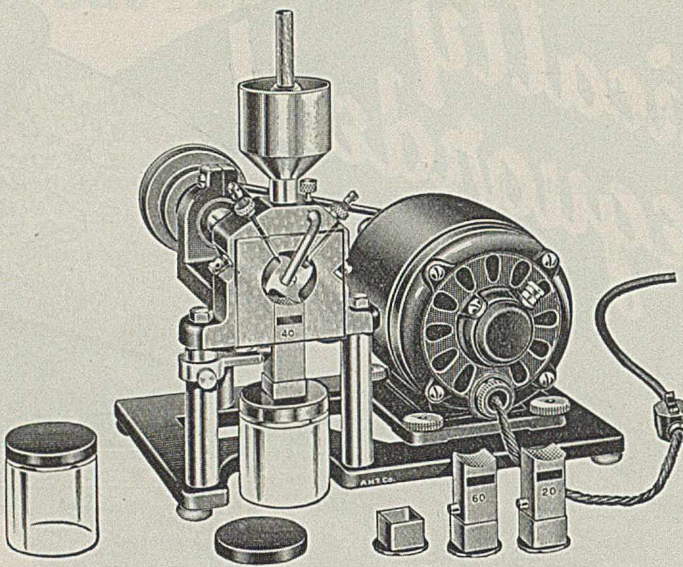

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Determination of Columbium and Tantalum in Stainless Steel

THOS. R. CUNNINGHAM

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THE addition of columbium to stainless steel to improve its corrosion resistance is increasing rapidly and has necessitated the development of an accurate method for separating this element. Weiss and Landecker (*4*) state that columbium and tantalum are precipitated from solution by evaporation with perchloric acid. Silverman (*3*) describes a method for the determination of columbium in 18 per cent chromium–8 per cent nickel steel and in low-titanium steel based on this separation. It has been the author's experience that columbium and tantalum are not quantitatively precipitated by evaporation with perchloric acid when appreciable amounts (> 0.10 per cent) of titanium are present. Furthermore, the columbium that is precipitated is badly contaminated with titanium. Silverman (*3*) mixed a 1-gram sample of steel containing columbium with 1 gram of 0.30 per cent titanium steel and, because the weight of the final residue, after putting through all of the steps of his method, showed excellent agreement with the weight obtained on direct treatment of the columbium steel alone, concluded that titanium, if present in a columbium steel up to 0.15 per cent, would have no effect on the columbium determination.

The author analyzed a sample of columbium- and titanium-bearing 18 per cent chromium–8 per cent nickel steel by the cupferron method described below, and found 0.83 per cent columbium and 0.45 per cent titanium. A test carried out on this steel by Silverman's (*3*) procedure gave a final residue which, when analyzed for titanium colorimetrically, showed 0.15 per cent. Lundell, Hoffman, and Bright (*1*) also point out that titanium interferes with the accurate determination of columbium and tantalum.

In the presence of titanium (> 0.1 per cent), columbium and tantalum may be determined by treating the steel with 200 to 300 ml. of 30 per cent hydrochloric acid at a temperature of approximately 80° C. When the action of the acid has practically ceased, a few drops of hydrofluoric acid are added and the heating is continued for several minutes longer. The solution is cooled to about 15° C., diluted with cold water to 400 ml., and the columbium, tantalum, and titanium are precipitated by the addition of an excess (20 to 30 ml. are usually sufficient) of a cold, freshly prepared 6 per cent solution of cupferron. Some ashless paper pulp is added, the solution is stirred vigorously for several minutes, filtered on two 11-cm. No. 42 Whatman filler papers (containing some ashless paper pulp) supported on a Büchner funnel, gentle suction being employed, and the paper and precipitate are washed at least 20 times with cold 10 per cent hydrochloric acid containing 20 ml. of the cupferron solution per liter. The paper is ignited in a 100-ml. platinum dish at a low temperature, fused with 3 to 5 grams of potassium pyrosulfate, and the melt, when cool, is dissolved in 200 ml. of 5 per cent tartaric acid containing 4 ml. of sulfuric acid (1 to 1). The solution is then treated with a brisk stream of hydrogen sulfide for 15 to 20 minutes. If a precipitate forms it is filtered on a 9-cm. paper containing some ashless paper pulp, washed 18 to 20 times with hydrogen sulfide water containing 0.5 per cent sulfuric acid and 5 per cent tartaric acid, and discarded.

An excess of about 2 ml. of ammonia (sp. gr. 0.90) is added and the solution is treated with hydrogen sulfide for 5 minutes longer. Some ashless paper pulp is introduced and after the precipitate of ferrous sulfide has been allowed to digest at a temperature of approximately 70° C. for 10 minutes, it is filtered, washed well with ammonium sulfide water containing 2 per cent ammonium chloride and 2 per cent tartrate, and discarded. The filtrate is boiled to expel hydrogen sulfide, 40 ml. of hydrochloric acid (sp. gr. 1.19) are added, and the boiling is continued until the volume has been reduced to about 300 ml. The solution is cooled to 15° C. and the columbium, tantalum, and titanium are precipitated with cupferron, filtered, and washed as previously described. The precipitate is ignited first at a low temperature and finally at 1000° to 1050° C., cooled, and weighed. The ignited and weighed precipitate is fused with about 12 times its weight of potassium pyrosulfate, the melt is dissolved in 100 ml. of 20 per cent sulfuric acid containing 1 gram of succinic acid and 1 ml. of 30 per cent hydrogen peroxide, and the titanium is determined colorimetrically. Then, 25 ml. of a 20 per cent sulfuric acid solution (containing 0.0500 gram of pure titanium dioxide fused with 2 to 3 grams of potassium pyrosulfate) are added and the columbium in the solution is estimated by the procedure described in the method given below.

Commercial columbium steels are essentially free from titanium; therefore, the determination may be carried out as described in the method. However, in case of doubt, the cupferron method should be used.

The total oxides of columbium and tantalum found on a sample of 18 per cent chromium–8 per cent nickel steel by the method described below showed excellent agreement with the total oxides obtained by this cupferron method. The proposed method can also be worked in considerably less time than the cupferron method.

The tantalum content of the total oxides obtained on a 10-gram sample of columbium-bearing 18 per cent chromium–8 per cent nickel steel can be obtained by the author's modification of Schoeller and Powell's (*2*) tannin procedure.

For this separation the precipitate is fused with 12 times its weight of potassium pyrosulfate and the melt, when cool, is dissolved in 100 ml. of hot 2 per cent ammonium oxalate. The solution is treated with 2 ml. of sulfuric acid (1 to 1), diluted to 250 ml. with hot water, and heated to boiling. Four drops of a 0.25 per cent solution of bromophenol blue (prepared by dissolving 0.25 gram of the indicator in 7.5 ml. of 0.05 *N* sodium hydroxide and diluting with cold water to 100 ml.) are added, followed by ammonia (1 to 2) drop by drop until the yellow color just

Table I. Tests Made on Columbium-Treated 18 Per Cent Chromium–8 Per Cent Nickel Steel

Sample	Sample Taken	Total Cb_2O_5 + Ta_2O_5 Found	Cb (+Ta)[a]	Total Cb_2O_5 + Ta_2O_5	Cb[b]	Ta	Tannin Procedure: Total Cb_2O_5 + Ta_2O_5	Tannin Procedure: Cb	Tannin Procedure: Ta
	Grams	*Gram*	%	*Gram*	%	%	*Gram*	%	%
38	3	0.0421	0.980	....	...	...	....	...	...
38	5	0.0705	0.986	0.0705	0.934	0.06	0.0700	0.932	0.058
38	2	0.0280	0.980	....	...	...	....	...	...
38	2	0.0282[c]	0.986	....	...	...	....	...	...
123	5	0.0320[c]	0.45	0.0320	0.426	0.029	....	...	...
123	10	....	...	....	...	...	0.0640	0.429	0.026
123	15	....	...	....	...	...	0.0960	0.424	0.027
123	5	....	...	0.0320	0.426	0.029	....	...	...

[a] Per cent total oxides found calculated to columbium.

[b] Results obtained by addition of TiO_2, fusion with $K_2S_2O_7$, and passing the solution through the reductor as described in the method.

[c] Result obtained by cupferron method.

changes to a distinct purple. This corresponds to a pH of approximately 4.6. From 25 to 30 ml. of a freshly prepared 1 per cent solution of tannin are added, followed by 10 grams of ammonium chloride and some ashless paper pulp, and the solution is gently boiled for at least 15 minutes.

The hot solution is filtered on an 11-cm. paper containing some ashless paper pulp, and the paper and precipitate are washed from 20 to 25 times with a hot 2 per cent solution of ammonium chloride and ignited in platinum at a low temperature to burn off the carbon of the filter paper. The precipitate is treated in platinum with 5 ml. of sulfuric acid (1 to 1) and 1 ml. of hydrofluoric acid, and the solution is evaporated to a volume of 1.5 to 2 ml., cooled, and transferred to a 250-ml. beaker by means of 150 ml. of cold 2 per cent hydrochloric acid. Twenty-five milliliters of sulfurous acid and some ashless paper pulp are introduced, the solution is boiled for at least 5 minutes, and allowed to stand for 30 minutes or longer at about 70° C. before filtering. The precipitate is ignited and weighed. A weight of 0.0200 gram of pure titanium dioxide is added, the mixture is fused with 12 times its weight of potassium pyrosulfate and the melt is dissolved as described in paragraph 3 of the method. The solution is passed through the reductor and titrated with standard 0.05 *N* potassium permanganate, all as described in paragraphs 4 and 5 of the method. A blank on the reductor and titanium dioxide is carried through as described and the difference in volume of permanganate between the sample and the blank is the volume equivalent to any Cb_2O_5. The weight of Ta_2O_5 (+ Cb_2O_5) less the Cb_2O_5 found, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum.

Tantalum oxide is white whether hot or cold, whereas columbium oxide is yellow when hot and white when cold. Silverman (*3*) states that Cb_2O_5 is nearly white when cold, which would indicate that his oxide was impure. In order to remove silica and to purify the precipitate obtained by evaporation with perchloric acid, it is ignited and treated with hydrofluoric, sulfuric, and perchloric acids, finally evaporating the solution to dense fumes of sulfuric acid. The columbium and tantalum in this solution are then precipitated by boiling with sulfurous acid, filtered, ignited, and weighed as oxides.

The following method has, with but few modifications, been used by this laboratory since 1932 and by other laboratories since 1933, and requires about 2.5 hours.

Method

From 2 to 5 grams of the sample are transferred to a 600-ml. covered beaker and treated with from 25 to 50 ml. of hydrochloric acid (sp. gr. 1.19) and 10 ml. of nitric acid (sp. gr. 1.42) at a temperature of approximately 90° C. When all action appears to have ceased, 30 to 60 ml. of perchloric acid (60 per cent) are introduced, the solution is boiled until dense fumes of perchloric acid are freely evolved, and the boiling is continued for about 5 minutes longer to ensure the complete conversion of the chromium to chromic acid. Two hundred milliliters of hot water, 50 to 100 ml. of sulfurous acid, and 10 ml. of hydrochloric acid (sp. gr. 1.19) are introduced and the solution is boiled for 5 minutes. Considerable ashless paper pulp is introduced, and the contents of the beaker are allowed to digest at a temperature of from 60° to 70° C. for 15 minutes, or until the supernatant liquid is clear, and filtered on an 11-cm. paper containing some ashless paper pulp. The beaker is scrubbed with a filter paper moistened with 2 per cent hydrochloric acid and added to the filter. The paper and precipitate are washed from 12 to 15 times with hot 2 per cent hydrochloric acid and ignited in a 50-ml. platinum dish at a low temperature to burn off the carbon of the filter paper.

Approximately 5 ml. of hydrofluoric acid (48 per cent) and 10 ml. of sulfuric acid (1 to 1) are introduced, the solution is evaporated to dense fumes of sulfur trioxide, and the fuming is continued until the volume has been reduced to approximately 2.5 ml. to ensure the complete expulsion of all hydrofluoric acid. Should the precipitate not dissolve after several minutes' heating, approximately 2 ml. of perchloric acid (60 per cent) are added and the solution is evaporated as described. If the evaporation is allowed to proceed almost to dryness, any separated columbic or tantalic acids may be dissolved by the addition of several milliliters of sulfuric acid (sp. gr. 1.84) and further heating for 1 or 2 minutes. The contents of the dish are allowed to cool somewhat and transferred to a 400-ml. beaker by means of about 200 ml. of hot 2 per cent hydrochloric acid. Any adhering precipitate is removed from the dish by means of an 11-cm. filter paper moistened with hydrochloric acid, and added to the beaker. An excess (about 50 ml.) sulfurous acid is added, and the solution is boiled for 5 minutes. Some ashless paper pulp is introduced, and the solution is digested at a temperature of from 60° to 70° C. for 15 minutes, or until the supernatant liquid is clear, filtered on an 11-cm. paper containing some ashless paper pulp, and washed 10 times with hot 2 per cent hydrochloric acid. The precipitate is ignited in a 50-ml. platinum dish, first at a low temperature to burn off the carbon of the filter paper, and finally to constant weight at 1000° to 1050° C., cooled, and weighed. (For a control analysis, the weight obtained multiplied by 69.9 and divided by the weight of sample taken, will give the approximate percentage of columbium.)

To the ignited and weighed precipitate of columbium and tantalum oxides is added 0.0500 gram of pure titanium dioxide, and the mixture is fused with 2 to 3 grams of potassium pyrosulfate. The dish and its contents are permitted to cool somewhat, 5 ml. of sulfuric acid (sp. gr. 1.84) are introduced, and the heating is continued on a hot plate until a clear solution is obtained. The contents of the dish are allowed to cool partially, are transferred to a dry 250-ml. beaker, and the dish is rinsed successively with three 5-ml. portions of sulfuric acid (sp. gr. 1.84). The dish is further rinsed with 20 ml. of 5 per cent succinic acid containing 1 ml. of 30 per cent hydrogen peroxide, and the rinsings are added to the beaker. The solution is stirred thoroughly, diluted to 100 ml. with cold water, heated to 60° to 70° C., passed through a Jones reductor into a solution of ferric sulfate, and titrated with a standard solution of potassium permanganate. The columbium and titanium are reduced from $Cb_2(SO_4)_5$ and $Ti(SO_4)_2$ to $Cb_2(SO_4)_3$ and $Ti_2(SO_4)_3$, respectively, whereas the tantalum is not affected. The titanium added serves to prevent hydrolysis of the columbium and tantalum in the reductor. The columbous and titanous sulfates immediately react with the ferric sulfate to form $Cb_2(SO_4)_5$ and $Ti(SO_4)_2$, respectively, and a corresponding amount of ferrous sulfate equivalent to the reduced columbium and titanium.

A Jones reductor having a column of 20-mesh zinc 75 cm. (30 inches) long is required. The zinc should be amalgamated by treating 800 grams, of very low iron content, with 400 ml. of a 2.5 per cent mercuric chloride solution in an 800-ml. beaker and stirring vigorously for 2 minutes. The solution is decanted off and the zinc washed with water, transferred to the 75-cm. (30-inch) reductor, and further washed with hot 2.5 per cent sulfuric acid and water. The reductor, filled with amalgamated zinc as described, is good for about 6 determinations, when it should be emptied and filled with new zinc freshly amalgamated. Immediately before using the reductor it is well to pass through it 200 ml. of almost boiling water in order to preheat the column of zinc. The reductor is then connected to a 1000-ml. suction flask with the delivery tube dipping beneath the surface of 25 ml. of ferric sulfate solution (prepared by dissolving 100 grams of ferric sulfate in a solution containing 150 ml. of phosphoric acid, sp. gr. 1.72, 20 ml. of 1 to 1 sulfuric acid, and 850 ml. of water), and the following solutions are passed through it in the order named: 100 ml. of hot (60° to 70° C.) 20 per cent sulfuric acid; the columbium solution, also heated to 60° to 70° C.; 100 ml. of hot (60° to 70° C.) 20 per cent sulfuric acid containing 1 gram of dissolved succinic acid; and three 50-ml. portions of cold water. At no time is the funnel that forms the reductor inlet permitted to become entirely empty, and the reductor when idle should always be kept full of distilled water to above the top of the zinc.

The solution is cooled to room temperature by addition of several ice cubes prepared from distilled water, transferred to an 800-ml. beaker, and titrated with 0.05 *N* potassium permanganate solution (1 ml. is equivalent to 0.002323 gram of columbium or 0.002395 gram of titanium) that has been standardized against sodium oxalate from the Bureau of Standards. A "blank" on the reagents and reductor is made by fusing a 0.0500-gram portion of pure titanium dioxide with 2 to 3 grams of potassium pyrosulfate (the same amount used in the analysis), dissolving the melt, and passing it through the Jones reductor, all as described in the third and fourth paragraphs. The solution is cooled to room temperature and titrated with 0.05 *N* potassium permanganate. The total volume of standard 0.05 *N* potassium permanganate solution required, less the "blank" (including 0.0500 gram of titanium dioxide) is multiplied by 0.002323 and divided by the weight of sample taken to give the per cent of columbium. The weight of columbium found is multiplied by 1.43 to give the corresponding weight of columbium pentoxide. The weight of the total oxides of columbium and tantalum obtained as described in the second paragraph, less the weight of columbium pentoxide found, gives the weight of tantalum pentoxide, which, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum in the steel.

A modification of this method is necessary for steels containing molybdenum and tungsten. When titanium is present in amounts greater than 0.10 per cent, it is necessary to use the cupferron method described above.

If desired, the ignited and weighed precipitate of columbium and tantalum pentoxides, obtained as described in the second paragraph, may be fused with potassium pyrosulfate without any titanium dioxide addition, the melt dissolved as described in the third paragraph, and the solution passed through the reductor, cooled, and titrated, all as described in the fourth and fifth paragraphs of the method. A "blank" in this case is run on the reductor by dissolving 2 to 3 grams of potassium pyrosulfate in 100 ml. of 20 per cent sulfuric acid containing the same amounts of succinic acid and hydrogen peroxide that were used in the analysis, and putting the solution through the reductor as described, cooling, and titrating. It is very difficult to obtain complete reduction of columbium by means of a Jones reductor (unless titanium is added) but, if the directions given are closely followed, the reduction is so nearly complete that the error thus introduced is not significant when dealing with the amount of columbium usually found in a sample of steel.

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Accurate Determination of Dew Point

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The apparatus features sensitive instrumental observation of dew, combined with minimization of systematic errors in the measurement of the temperature at the gas-liquid interface.

The technic is such as to eliminate the marked hysteresis error characteristic of methods involving continuous temperature change. An accuracy of ±0.01° C. is reached.

A double gaseous film adjacent to the liquid phase is hypothesized in explanation of observed phenomena.

DIRECT dew-point determination affords a sensitive means of determining vapor concentrations. The formation of dew has been utilized as a criterion in the investigation of phase equilibria with reference to motor fuels (*2*, *6*, *12*) and hydrocarbon systems under pressure (*8*, *9*). Improvement in the accuracy of dew-point indication should increase its usefulness as a research tool.

Reviews of hygrometric methods (*10*, *11*) indicate that the means of dew-point determination used in 1916 offered little advantage in dependability over the ether-cooled silver thimble of Regnault (*7*). The accuracy of preferred forms of apparatus varied from 0.2° to 2° C. with decrease in relative humidity.

It appears that these errors were due largely to the unmeasured temperature gradient between the gas-liquid interface and the temperature-recording device. This temperature gradient has two components: (1) the drop across the dew itself, and (2) the drop within the apparatus.

Griffiths (*1*) reduced the second component by inserting the thermometer in a metal block upon whose surface the dew deposited. Readings at appearance and disappearance of dew differed by 0.1° to 2.2° C. Holtzmann (*3*) accomplished virtual elimination of the second component by use of a thermocouple mounted close to the metal deposition surface. An ingenious technic of observation yielded a precision (reproducibility) of some 0.03° C., dependent upon the experience and skill of the observer. Accuracy was not established, results differing from psychrometer readings by the equivalent of some 0.1° C. variation in dew point. It is to be noted especially that this method must be classified among those depending upon the presence at the dew point of sufficient dew to be detected with certainty by visual means. This would cause error in determinations on confined systems, through coincident decrease of vapor concentration in the sample whose composition is sought.

Dew indication through alteration in surface resistance was investigated by Johnstone (*4*) and Tchang (*13*). The ease of visual observation of dew deposit was improved by the use of a platinum-blacked surface by Stevenson and Babor (*12*), who applied their method to the study of the volatility of gasoline. Sage and Lacey (*8*, *9*) applied a modification of the dew-point method to the investigation of phase equilibria in hydrocarbon mixtures. In this case dew was detected through thermal effects caused by the formation of a single hanging droplet 0.1 mm. in diameter. It is again noted that formation

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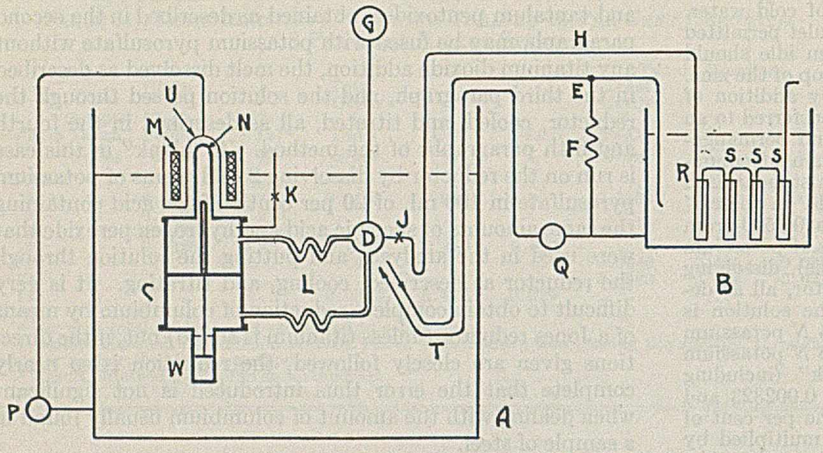

FIGURE 1. APPARATUS FOR INVESTIGATION OF DEW DEPOSITION

of such an amount of liquid occasions change in the composition of the gaseous phase. Tomlinson (*14*) made use of a photoelectric method for detection only, an arbitrarily selected quantity of dew deposit causing actuation, through amplifier and relay, of a signal lamp.

None of these methods succeeded in producing a satisfactory reduction of the first component of the temperature gradient error previously mentioned. This might be accomplished by a method in which the amount of dew approached zero at the dew point. Such a method could be applied to confined systems without introducing further error through depletion of vapor in the gaseous phase. Requirements include extreme sensitivity coupled with a technic of continuous quantitative estimation of variation in dew quantity in the temperature range near the dew point. The apparatus described below was designed to meet these requirements.

Method

Accurate direct determination of the dew point of confined samples is accomplished through a sensitive photoelectric means of dew observation, combined with a technic of intermittent temperature rise calculated to minimize the quantity of dew present at the time the deposition surface reaches the dew-point temperature.

Apparatus

Figure 1 is a diagrammatic representation of the apparatus, whose design included provision for operation above atmospheric pressure.

In thermostat *A* is the dew chamber, *D*, through which a periodically reversed circulation of the gas body is maintained by the 10.2-cm. (4-inch) stroke of a brass piston 12.7 cm. (5 inches) in diameter moving in a steel cylinder, *C*. The connecting coils, *L*, each composed of 0.9 meter (3 feet) of tubing 1.3 cm. (0.5 inch) in diameter, provide added surface for the maintenance of constant and uniform temperature of the gas. The Bourdon pressure gage, *G*, is connected with chamber *D* through an oil- and mercury-filled loop to minimize dead-end space. Bath temperature is measured by a calibrated thermometer graduated in 0.1° C.

For introduction of a sample, gas is passed through Milligan saturators *S*, cotton-packed spray catcher *R*, heated vapor line *H*, valve *J*, chamber *D*, coils *L*, and cylinder *C* to outlet valve *K*, the piston being in operation during the process.

MAGNETICALLY OPERATED PISTON. The circulating piston is raised by the fan-cooled solenoid, *M*, contained in the thermally insulated brass can, *U*. The brass cylinder extension, *N*, is bathed in water circulated from thermostat *A* by gear pump *P* through an insulated pipe. The rate of rise of the piston is controlled by an attached auxiliary piston working in mercury well *W*, displacement of mercury occurring through channels controlled by needle valves situated within the apparatus. Rise of piston was set to about 1 minute, fall requiring 2 minutes. A motor-driven mercury switch controls the solenoid operating cycle, which totals 3.6 minutes.

DEW-MIRROR TEMPERATURE. The temperature of the dew mirror is controlled by circulation of water from thermostat *B* through pump *Q* and insulated lines *T*. Temperature of thermostat *B* is measured by a thermometer similar to that used in the large bath. For easier and more reliable readings of temperature intervals, a Beckman graduated to 0.01° C. is also employed. Rapid chilling of mirror for initial dew deposition is effected by use of cock *E* and water-cooled coils *F*.

Figure 2 shows the submerged dew chamber, in which is the mirror, *M*, of diameter 1.27 cm. (0.5 inch). The flow of the sample is directed horizontally across and immediately adjacent to this mirror. The mirror is integral with the brass billet, *C*, which is thermally insulated by means of Bakelite disks *B* and plastic insulation *I*. Two holes were drilled through the billet at *M*, and countersunk. The enameled thermocouple wires, *W*, were brought up through these holes and fastened by filling the countersinks with solder. Surface *M* was then polished and chromium-plated in order to assist the deposition of dew in the form of many discrete droplets. The actual thermocouple junction is 0.8 mm. (0.03 inch) below mirror *M*. The temperature difference between these two points is calculated to be less than 0.01° C. when the mirror is 50° C. below the temperature of the gas body.

The copper-constantan thermocouple wire, specially drawn, was tested for inhomogeneity, insulated with fine rubber tube, and enclosed in a flexible waterproof metal conduit, which formed part of the interconnected equipotential shield protecting the entire measuring circuit from leakage currents. The cold junction is in thermostat *B*. The couple thus serves to measure merely the temperature drop along the water-circulating system, and is directly connected through an all-copper circuit with a sensitive galvanometer. Before the billet, *C*, was bolted into place, the thermocouple and galvanometer set-up was calibrated directly against carefully compared Beckman thermometers, yielding a mean value 0.023° C. per mm. of scale deflection. From the temperature of bath *B*, the mirror temperature can thus be calculated.

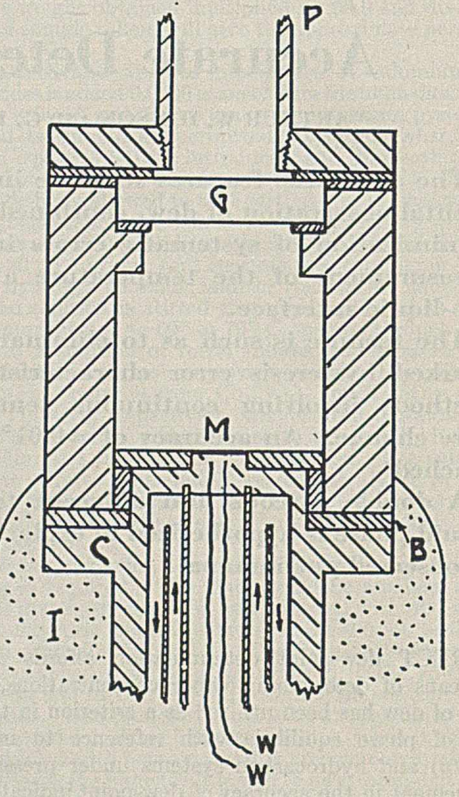

FIGURE 2. DEW CHAMBER

OPTICAL SYSTEM. The source of light is a concentrated filament storage battery lamp. The parallel beam produced by a collimating system passes through an infrared filter and is reflected down along one side of pipe *P* through window *G* to a small total reflecting prism. From this prism the beam reaches the mirror at an angle of some 10° to its surface, and thence, by means of a second reflecting prism, is made to travel back up the other side of pipe *P* to be reflected to a sensitive photoelectric cell.

Owing to the small angle between the incident beam and the mirror surface, the large number of discrete dew droplets intercept and disperse a large fraction of the light, increasing the sensitivity of dew detection.

Amplifier. The photoelectric cell controls the grid circuit of a three-element vacuum-tube amplifier. To attain satisfactory constancy of operating conditions, heavy-duty B-batteries are used in conjunction with a storage A-battery. Plate current is read to 0.02 ma. Drift is determined before and after each run.

Results

A series of preliminary investigations indicated that a gradual decrease in light transmission occurs with decrease in mirror temperature, even when the latter remains well above the dew point. No such effect was noted when the apparatus was evacuated, nor when it was filled with dried air. It appears that the apparatus is sufficiently sensitive to register the presence of gaseous films adjacent to the mirror, of composition differing somewhat from the body of gas due to localized cooling at nearly constant pressure.

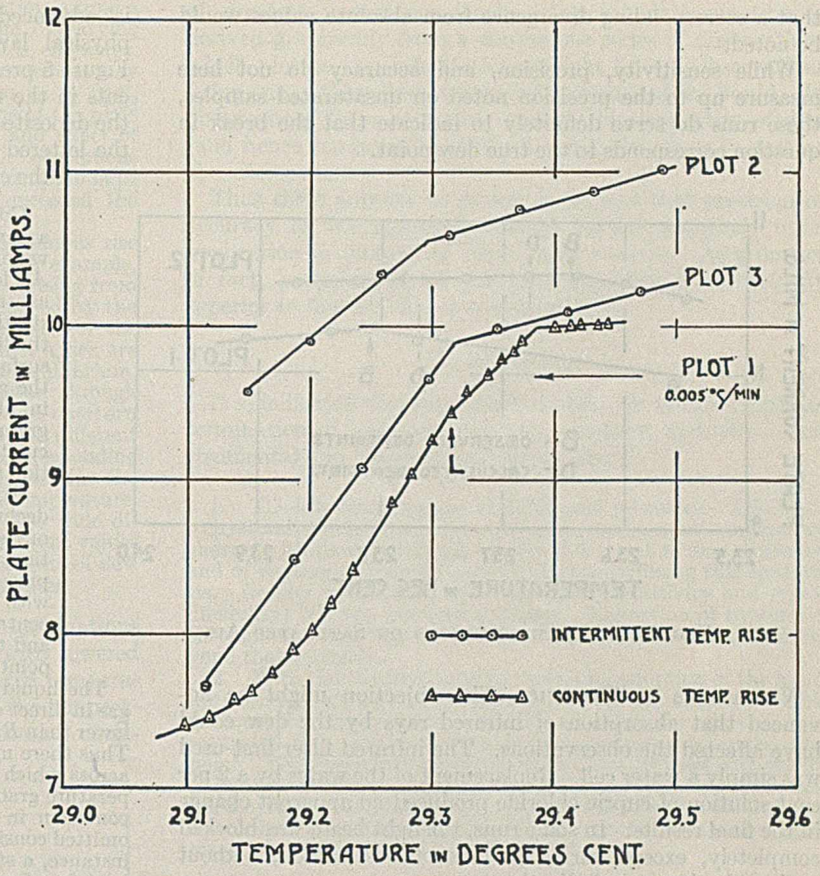

Figure 3. Comparison of Technics of Determination

Continuous Temperature Change. For slow cooling, the plot of plate current versus mirror temperature showed no sharp break, but changed direction gradually over a range of several tenths of a degree. Determination on falling temperature was discarded in favor of a slow temperature rise following preliminary deposition of dew.

Plot 1, Figure 3, illustrates the form of graph obtained through runs by the latter method. There are two breaks, the less distinct lower break, *L*, and the sharp upper break which no doubt would be the only one observable by direct visual means. However, in runs on the same sample at a heating rate of about 0.004° C. per minute, the lower breaks checked one another within 0.01° C., while the upper breaks differed by over 0.1° C. Varying the heating rate from 0.004° C. per minute in one run to 0.014° C. per minute in another, the discrepancy between upper breaks increased to 0.2° C., while the lower breaks again checked each other. It appears that the lower break, not the upper one, corresponds to the true dew point. Unfortunately, the lower break is poorly defined.

Intermittent Temperature Change. To eliminate the lag of dew evaporation with rising temperature, further runs were conducted in a stepwise manner. After preliminary deposition of dew, the rise was accomplished by rapid heating through suitable small temperature intervals, in each case maintaining temperature at the new level until plate current became constant, the criterion of the latter being in most cases a maximum change of about 0.04 milliampere per cycle (3.6 minutes). The final reading of plate current, in each series, was plotted against temperature.

Four such determinations checked within an extreme range of 0.02° C., the plots consisting of two well-defined intersecting straight lines. In two of these runs the point nearest the intersection fell off the lines. This defect was remedied by extrapolating to infinite time (zero rate of plate current change) each series of observations at a given temperature. Plots 2 and 3, Figure 3, drawn from the extrapolated values, also agree within 0.02° C. Moreover, no readable difference in dew point resulted, in either case, from use of extrapolated instead of final readings. It appears that the work of extrapolation may be omitted.

Comparison of Technics. Determinations represented in Figure 3 were all on the same sample, of about 90 per cent relative humidity. It now seems clear that the break, *L*, of plot 1 is to be identified with the true dew point as determined by plots 2 and 3.

The intermittent rise method presents advantages of improved sensitivity and superior convenience. Its success depends upon the use of sensitive instrumental observation, such as the photoelectric system herein described.

Saturated Samples. The means leading to precision of dew-point determination having been investigated, it was desired to discover if the accuracy attainable was of comparable degree. It was found impossible to introduce into the apparatus a prepared partially saturated sample without change in composition far greater than the precision of the determination. It was accordingly decided to work with saturated samples, prepared by introduction of water directly into the tubes connecting cylinder with dew chamber.

The continuous rise method produced in this case no definite break in the plotted results, but the intermittent rise technic yielded the plots of Figure 4. Letters *D* indicate the dew points of the respective samples, calculated to the temperature scale plotted by consideration of thermometer corrections and reading of the differential galvanometer. Letters *B* indicate the observed breaks. *B* and *D* differ in each case by some 0.04° C. There is uncertainty as to the exact point of intersection, occasioned by the relatively great angle between the component sections of each plot. It is thus to be expected that a corresponding divergence from absolute values would be noted.

While sensitivity, precision, and accuracy do not here measure up to the precision noted on unsaturated samples, these runs do serve definitely to indicate that the break in question corresponds to the true dew point.

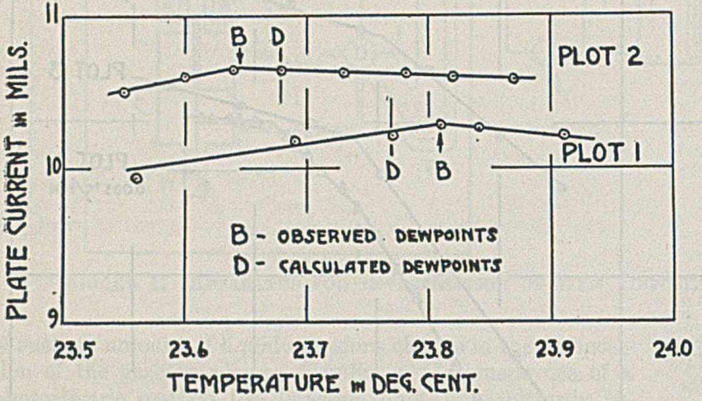

Figure 4. Determinations on Saturated Air

Variations in Technic. The objection might be advanced that absorption of infrared rays by the dew could have affected the observations. The infrared filter first used was simply a water cell. Replacement of the water by a 2 per cent solution of cupric chloride produced no apparent change in the final results. In some runs, the light beam was blocked completely, except during periods of observation, without noticeable change in indications.

No improvement resulted from coating the mirror with platinum black (*12*), suspending gas circulation, or varying the rate of transition between test temperatures.

Discussion

The data give rise to a number of questions concerning the mechanism through which occurs the interchange between liquid and gaseous phases. Chief among these are:

1. Equilibrium when mirror is below the dew point. During intermittent rise runs it was observed, at each temperature level, that the light transmission became greater than that at the preceding level, but slowly approached constancy. From usual considerations, it would be expected that dew would deposit on, rather than evaporate from, a surface remaining at a temperature below the dew point.
2. Break in plot for unsaturated samples, intermittent rise runs. An explanation is needed for the abrupt change in slope. Note that since these were equilibrium readings, no rates of evaporation or diffusion are involved.
3. Break in plot for saturated samples, intermittent rise runs. Why is the change in slope less than in the case of unsaturated samples?
4. Breaks in plots for unsaturated samples, continuous rise runs. Why is the lower break lacking in sharpness? What is the significance of the upper break, and why does its position vary widely in runs under different conditions of dew and heating rate?

In correlating these ideas, it should be borne in mind that the amount of light transmitted to the photocell is affected by changes in the gaseous phase as well as in the liquid phase. Such changes may include convection currents or the formation of films of varying thickness and vapor content. They may partially deflect the light beam from its normal course through mirror and aperture system, or alter its intensity by absorption. It is also to be remembered that the temperature gradient, between the dew mirror and the body of the gaseous phase, will be largely across the gas film rather than the liquid.

Double-Film Hypothesis. To coördinate the observed qualitative and quantitative data the double-film hypothesis is advanced. This concept is in accord with accepted physical laws governing behavior of gases and vapors. Figure 5 presents temperature and vapor concentration gradients in the thin films immediately adjacent to the surface of the deposited liquid. The precise form of the plots, between the lettered points, is not material to the development of the concept.

Consider a general case, wherein a liquid surface is at a temperature T' below the dew point of a body of vapor-gas of temperature Tg and vapor concentration A, less than saturation. The temperature gradient causes a corresponding density gradient, producing a stratification in the gas phase immediately adjacent to the liquid. This will be most marked when the liquid surface is horizontal and there is but little circulation in the gas phase, but will probably exist to lesser degree in absence of either of these conditions. In the diagram, the range above Tg and A is that wherein circulation maintains approximate uniformity in composition and temperature of the gas phase.

Approaching the liquid-gas interface, the temperature declines. The first effect of this, indicated by section AB of the concentration line, is to increase vapor concentration, since this localized cooling is at essentially constant pressure. The film so produced is still unsaturated, until with decreasing temperature and increasing vapor concentration, saturation is reached at concentration B and temperature T. This temperature T is the true dew point.

The liquid surface is at a still lower temperature, T', and the gas in direct contact with it has a vapor concentration C, which is lower than B, owing to condensation of liquid from the gas phase. Thus there must exist between points B and C a saturated film, across which there is a concentration gradient as well as a temperature gradient. Keevil and Lewis (*5*) discussed a comparable condition in connection with the dehumidification of air, but omitted consideration of the unsaturated film AB. In the present instance, a steady state exists at each test temperature, without transfer of vapor across the double film. If the system reached this state by prior lowering of the liquid surface from a higher temperature, the saturated film may contain, suspended in it, a fog of liquid droplets, whose source was the condensation above mentioned.

Were the original vapor-gas mixture saturated, there would be no unsaturated film. The temperature gradient, TgT, and the concentration gradient, AB, would become zero. The character of the saturated film would remain as indicated in the diagram.

Correlation with the Data. From the standpoint of the concept above developed, the major questions raised by the experimental data can now be answered.

1. Equilibrium when mirror is below the dew point. The above concept makes it clear that the liquid surface is in equilibrium with a gas carrying vapor concentration C, Figure 5. This concentration may be less than that in the body of the gas, owing to prior condensation within the saturated film. Hence for each mirror temperature, an equilibrium condition may be established, even though the mirror is below the dew point.
2. Break in plot for unsaturated samples, intermittent rise runs. Referring again to Figure 5, if the temperature of the liquid surface be raised through a small interval, and held at the new level, a readjustment of both films may be expected to occur. Changes will involve temperature gradients, concentration gradients, and thicknesses, the general relationships remaining as before, so long as T' is still below the true dew point T. Changes in light reflection between temperature levels are represented by the left section of, for example, plot 2, Figure 3. These changes are affected also by alterations in amount of dew on the mirror. When T' is raised to coincide with T, there is no longer a saturated film, nor will the liquid phase persist above this temperature. Further temperature increase causes variations in the remaining single unsaturated film, represented by the right section of plot 2, Figure 3. The abrupt change of slope is a consequence of the abrupt change in physical nature of the entities affecting the transmission of the light. Another break might be expected if T' were raised high enough to coincide with Tg, the temperature of the gaseous body, at which point the unsaturated film would in turn disappear.
3. Break in plot for saturated samples, intermittent rise runs. In this case there is at no point an unsaturated film. The cause of the breaks in the plots, Figure 4, is entirely different from that discussed in the preceding paragraph in connection with un-

saturated samples. In saturated samples, the transition is from a condition wherein there is present a saturated film of varying thickness, to one wherein there is no film of this character. When T' becomes greater than T_g slight convection currents may be set up, whose disturbance of light transmission is, in part, the cause of the negative slopes of the right sections of the plots in Figure 4. Definite indication of the existence and effect of such convection currents has been noted. With rapid continuous heating of the mirror, in the absence of dew, sudden drops in light transmission occurred when mirror temperature exceeded the temperature of the gas body by some 0.1° C.

4. Breaks in plots for unsaturated samples, continuous rise runs. The lack of sharpness in the lower break of, for example, plot 1, Figure 4, may be attributed to disturbances arising from irregular convection currents. Such currents are caused by the relatively rapid and continuous rise of the temperature of the dew surface. Temperature gradients set during such a rise are the reverse of those existing in the double film at equilibrium, and, time being insufficient to allow their dissipation through conduction or readjustment of the film, a convection overturn occurs. The upper break is thought to arise from a still different source from those previously discussed, in this case corresponding to the completion of the processes which, were it not for the hysteresis introduced by the continual variation in temperature, would have been completed at the lower break. The wide divergence in upper breaks in different runs reflects different values of this hysteresis, brought about by variation in amounts of dew originally deposited, and by variation in the heating rates.

DETERMINATION AT OTHER HUMIDITIES. In determinations of dew point by usual means, error increases with lowered humidity. This is due primarily to the augmented temperature gradient between the body of vapor-gas and the temperature-measuring device. As set forth in the discussion of design of apparatus, this causes error in two ways.

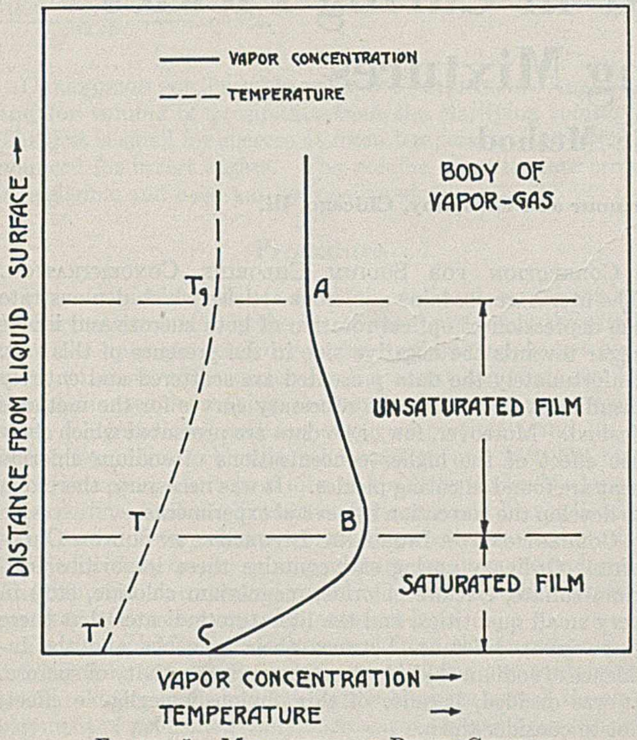

FIGURE 5. MECHANISM OF PHASE CHANGE

In the present apparatus, error due to temperature gradient between thermocouple and mirror surface has been reduced to an estimated 0.01° C. for a 50° differential between temperatures of sample and dew-point mirror. Error due to temperature gradient across the dew film is eliminated by two means. First, an exceedingly sensitive instrumental method of detection is employed, which reveals the presence of very small amounts of dew, thus permitting temperature observation at a time when error is very small. Second, and of greatest importance, each dew-point determination is derived graphically from a continuous series of observations which plot as two intersecting straight lines. Observations fixing one of these lines are made in absence of the liquid. In observations fixing the other straight line, quantity of dew (and hence temperature gradient error) decreases to zero at the intersection.

Thus there appears no reason to suspect that precision or accuracy of this apparatus should fall off materially upon application to samples of lower vapor content. As a matter of fact, precision at 90 per cent humidity was markedly superior to that at 100 per cent humidity.

Application

It is indicated that fundamental obstacles to dew-point determination of high precision and accuracy, exclusive of instrumental and observational errors, are:

1. The inherent slowness of diffusional processes. This leads to hysteresis in determinations involving continuous temperature change. Methods involving control of amount of dew deposited and of heating rate might succeed in standardizing this hysteresis. Results would then show precision (sensitivity and reproducibility) but not absolute accuracy. Reduction of hysteresis, through slow heating, increases the time of a determination beyond that desirable.
2. With the elimination of hysteresis by adoption of the intermittent rise technic, there is indication of the presence of a double gaseous film adjacent to the liquid, of which the upper or unsaturated film is still present at temperatures above the dew point. This film appears to produce an effect, at least with regard to light transmission, similar in nature to a persistence of the dew itself. This effect affords explanation of the difficulty of obtaining concordant indications of dew point where reliance is placed upon visual observation.

The apparent way to obtain still sharper indications of dew point, and simultaneously to realize a shorter period of determination, is to cause the sample to move at high velocity across the surface on which dew is deposited. The object is to minimize film thicknesses, and also to increase diffusion rates. Correction for pressure changes would be necessary.

Such an application, in combination with photoelectric or other instrumental means of dew observation, would appear to be a useful research tool, as, for example, in the determination of pressure-phase relationships in complex hydrocarbon mixtures at constant temperature. Sensitive control of vapor mixtures in industrial processes presents another possibility.

The accuracy of dew-point determination which has been developed opens the way to possible new applications. For example, the measurement of very low concentrations of a vapor in a gas is rendered practicable by the combination of such accurate determination with the following suggested principle of operation: A reference mixture is first prepared, consisting of gas partially saturated with a selected vapor, and the dew point (with respect to that vapor) is determined. The sample, of unknown vapor concentration, is now pumped into the space occupied by the reference mixture, and the new dew point is determined. The difference in dew points is a sensitive measure of the added vapor concentration carried in by the unknown sample. Multiplied sensitivity could be attained by continuing to pump in the unknown sample until a total pressure of several atmospheres had been reached. In the latter case the effects of dissolved gas, and of increased pressure, upon the vapor pressure of the liquid phase should be considered.

Summary and Conclusions

An apparatus has been designed which minimizes the known instrumental and observational errors in the determination of dew point.

The technic of applying this apparatus to the elucidation of the inherent difficulties of dew point determination has been developed.

Wide discrepancies are introduced by hysteresis in dew evaporation. These have been investigated and their extent has been indicated.

A technic for eliminating hysteresis, at the expense of time consumption, has been evolved.

It has been shown possible to obtain a precision of about ±0.01° C. at 90 per cent humidity, and ±0.05° C. at 100 per cent humidity. Observations on the saturated samples checked absolute values within the stated limits of precision (reproducibility).

A hypothesis has been advanced with regard to the structure of gaseous films adjacent to the liquid phase. From this hypothesis has been formulated a concept of the mechanism of dew formation and evaporation, which affords explanation of the difficulty in obtaining concordant dew point indications by visual means.

A means of increasing further the sharpness of dew indication, simultaneously decreasing the time required for a determination, has been outlined.

Application of accurate dew-point determination as a research tool has been considered.

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Determination of Sugar in Curing Pickles and Dry-Curing Mixtures

A Polarimetric Method

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ONE important phase of packing-house laboratory control over plant operations is the analysis of curing pickles both new and used, and dry-curing mixtures. The former are solutions of sodium chloride containing sucrose in the form of raw or granulated sugar and the regular curing ingredients, sodium nitrite and sodium nitrate, either singly or together. The concentration of sodium chloride varies from about 15 per cent to saturation, while the sugar range is from zero to about 5 per cent. Sodium nitrite and nitrate are present in considerably less amount, seldom exceeding 0.5 per cent for the nitrate and 0.2 per cent for the nitrite. Dry-curing mixtures differ from pickles in that they contain these ingredients in the dry state.

The sugar determination (by any of the recognized gravimetric or volumetric methods) consumes the most time and is the least accurate of the ingredient tests, and a quick and reasonably accurate method would greatly facilitate pickle and dry-cure control and save much time and labor in the laboratory.

Use of Polariscope

The polariscope in the field of sugar chemistry is employed ordinarily on solutions containing sugars with no inorganic substances present. On account of its dependability and production of uniform results, particularly on sucrose, the instrument was considered suitable for this study, despite the corrections that necessarily would have to be applied with its use.

CORRECTION FOR SODIUM CHLORIDE CONCENTRATION. The literature contains numerous articles which demonstrate the depression of optical rotation of both sucrose and invert sugar towards the negative side in the presence of this salt. Unfortunately the data presented are scattered and entirely insufficient to develop the necessary curves for the methods desired. Moreover, few or no data are presented which show the effect of the higher concentrations of sodium chloride that are found in curing pickles. It was necessary, therefore, to develop the correction by several experiments.

CORRECTION FOR INORGANIC IMPURITIES IN SODIUM CHLORIDE. Ordinary curing salt contains these impurities (calcium sulfate, calcium chloride, magnesium chloride, etc.) in very small quantities, and the literature indicates that there is no great difference between their influence and the influence of sodium chloride upon the optical activity of sucrose. It was decided, because of this obviously negligible effect, not to consider them.

CORRECTION FOR SODIUM NITRITE AND SODIUM NITRATE. As only scattered data are available, it became necessary to develop this by experimentation.

CORRECTION FOR PRESENCE OF INVERT SUGAR IN SUCROSE. This factor possesses some significance. It would be possible to invert the solution containing the sucrose and calculate total sugar as invert, but this would add another step of considerable length. A study of numerous analyses of raw and granulated sugar disclosed that the invert content was fairly constant in both types. For all practical purposes an assumption could be made that there is 1.5 per cent of invert sugar in the raw sugar, and 0.50 per cent in the granulated sugar. The errors due to the ordinary variations from these values are not appreciable. (For convenience, however, a formula giving the correction to apply to sugars having different invert values from these is presented later.)

Table I. Sucrose Determinations

Sucrose	Sodium Chloride	Sodium Nitrate	Sodium Nitrite	Reading	Sucrose Pounds per 100 gallons[a,b]	Sucrose Added for correction[c]
Pounds per 100 gallons				° V.		%
15.00	...	..	..	+ 7.00	15.25	0.0
	50	..	..	+ 6.90	15.03	1.5
	100	..	..	+ 6.71	14.62	4.3
	150	..	..	+ 6.63	14.44	5.6
	200	..	..	+ 6.57	14.31	6.5
	250	..	..	+ 6.49	14.13	7.9
30.00	...	..	..	+13.77	29.99	0.0
	100	..	..	+13.37	29.12	3.0
	200	..	..	+13.07	28.47	5.3
	250	..	..	+12.87	28.03	7.0
	...	5.0	..	+13.78	30.01	0.0
	...	10.0	..	+13.85	30.17	0.0
	...	..	5.0	+13.74	29.93	0.0
	...	..	10.0	+13.79	30.03	0.0
40.00	...	..	..	+18.50	40.29	0.0
	50	..	..	+18.11	39.44	2.2
	100	..	..	+17.83	38.83	3.8
	150	..	..	+17.66	38.46	4.8
	200	..	..	+17.40	37.90	6.3
	225	..	..	+17.22	37.51	7.4
	256	..	..	+17.16	37.37	7.8
	...	2.5	..	+18.37	40.01	0.1
	...	..	1.0	+18.52	40.34	0.0

[a] Pounds per 100 U. S. gallons × 0.1198 = grams per 100 ml. Reading in ° V. × 2.1782 = pounds of sucrose per 100 gallons at 32° C. (*3*).

[b] Calculated from the readings obtained.

[c] The % corrections are based on the decrease obtained from zero salt. Thus, for 15 pounds of sucrose and 250 pounds of sodium chloride, the % to be added to the sucrose value already obtained (14.13 pounds) equals $\frac{(15.25 - 14.13) \times 100}{14.13}$ or 7.9%.

Correction for Temperature of Polarimetric Reading and for volume of precipitate from the clarifying solution. The first is small for sucrose at room temperature but is pronounced for invert sugars. The volume of precipitate error is negligible and need not be considered.

Procedure

For new pickles—that is, fresh, as made up, containing no protein matter and only the invert sugar present in the original make-up sugar—and dry-curing mixtures, apply two correction factors: (1) a value for the invert sugar present in the sugar used in making the pickle, assuming a constant value for granulated and raw sugar, respectively, and (2) a factor for sodium chloride concentration and possibly one each for sodium nitrite and nitrate, the latter to be developed by experimentation. These two factors would be applied in order to the direct polarimetric reading on the clarified or unclarified pickle, or dry-curing mixture made up to volume. The temperature correction would be avoided by always reading at 25° C. or at some other constant level.

For used pickles (pickles removed from the tierce or box holding the meat during the process of curing and containing protein matter and a high proportion of invert sugar), the employment of polarimetric methods was inadvisable for several reasons: (1) A large factor must be used in the calculations, which limits accuracy; (2) the correction for sodium chloride is very large, also limiting accuracy; and (3) clarification of used pickles followed by inversion is an awkward operation. Consequently, extension of the work to used pickles was abandoned.

Sucrose

Pure, dried Difco sucrose was made up into a solution of known strength. Varying quantities of chemically pure sodium chloride were weighed into 100-ml. volumetric flasks, and known amounts of the sucrose solution were then added to each. In a few cases, solutions containing sodium nitrite or sodium nitrate alone were prepared with sucrose. These were then made up to volume, mixed thoroughly, and polarized directly in a 200-mm. tube with white light filtered through a potassium dichromate cell, the solution being of such concentration that the percentage content of potassium dichromate multiplied by the length of the column in centimeters was equal to 9. The instrument employed in these tests was a J. and J. Fric, Bates-type saccharimeter, 200 mm. All readings were made at 32° C. The results are shown in Table I.

It follows from these data that there is a regular decrease in apparent values of sucrose with an increase in sodium chloride concentration. Another fact brought out is that sodium nitrite and sodium nitrate in the concentrations employed in pickle exert no appreciable effect on the rotation and consequently may be neglected as factors influencing the readings.

Table II presents the sucrose correction to be added to the uncorrected sucrose obtained from the polarimetric reading compensating for the presence of invert sugar.

Table II. Initial Correction, for Invert Sugar

(Based on the assumption of 1.50% invert sugar and 98.50% sucrose in raw sugar and 0.50% invert sugar and 99.50% sucrose in granulated sugar. Add to sucrose from direct polarimetric reading, expressed in any unit of weight per volume at 20° C. such as grains per 100 ml. or pounds per 100 gallons. The correction will be in the same unit of weight per volume. Example: The correction for 10 pounds per 100 gallons at 25° C. is 0.21 pound per 100 gallons. For 10 grams per 100 ml. at 25° C. it is 0.21 gram per 10 ml.)

Sucrose Calculated from Polarimetric Reading[a]	Correction for Raw[b] Sugar	Correction for Granulated[b] Sugar	Sucrose Calculated from Polarimetric Reading[a]	Correction for Raw[b] Sugar	Correction for Granulated[b] Sugar
1	0.02	0.01	26	0.54	0.20
2	0.04	0.02	27	0.56	0.21
3	0.06	0.02	28	0.59	0.22
4	0.08	0.03	29	0.61	0.23
5	0.10	0.04	30	0.63	0.24
6	0.13	0.05	31	0.65	0.25
7	0.15	0.06	32	0.67	0.25
8	0.17	0.06	33	0.69	0.26
9	0.19	0.07	34	0.71	0.27
10	0.21	0.08	35	0.74	0.28
11	0.23	0.09	36	0.76	0.29
12	0.25	0.10	37	0.78	0.30
13	0.27	0.10	38	0.80	0.30
14	0.29	0.11	39	0.82	0.31
15	0.31	0.12	40	0.84	0.32
16	0.33	0.13	41	0.87	0.33
17	0.35	0.14	42	0.89	0.33
18	0.38	0.14	43	0.91	0.34
19	0.40	0.15	44	0.93	0.35
20	0.42	0.16	45	0.95	0.36
21	0.44	0.16	46	0.97	0.37
22	0.46	0.17	47	0.99	0.37
23	0.48	0.18	48	1.01	0.38
24	0.50	0.19	49	1.03	0.39
25	0.52	0.19	50	1.05	0.39

[a] In any unit of weight per volume at 25° C.

[b] In same unit of weight per volume as sucrose in first column at 25° C

On the basis of the data developed, Table III was drawn up. It shows the sucrose correction to be added to the sucrose already corrected for invert sugar, as described above, for the presence of sodium chloride.

The methods outlined below utilize the facts which were brought out in the foregoing work. They are recommended for use in routine testing or for determinations where extreme accuracy is not required.

New Pickles

Pickles Made from Raw Sugar. Fill a 100-ml. volumetric flask to the mark with pickle at a temperature of 25° C. Add 2 to 4 ml. (as necessary) of basic lead acetate and mix. (To prepare this reagent, boil 430 grams of neutral lead acetate, 130 grams of litharge, and 1 liter of distilled water for 30 minutes. Allow the mixture to cool and settle and then dilute the supernatant liquid to a specific gravity of 1.25 with recently boiled, distilled water.

Table III. Final Correction, for Sodium Chloride Concentration

(Add to sucrose, expressed in any unit of weight per volume at 25° C., such as grams per 100 ml. or pounds per 100 gallons, corrected for invert sugar. The correction will be in the same unit of weight per volume. Example: The correction for 30 pounds of sucrose per 100 gallons at 25° C. for a sodium chloride concentration of 30 pounds per 100 gallons at 25° C. is 0.31 pound per 100 gallons. For 30 grams of sucrose per 100 ml. at 25° C. for a sodium chloride concentration of 30 grams per 100 ml. at 25° C. it is 0.31 gram per 100 ml.

The table applies for values of sugar up to the equivalent of 50 pounds per 100 gallons as the experimental data went only that high. For example, if the units are expressed in grams per 100 ml., the table should not be used for sucrose values in excess of 6 grams per 100 ml.)

Sucrose Corrected for Invert[a] Sugar	Salt Concentration[b]																										
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	265
1	0.00	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.08	0.08	0.08
2	0.01	0.01	0.02	0.03	0.04	0.04	0.05	0.06	0.06	0.07	0.07	0.08	0.09	0.09	0.10	0.10	0.11	0.11	0.12	0.13	0.13	0.14	0.14	0.15	0.15	0.16	0.16
3	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15	0.15	0.16	0.17	0.18	0.19	0.19	0.20	0.21	0.22	0.23	0.24	0.24
4	0.01	0.03	0.04	0.06	0.07	0.08	0.10	0.11	0.12	0.14	0.15	0.16	0.17	0.18	0.20	0.20	0.22	0.23	0.24	0.25	0.26	0.27	0.28	0.29	0.30	0.32	0.32
5	0.02	0.03	0.05	0.07	0.09	0.10	0.12	0.14	0.15	0.17	0.18	0.20	0.21	0.23	0.24	0.25	0.27	0.28	0.30	0.31	0.32	0.34	0.35	0.36	0.38	0.39	0.40
6	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24	0.26	0.28	0.30	0.30	0.32	0.34	0.36	0.38	0.38	0.40	0.42	0.44	0.46	0.48	0.48
7	0.02	0.05	0.07	0.10	0.13	0.15	0.17	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.35	0.35	0.38	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.53	0.55	0.57
8	0.03	0.06	0.08	0.12	0.14	0.16	0.20	0.22	0.24	0.28	0.30	0.32	0.34	0.36	0.40	0.40	0.44	0.46	0.48	0.50	0.53	0.54	0.56	0.58	0.60	0.64	0.64
9	0.03	0.06	0.09	0.13	0.16	0.19	0.22	0.25	0.28	0.31	0.33	0.36	0.39	0.41	0.44	0.46	0.49	0.51	0.54	0.57	0.59	0.61	0.64	0.66	0.68	0.71	0.73
10	0.03	0.07	0.10	0.14	0.18	0.21	0.24	0.28	0.31	0.34	0.37	0.40	0.43	0.46	0.49	0.51	0.54	0.57	0.60	0.63	0.65	0.68	0.71	0.73	0.76	0.79	0.81
11	0.04	0.08	0.12	0.15	0.20	0.23	0.26	0.31	0.34	0.37	0.41	0.44	0.47	0.51	0.54	0.56	0.59	0.63	0.66	0.69	0.72	0.75	0.78	0.80	0.84	0.87	0.89
12	0.04	0.08	0.13	0.17	0.22	0.25	0.29	0.34	0.37	0.41	0.44	0.48	0.52	0.55	0.59	0.61	0.65	0.68	0.72	0.76	0.78	0.82	0.85	0.88	0.91	0.95	0.97
13	0.05	0.09	0.14	0.18	0.23	0.27	0.31	0.36	0.40	0.44	0.48	0.52	0.56	0.60	0.64	0.66	0.70	0.74	0.78	0.82	0.85	0.88	0.92	0.95	0.99	1.03	1.05
14	0.05	0.10	0.15	0.20	0.25	0.29	0.34	0.39	0.43	0.48	0.52	0.56	0.60	0.64	0.69	0.72	0.76	0.80	0.84	0.88	0.91	0.95	0.99	1.02	1.06	1.11	1.13
15	0.05	0.10	0.16	0.21	0.27	0.31	0.36	0.42	0.46	0.51	0.55	0.60	0.64	0.69	0.74	0.77	0.81	0.85	0.90	0.94	0.98	1.02	1.07	1.10	1.14	1.19	1.22
16	0.06	0.11	0.17	0.22	0.29	0.34	0.38	0.45	0.50	0.54	0.59	0.64	0.69	0.74	0.79	0.82	0.86	0.91	0.96	1.01	1.04	1.09	1.14	1.17	1.22	1.26	1.30
17	0.06	0.12	0.18	0.24	0.31	0.36	0.41	0.48	0.53	0.58	0.63	0.68	0.73	0.78	0.83	0.87	0.92	0.97	1.02	1.07	1.11	1.16	1.21	1.24	1.29	1.34	1.38
18	0.06	0.13	0.19	0.25	0.32	0.38	0.43	0.50	0.56	0.61	0.67	0.72	0.77	0.83	0.88	0.92	0.97	1.03	1.08	1.13	1.17	1.23	1.28	1.32	1.37	1.42	1.46
19	0.07	0.13	0.20	0.27	0.34	0.40	0.46	0.53	0.59	0.65	0.70	0.76	0.82	0.87	0.93	0.97	1.03	1.09	1.14	1.20	1.24	1.29	1.35	1.39	1.44	1.50	1.54
20	0.07	0.14	0.21	0.28	0.36	0.42	0.48	0.56	0.62	0.68	0.74	0.80	0.86	0.92	0.98	1.02	1.08	1.14	1.20	1.26	1.30	1.36	1.42	1.46	1.52	1.58	1.62
21	0.07	0.15	0.22	0.29	0.38	0.44	0.50	0.59	0.65	0.71	0.78	0.84	0.90	0.97	1.03	1.07	1.14	1.20	1.26	1.33	1.37	1.43	1.49	1.53	1.60	1.66	1.70
22	0.08	0.15	0.23	0.31	0.40	0.46	0.53	0.62	0.68	0.75	0.81	0.88	0.94	1.01	1.08	1.12	1.19	1.25	1.32	1.39	1.43	1.50	1.56	1.61	1.67	1.74	1.78
23	0.08	0.16	0.24	0.32	0.41	0.48	0.55	0.64	0.71	0.78	0.85	0.92	0.99	1.06	1.13	1.17	1.24	1.31	1.38	1.45	1.50	1.57	1.63	1.68	1.75	1.82	1.86
24	0.08	0.17	0.25	0.34	0.43	0.50	0.58	0.67	0.74	0.82	0.89	0.96	1.03	1.10	1.18	1.22	1.30	1.37	1.44	1.51	1.56	1.63	1.71	1.75	1.82	1.90	1.94
25	0.09	0.17	0.26	0.35	0.45	0.52	0.60	0.70	0.78	0.85	0.92	1.00	1.07	1.15	1.23	1.27	1.35	1.43	1.50	1.58	1.63	1.70	1.78	1.83	1.90	1.98	2.02
26	0.09	0.18	0.27	0.36	0.47	0.55	0.62	0.73	0.81	0.88	0.96	1.04	1.12	1.20	1.27	1.33	1.41	1.48	1.56	1.64	1.69	1.77	1.85	1.90	1.98	2.05	2.11
27	0.09	0.19	0.28	0.38	0.49	0.57	0.65	0.76	0.84	0.92	1.00	1.08	1.16	1.24	1.32	1.38	1.46	1.54	1.62	1.70	1.76	1.83	1.92	1.97	2.05	2.14	2.19
28	0.10	0.20	0.29	0.39	0.50	0.59	0.67	0.78	0.87	0.95	1.04	1.12	1.20	1.29	1.37	1.43	1.51	1.60	1.68	1.77	1.82	1.90	1.99	2.05	2.13	2.21	2.27
29	0.10	0.20	0.30	0.41	0.52	0.61	0.70	0.81	0.90	0.99	1.07	1.16	1.25	1.33	1.42	1.48	1.57	1.65	1.74	1.83	1.89	1.98	2.06	2.12	2.21	2.29	2.35
30	0.10	0.21	0.31	0.42	0.54	0.63	0.72	0.84	0.93	1.02	1.11	1.20	1.29	1.38	1.47	1.53	1.62	1.71	1.80	1.89	1.95	2.04	2.13	2.19	2.28	2.37	2.43
31	0.11	0.22	0.32	0.43	0.56	0.65	0.74	0.87	0.96	1.05	1.15	1.24	1.33	1.43	1.52	1.58	1.67	1.77	1.86	1.95	2.02	2.11	2.20	2.27	2.36	2.45	2.51
32	0.11	0.22	0.34	0.45	0.58	0.67	0.77	0.90	0.99	1.09	1.18	1.28	1.38	1.47	1.57	1.63	1.73	1.83	1.92	2.02	2.08	2.18	2.27	2.34	2.43	2.53	2.59
33	0.12	0.23	0.35	0.46	0.59	0.69	0.79	0.93	1.02	1.12	1.22	1.32	1.42	1.52	1.62	1.68	1.78	1.88	1.98	2.08	2.15	2.24	2.35	2.41	2.51	2.61	2.68
34	0.12	0.24	0.36	0.48	0.61	0.71	0.82	0.95	1.05	1.15	1.26	1.36	1.46	1.57	1.67	1.73	1.84	1.94	2.04	2.14	2.21	2.31	2.42	2.48	2.58	2.69	2.76
35	0.12	0.25	0.37	0.49	0.63	0.74	0.84	0.98	1.09	1.19	1.30	1.40	1.50	1.61	1.72	1.78	1.89	2.00	2.10	2.21	2.28	2.38	2.49	2.56	2.66	2.76	2.84
36	0.13	0.25	0.38	0.50	0.65	0.76	0.86	1.01	1.12	1.23	1.33	1.44	1.55	1.66	1.77	1.83	1.95	2.05	2.16	2.27	2.34	2.45	2.56	2.63	2.74	2.84	2.92
37	0.13	0.26	0.39	0.52	0.67	0.78	0.89	1.04	1.15	1.26	1.37	1.48	1.59	1.70	1.81	1.89	2.00	2.11	2.22	2.33	2.41	2.52	2.63	2.70	2.81	2.93	3.00
38	0.13	0.27	0.40	0.53	0.68	0.80	0.91	1.07	1.18	1.29	1.41	1.52	1.63	1.75	1.86	1.93	2.05	2.17	2.28	2.40	2.47	2.58	2.70	2.77	2.89	3.00	3.08
39	0.14	0.27	0.41	0.55	0.70	0.82	0.94	1.09	1.21	1.33	1.44	1.56	1.68	1.80	1.91	1.99	2.11	2.22	2.34	2.46	2.54	2.65	2.77	2.85	2.96	3.08	3.16
40	0.14	0.28	0.42	0.56	0.72	0.84	0.96	1.12	1.24	1.36	1.48	1.60	1.72	1.84	1.96	2.04	2.16	2.27	2.40	2.53	2.60	2.72	2.84	2.92	3.04	3.16	3.24
41	0.14	0.29	0.43	0.57	0.74	0.86	0.98	1.15	1.27	1.39	1.52	1.64	1.77	1.88	2.01	2.09	2.22	2.34	2.46	2.58	2.67	2.79	2.91	3.00	3.11	3.24	3.32
42	0.15	0.29	0.44	0.59	0.76	0.88	1.01	1.18	1.30	1.43	1.56	1.68	1.81	1.93	2.06	2.14	2.27	2.39	2.52	2.65	2.73	2.86	2.97	3.07	3.19	3.32	3.40
43	0.15	0.30	0.45	0.60	0.77	0.90	1.03	1.20	1.33	1.46	1.59	1.72	1.85	1.98	2.11	2.19	2.32	2.45	2.58	2.71	2.80	2.93	3.05	3.14	3.27	3.40	3.48
44	0.15	0.31	0.46	0.62	0.79	0.92	1.06	1.23	1.37	1.50	1.63	1.76	1.89	2.02	2.16	2.25	2.38	2.51	2.64	2.77	2.86	2.99	3.12	3.22	3.34	3.47	3.57
45	0.16	0.32	0.47	0.63	0.81	0.95	1.08	1.26	1.40	1.53	1.67	1.80	1.93	2.07	2.20	2.30	2.43	2.56	2.70	2.84	2.93	3.06	3.20	3.29	3.42	3.55	3.65
46	0.16	0.32	0.48	0.64	0.83	0.97	1.10	1.29	1.43	1.57	1.70	1.84	1.98	2.12	2.25	2.35	2.49	2.62	2.76	2.90	2.99	3.13	3.27	3.36	3.50	3.63	3.75
47	0.16	0.33	0.49	0.66	0.85	0.99	1.13	1.32	1.46	1.60	1.74	1.88	2.02	2.16	2.30	2.40	2.54	2.68	2.82	2.96	3.06	3.20	3.33	3.43	3.57	3.72	3.81
48	0.17	0.34	0.50	0.67	0.86	1.01	1.15	1.34	1.49	1.63	1.78	1.92	2.07	2.21	2.35	2.45	2.59	2.74	2.88	3.03	3.12	3.27	3.41	3.51	3.65	3.79	3.89
49	0.17	0.34	0.51	0.69	0.88	1.03	1.18	1.37	1.52	1.67	1.82	1.96	2.11	2.25	2.40	2.50	2.65	2.79	2.94	3.09	3.19	3.33	3.48	3.58	3.72	3.87	3.97
50	0.17	0.35	0.52	0.70	0.90	1.05	1.20	1.40	1.55	1.70	1.85	2.00	2.15	2.30	2.45	2.55	2.70	2.85	3.00	3.15	3.25	3.40	3.55	3.65	3.80	3.95	4.05

[a] In any unit of weight per volume at 25° C.

[b] In same unit of weight per volume at 25° C. as sucrose in first column.

Solid basic lead acetate may be substituted for the normal salt and litharge in the preparation of the solution, *1.*) Filter through a dry filter paper and reject the first 10 ml. Polarize the filtrate in a 200-mm. tube, using sodium light or its equivalent.

CALCULATIONS. Sucrose (in pounds per 100 gallons at 25° C.) = reading × 2.1735 or, sucrose (in grams per 100 ml. at 25° C.) = reading × 0.2604.

If the result is expressed in pounds per 100 gallons, apply Table II under "raw sugar" for invert sugar and add the correction to the sucrose obtained above.

Apply Table III for the sodium chloride concentration, adding the correction to the sucrose corrected for invert sugar.

Correct for the dilution by the clarifying reagent, which gives the correct total sugar expressed as sucrose in pounds per 100 gallons at the temperature of the reading (or in grams per 100 ml., depending upon the method of calculation that has been employed).

To calculate to pounds per 100 gallons or grams per 100 ml. at another temperature, multiply the result by S_2/S_1 where

$$S_2 = \text{specific gravity } \frac{(\text{at temperature desired, } ^\circ\text{ C.})}{(4^\circ\text{ C.})}$$

$$\text{and} \qquad S_1 = \text{specific gravity } \frac{(25^\circ\text{ C.})}{(4^\circ\text{ C.})}$$

PICKLES MADE FROM GRANULATED SUGAR. Polarize the sample direct without clarification. The corrections and calculations are the same as for raw-sugar pickles, except that the corrections under "granulated sugar" in Table II should be used, and there is no adjustment for dilution by the clarifying agent.

In case a sugar is employed known to contain invert sugar in significantly different amount than the values assumed here (1.5 per cent for raw sugar and 0.5 per cent for granulated sugar) the following formula may be used to obtain the correct factor to add.

If results are expressed as pounds per 100 gallons:

$$\frac{\text{Pounds of sucrose per 100 gallons at } 25^\circ\text{ C. (uncorrected)} \times 100}{\text{Reading when 25 grams of sugar are made to 100 ml. at } 25^\circ\text{ C.}^1} - \text{pounds of sucrose per 100 gallons at } 25^\circ\text{ C. (uncorrected)}$$

If results are expressed as grams per 100 ml.:

$$\frac{\text{Grams of sucrose per 100 ml. at } 25^\circ\text{ C. (uncorrected)} \times 100}{\text{Reading when 25 grams of sugar are made to 100 ml. at } 25^\circ\text{ C.}^1} - \text{grams of sucrose per 100 ml. at } 25^\circ\text{ C. (uncorrected)}$$

(26 grams of sucrose will read 99.85° V. at 25° C., the value dropping 0.03° for each ° C. above 20° C., *2.*)

Dry-Curing Mixtures

A solution of satisfactory sugar concentration is prepared from the sample and polarized directly in a 200-mm. tube at 25° C., when granulated sugar is used.

CALCULATION. Sucrose (in pounds per 100 gallons at 25° C. = reading × 2.1735 or, sucrose (in grams per 100 ml. at 25° C.) = reading × 0.2604.

Apply Table II under "granulated sugar" for the invert sugar correction, adding it to the sucrose obtained above.

Apply Table III for the sodium chloride concentration correction (the concentration of sodium chloride in the solution of dry-curing mixture must be determined in pounds per 100 gallons) and add this to the sucrose corrected for invert sugar.

Then the percentage of total sugar as sucrose equals:

$$\frac{\text{Corrected total sugar (in pounds per 100 gallons at } 25^\circ\text{ C.)} \times \text{volume of solution prepared (in ml.)}}{8.344 \times \text{weight of dry-curing mixture made to volume (in grams)}}$$

or

$$\frac{\text{Corrected total sugar (in grams per 100 ml. at } 25^\circ\text{ C.)} \times \text{volume of solution prepared (in ml.)}}{\text{Weight of dry-curing mixture made to volume (in grams)}}$$

If raw sugar is used, the same procedure applies, except that a clarifying agent is employed with subsequent filtration. Add the clarifying agent to the flask before making up to volume, thus avoiding the correction for dilution which is necessary with pickles. In the calculations, apply the raw sugar correction for invert sugar.

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[1] Equals: $\frac{(\%\text{ of sucrose} \times 99.85)}{100} + \frac{(\%\text{ of invert sugar} \times -27.50)}{100}$

The Effect of Phosphate on the Determination of Tungsten

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IT HAS long been recognized that phosphates interfere with the quantitative determination of tungsten, yet very little work has been conducted to determine the cause and the extent of that interference. It has generally been conceived as due to the formation of a phosphotungstic acid complex; the extent of that interference is virtually unknown. Hutchin (*1*, *3*) concluded that phosphates do not interfere with the determination of tungsten by the cinchonine method; but Hillebrand and Lundell (*2*) give four analyses, the results of which would indicate that phosphates cause low results in the determination of tungsten by the acid precipitation method and high results when the cinchonine method is used. Aside from these five analyses, no other relevant quantitative data were found in the literature.

The present work was therefore undertaken in order to ascertain the extent, and, if possible, the cause of the interference of phosphate in the quantitative determination of tungsten by the acid precipitation and by the cinchonine precipitation procedures. The method of attack consisted essentially of adding increments of phosphate solution to a fixed amount of a sodium tungstate solution and determining the tungsten trioxide by the two methods, standard procedures being followed.

Preparation and Standardization of Solutions

SODIUM TUNGSTATE. A solution of this salt was prepared containing approximately 0.1000 gram of WO_3 per 40 ml., and was standardized by the cinchonine method (*5*) and by the benzidine method of von Knorre (*4*).

DISODIUM HYDROGEN PHOSPHATE. A stock solution of this salt was prepared which contained 0.2980 gram of P_2O_5 per 40.00 ml. Its concentration was determined by precipitation of

$MgNH_4PO_4 \cdot 6H_2O$, ignition to $Mg_2P_2O_7$, and calculation of the results to P_2O_5. The solution was diluted for use.

Cinchonine Reagent. Fifty grams of cinchonine were dissolved in 400 ml. of 6 *N* hydrochloric acid and the solution was filtered before use.

Acid Precipitation Procedure

To 40.00 ml. of the standardized tungstate solution contained in a 250-ml. beaker a definite amount of the phosphate solution was added. The solution was brought nearly to boiling on a hot plate, and 40 ml. of concentrated hydrochloric acid and 15 ml. of concentrated nitric acid were added. The solution was boiled down to a volume of 50 ml., 5 ml. of concentrated nitric acid were added, and the solution was further evaporated to a volume of 10 ml. It was then made up to 150 ml. with hot water, allowed to simmer for half an hour, and left to stand in the cold overnight.

The precipitated tungsten trioxide was filtered with the aid of filter pulp (made by digesting ashless filter paper with concentrated hydrochloric acid and diluting with water), washed with dilute hydrochloric acid (1 to 19), dried, and ignited at 800° ± 10° C. in an electric muffle furnace to constant weight. Determinations were made in triplicate.

Table I. Effect of Phosphate on Precipitation of Tungsten by Acid

(WO_3 present in all solutions, 0.1003 gram)

	WO_3 Precipitated				
	By HCl-HNO_3				
P_2O_5				Av.	By $HClO_4$
Mg.	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.37	0.0948	0.0947	0.0936	0.0944	0.0891
0.75	0.0902	0.0900	0.0904	0.0902	0.0769
1.45	0.0822	0.0818	0.0837	0.0826	0.0605
2.24	0.0743	0.0743	0.0772	0.0752	0.0356
2.98	0.0687	0.0689	0.0700	0.0692	0.0244
4.47	0.0568	0.0584	0.0592	0.0581	0.0202
5.96	0.0523	0.0528	0.0512	0.0523	0.0173
7.45	0.0476	0.0479	0.0459	0.0472	0.0150
8.94	0.0409	0.0440	0.0469	0.0439	....
10.4	0.0333	0.0363	0.0364	0.0354	....
11.9	0.0332	0.0334	0.0367	0.0344	....
13.4	0.0295	0.0309	0.0347	0.0317	....
14.9	0.0307	0.0360	0.0268	0.0312	....
16.4	0.0413	0.0322	0.0129	0.0288	....
17.9	0.0211	0.0374	0.0151	0.0245	....

Because of the recent widespread use of perchloric acid as an oxidizing acid of low volatility, and more particularly because of certain discrepancies which arose in the use of the hydrochloric-nitric acid procedure with the higher amounts of added phosphate, it was decided to try the effect of 15 ml. of perchloric acid in place of the hydrochloric-nitric acid mixture. One determination using the perchloric acid modification was carried out along with the triplicates by the hydrochloric-nitric acid method. Results are recorded in Table I and plotted in Figure 1.

In the absence of phosphate, the use of perchloric acid in place of the usual hydrochloric-nitric acid mixture in the acid precipitation method results in complete precipitation of the tungsten, as is shown by Table II, which represents a typical standardization of tungstate solution.

Table II. Effectiveness of Perchloric Acid in Tungstate Standardization

(WO_3 present in all solutions, 0.1003 gram)

WO_3 Precipitated		
Cinchonine method	Benzidine method	$HClO_4$ method
Gram	*Gram*	*Gram*
0.1005	0.1001	0.1002
0.1003	0.1001	0.1002
0.1002	0.1000	0.1004
0.1005	0.1002	....
Av. 0.1004	0.1001	0.1003

The use of perchloric acid in the standardization procedure obviates the annoying characteristic of the tungsten trioxide precipitate to cling tenaciously to the sides of the beaker, a tendency which is so noticeable in the hydrochloric-nitric acid treatment. The possibility of the solutions evaporating to complete dryness and baking is practically eliminated, and the tungsten trioxide is precipitated in a form which is easily filtered. The use of perchloric acid in place of the hydrochloric-nitric acid mixture is therefore highly recommended.

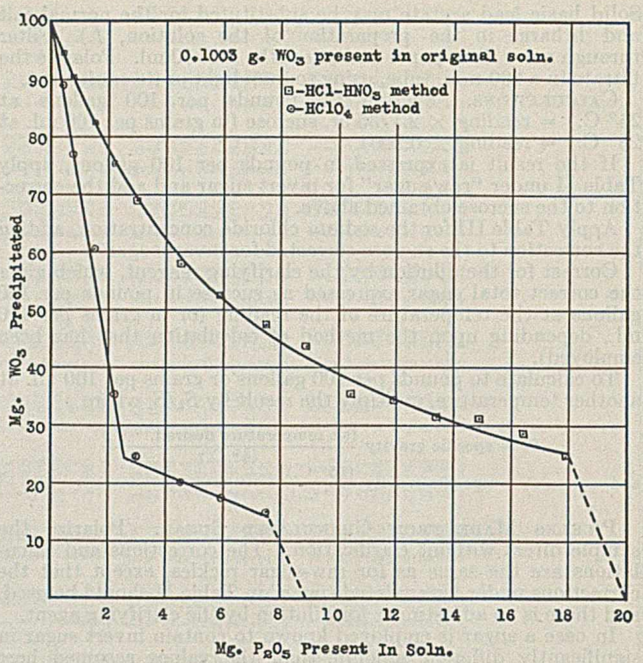

Figure 1. Effect of Phosphate on Determination of Tungsten by Acid Precipitation Method

Cinchonine Method

The cinchonine method was similar to the acid precipitation procedure, but with the addition of 10 ml. of cinchonine reagent after the dilution to 150 ml. The precipitate upon the filter was washed with a hot cinchonine wash solution prepared by diluting 30 ml. of cinchonine reagent and 30 ml. of concentrated hydrochloric acid to 1 liter with water. In the cinchonine method, increasing amounts of phosphate solution caused decreasing amounts of tungsten trioxide to be precipitated by the acid digestion treatment, but the addition of the cinchonine produced a copious white precipitate, later found to be cinchonine phosphotungstate. Solutions containing phosphate equivalent to 20 mg. or more of P_2O_5 formed no tungsten trioxide precipitate by the acid digestion treatment, but the addition of cinchonine produced copious precipitation. In view of this fact, the acid digestion procedure was omitted with solutions containing more than 20 mg. of phosphorus pentoxide. (Where the acid digestion was omitted, 3.5 ml. of concentrated nitric acid were added to the original solution, which, with the 60 milliequivalents of H^+ included with the cinchonine reagent, then contained 118 milliequivalents of H^+. This acidity was previously determined to be present in the final filtrate of solutions carried out by the acid precipitation method. It was thought best to make the acidity the same in the two methods.)

The results of determinations by this method appear in Table III.

Because of the consistency of the high results obtained with 20 mg. or more of phosphorus pentoxide, it was felt that there was being precipitated a cinchonine phosphotungstate, which on ignition yielded one of the phosphotungstic anhydrides. On the assumption that the ignited residue contained all the original tungsten trioxide, and that the excess in weight was due to phosphorus pentoxide, the composition of the residue was calculated to correspond to that of the anhydride of one of the well-known phosphotungstic acids, $P_2O_5 \cdot 24WO_3 \cdot nH_2O$.

Further evidence of the truth of this assumption was obtained by precipitating the tungsten trioxide by the cinchonine procedure from a solution containing one and one-half times the amount of tungsten trioxide previously used, together with a sufficient quantity of phosphorus pentoxide. Thus, with 0.1497 gram of tungsten trioxide present in the original solution, together with 0.0569 gram of phosphorus pentoxide, the average of three determinations gave 0.1535 ± 0.0002 gram of residue. This checks with the theoretical yield of 0.1535 gram calculated on the assumption that the composition of the residue is $P_2O_5 \cdot 24WO_3$.

TABLE III. EFFECT OF PHOSPHATE ON PRECIPITATION OF TUNGSTEN BY CINCHONINE

(WO_3 present in all solutions, 0.0998 gram)

P_2O_5	Weight of Residue			
				Av.
Mg.	*Gram*	*Gram*	*Gram*	*Gram*
3.0	0.1003	0.1007	0.1005	0.1005
6.0	0.1008	0.1011	0.1011	0.1010
10.0	0.1014	0.1015	0.1015	0.1015
15.0	0.1017	0.1015	0.1016	0.1016
20.0	0.1024	0.1023	0.1025	0.1024
37.3	0.1023	0.1024	0.1022	0.1023
55.9	0.1016	0.1025	0.1023	0.1021
74.5	0.1020	0.1020	0.1023	0.1021
93.1	0.1019	0.1023	0.1025	0.1024
120.0	0.1016	0.1020	0.1023	0.1020
149.0	0.1018	0.1019	0.1036	0.1024
447.0	0.1025	0.1028	0.1030	0.1027

To prove further the composition of the residue, analyses for phosphorus pentoxide and for tungsten trioxide were carried out on samples prepared from the ignited residues of the precipitates obtained by the cinchonine precipitation from solutions containing 0.6 gram of WO_3 and 0.3 gram of P_2O_5. A number of such precipitations and ignitions yielded a combined residue of 4.46 grams.

The phosphorus pentoxide was determined by fusion of portions of the residue with anhydrous sodium carbonate in a nickel crucible, leaching with acidified water, boiling, precipitating with magnesia mixture in the presence of tartaric acid, and subsequent ignition to $Mg_2P_2O_7$. The results are given in Table IV.

TABLE IV. ANALYSIS OF RESIDUE FOR P_2O_5

Weight of Sample	Weight of $Mg_2P_2O_7$	Weight of P_2O_5	
		Observed	Calcd. for $P_2O_5 \cdot 24WO_3$
Gram	*Gram*	*Gram*	*Gram*
0.4930	0.0194	0.0124	0.0123
0.5211	0.0197	0.0126	0.0130
0.5095	0.0199	0.0127	0.0127
0.5171	0.0200	0.0128	0.0129
	Av.	0.0126	0.0127

Two further samples were taken and both the phosphorus pentoxide content and the tungsten trioxide content were determined. Each sample was fused and the phosphorus pentoxide determined as before. The filtrate from the phosphorus pentoxide determination was diluted to 500 ml. in a volumetric flask and tungsten was determined in a 100-ml. aliquot by the benzidine method of von Knorre (*4*). The results are given in Table V.

TABLE V. ANALYSIS OF RESIDUE

Weight of Sample	Weight of $Mg_2P_2O_7$	Weight of P_2O_5		Weight of WO_3	
		Observed	Calcd. for $P_2O_5 \cdot 24WO_3$	Observed	Calcd. for $P_2O_5 \cdot 24WO_3$
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.5543	0.0214	0.0137	0.0138	....	....
0.1109	....	....	....	0.1078	0.1081
0.5778	0.0227	0.0145	0.0144	....	....
0.1156	....	.....	....	0.1125	0.1127

TABLE VI. COMPOSITION OF RESIDUE

(0.0998 gram of WO_3 present in original solutions)

P_2O_5	WO_3 Pptd.	WO_3 in Soln.	$P_2O_5 \cdot 24WO_3$ Equivalent to WO_3 in Soln.	Weight of Residue Calcd. as WO_3 Plus $P_2O_5 \cdot 24WO_3$	Actual Weight of Residue
Mg.	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
3.0	0.0692	0.0306	0.0314	0.1006	0.1005
6.0	0.0523	0.0475	0.0487	0.1010	0.1010
10.0	0.0377	0.0621	0.0636	0.1013	0.1015
15.0	0.0312	0.0686	0.0703	0.1015	0.1016

The composition of the residue having been ascertained, attention was directed to the results obtained in the cinchonine procedure, where relatively small amounts of phosphate (< 20 mg. of P_2O_5) were present. In this range, experiment showed some precipitation of tungsten trioxide by the acid digestion procedure, followed by the formation of an additional precipitate by cinchonine. It was felt that the residues obtained were a mixture of WO_3 and $P_2O_5 \cdot 24WO_3$. To show this, the amounts of tungsten trioxide present in a series of ignited precipitates were determined from Table I. The tungsten trioxide held in solution was then assumed to be precipitated as the phosphotungstate by the addition of the cinchonine, and the corresponding weight of $P_2O_5 \cdot 24WO_3$ was then calculated. The results are shown in Table VI.

The close agreement of the actual and calculated values for weights of the residues indicates the validity of the assumption of the composition of the residue in the range of phosphate concentration employed.

Discussion

Examination of the results obtained by the acid precipitation method yields two facts, one of practical importance, the other of theoretical interest. It is evident, in the first place, from both Table I and Figure 1, that the acid precipitation method for the determination of tungsten leads to low results in the presence of even small amounts of phosphate, and that the error increases with increasing amounts of phosphate. The second point of interest lies in the failure to obtain check results with solutions containing relatively large amounts of phosphate. This was attributed to the probable formation of some paratungstate in the highly acidified, hot phosphate-tungstate solution, the paratungstate not being decomposed by acids as are normal tungstates. The presence of the phosphate retards the tungsten trioxide precipitation and, therefore, allows time for paratungstate formation.

In the cinchonine method, any amount of phosphate causes high results. Increasing amounts of phosphate up to about 20 mg. of P_2O_5 per 100 mg. of WO_3 give increasing weights of residue, because of the precipitation of a decreasing amount of tungsten trioxide and a correspondingly increasing amount of the cinchonine phosphotungstate. Amounts of phosphate greater than 20 mg. of P_2O_5 per 100 mg. of WO_3 give uniform but high results because of the precipitation of only cinchonine phosphotungstate, the ignition of which yields $P_2O_5 \cdot 24WO_3$.

Summary

The acid precipitation method for the determination of tungsten is unreliable in the presence of even small amounts of phosphate.

An explanation for the erratic results obtained in a series of triplicate determinations has been attributed to the formation of paratungstate under the experimental conditions.

Increasing amounts of phosphate up to about 20 mg. of P_2O_5 per 100 mg. of WO_3 give increasingly higher results in the determination of tungsten by the cinchonine method.

Amounts of phosphate greater than about 20 mg. of P_2O_5 per 100 mg. of WO_3 cause uniform but high results in the cinchonine procedure. This has been shown to be due to the precipitation of a cinchonine phosphotungstate, the ignition of which leaves a residue of the formula $P_2O_5 \cdot 24WO_3$.

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Determination of Total Reducing Sugars and of Dextrose and Levulose in Cane Molasses

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THE work previously reported on the determination of dextrose and levulose in raw sugars (*9*, *10*) has been extended to the analysis of cane molasses, the same principles being applied. However, the Munson and Walker method was selected for the determination of the total reducing sugars, in place of the Lane and Eynon method, because the former method is used almost exclusively in this country for trade analyses of molasses, is the official method of the U. S. Treasury Department, and has been adopted tentatively also by the International Commission for Uniform Methods of Sugar Analysis (*4*). The present Munson and Walker tables give only invert sugar in the presence of sucrose, and it was therefore necessary first to establish a table for dextrose and for levulose, separately, in the presence of sucrose, at a total sugar concentration of 0.4 gram in 50 ml. of solution. The pure dextrose and levulose used for this purpose were obtained from the National Bureau of Standards, the moisture being first removed by careful drying at low temperature *in vacuo*.

Twenty different weights of dextrose and of levulose, ranging from 20 to 228 mg., plus the required amount of pure sucrose, were used for the fundamental data, and also thirteen different weights of mixtures of equal parts of dextrose and levulose, plus sucrose, in order to compare the results with those obtained by Munson and Walker with invert sugar prepared from sucrose. The copper was weighed as cupric oxide, a method which is recognized as one of the most accurate when no impurities are present besides the sugars (*1*).

The method of least squares, applied to the fundamental data by Louis Sattler, of this laboratory, gave the following equations, where D, L, I, and CuO signify milligrams of dextrose, levulose, invert sugar, and cupric oxide, respectively:

$$D = 0.38476\,CuO + 0.00009436\,CuO^2 - 3.177$$
$$L = 0.4305\,CuO + 0.0000611\,CuO^2 - 3.412$$
$$I = 0.40016\,CuO + 0.00009631\,CuO^2 - 2.9911$$

The milligrams of invert sugar corresponding to given quantities of cupric oxide were found to be slightly different from those given by Munson and Walker, as may be noted from Table I.

TABLE I. DETERMINATION OF INVERT SUGAR

CuO	Invert Sugar M. and W.	Invert Sugar E. and Z.
Mg.	*Mg.*	*Mg.*
50	17.5	17.3
100	38.1	38.0
150	59.2	59.2
200	80.7	80.9
250	102.7	103.1
300	125.0	125.7
350	147.9	148.9
400	171.4	172.5
450	195.5	196.6
500	220.1	221.2

Below 150 mg. of cupric oxide the invert sugar figures of the writers are a little lower than those of Munson and Walker, but above that point the values found by the writers become increasingly larger than those given by Munson and Walker. The complete table (Table V) based on the experiments of the writers has been arranged in a form somewhat different from that usually employed, to facilitate its use for the particular purpose in hand.

The method of Jackson and Mathews (*5*) was used, as heretofore, to determine the apparent levulose. In order to find dextrose, D, and levulose, L, the total reducing sugars, R_1, and the apparent levulose, R_2, are expressed as mg. of levulose, and the following formulas are used for the calculation:

$$aD + L = R_1$$
$$0.081D + L = R_2$$

where a is the variable reducing ratio of dextrose to levulose for the Munson and Walker method, found from Table V for all possible proportions between dextrose and levulose; and 0.081 is the constant reducing ratio of dextrose to levulose in the method of Jackson and Mathews.

Solving for D and L:

$$D = \frac{R_1 - R_2}{a - 0.081}$$

$$L = R_1 - aD$$

The results are calculated by a series of approximations. In the first calculation the value of a is taken from the column for invert sugar (50 D, 50 L) in Table V. If the result shows a different ratio of dextrose to levulose, a second calculation is made with the value of a corresponding to that ratio. A third approximation is usually unnecessary.

TABLE II. CHECK ANALYSES WITH KNOWN MIXTURES OF DEXTROSE, LEVULOSE, AND SUCROSE

No.	Sucrose Taken	Dextrose Taken	Dextrose Found	Levulose Taken	Levulose Found
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	320.0	56.0	56.3	24.0	23.5
2	320.0	32.0	30.6	48.0	48.4
3	280.0	84.0	83.0	36.0	36.2
4	280.0	48.0	47.4	72.0	71.5
5	240.0	112.0	113.9	48.0	48.3
6	240.0	64.0	61.4	96.0	97.1
7	200.0	140.0	137.3	60.0	60.8
8	320.0	40.0	41.0	40.0	38.4
9	240.0	80.0	80.3	80.0	79.9
10	200.0	100.0	102.1	100.0	98.7
Av.	...	75.6	75.3	60.4	60.3

This method was tested by analyzing a number of sugar mixtures containing known proportions of dextrose, levulose, and sucrose. In these analyses the copper was not determined gravimetrically, however, because the method is to be used for the analysis of low-purity products like molasses, in which case the copper precipitate is always contaminated with organic and mineral impurities, and consequently too high results are apt to be obtained by weighing in the form of cupric oxide. Although the organic impurities can be removed by ignition to cupric oxide, the mineral matter cannot. Reduction of the cupric oxide to metallic copper, by means of hydrogen or alcohol vapors, as described in the U. S. Treasury method, does not obviate this difficulty, because the mineral impurities still remain with the copper. This has been shown by Meade (*6*) who reports that the copper calculated from the cupric oxide usually checks with the copper reduced by alcohol vapor within a fraction of a milligram, which is well within the permissible difference between duplicate determinations as either oxide or metal. This observation has been fully confirmed in this laboratory.

For the reasons indicated it was decided to determine the copper in the precipitate by a volumetric method, and the widely used ferric sulfate–permanganate method was chosen for this purpose. The voluminous literature on this subject will not be reviewed in detail, but attention is called to the work of Schoorl and Regenbogen (*8*) and of Bruhns (*3*). These authors found that the low results usually obtained with the permanganate method are caused by reoxidation of the ferrous sulfate when the cuprous oxide is dissolved in a mixture of ferric sulfate and sulfuric acid. If, however, the cuprous oxide is first dissolved in ferric sulfate or ferric alum solution, and the sulfuric acid not added until immediately before the titration with permanganate, correct results are obtained. The writers have therefore adopted the method as modified by Pick (*7*). The end point of the permanganate titration can be fixed more sharply by the use of phenanthroline indicator. The ferric sulfate–permanganate method in the modified form has given very satisfactory results in this laboratory.

The results of the check analyses made by the combined method as described are shown in Table II.

Considering that the method is an indirect one, and that the experimental errors in both determinations are reflected in the final figures, the results are satisfactory.

TABLE III. ANALYSES OF MOLASSES AND SIRUPS

No.	Source	Combined Method: Total reducing sugars	Combined Method: Dextrose in reducing sugars	Reducing Sugars as Invert Sugar: Old M. and W. Table: Gravimetric	Old M. and W. Table: Volumetric	New M. and W. Table: Gravimetric	New M. and W. Table: Volumetric	$\frac{S-P}{I}$
		%	%	%	%	%	%	
		Raw Sugar Blackstraps						
10	Cuba	12.31	29.3	12.38	12.06	12.43	12.11	0.569
18	Cuba	15.84	33.2	15.73	15.54	15.81	15.63	0.630
26	Cuba	10.96	26.1	10.80	10.69	10.83	10.72	0.753
2	Puerto Rico	24.41	48.0	25.03	24.18	25.20	24.31	0.218
4	Puerto Rico	20.11	40.0	19.74	19.86	19.81	19.99	0.458
15	Puerto Rico	21.81	40.3	22.34	21.54	22.49	21.67	0.354
1	Sto. Domingo	14.43	35.5	14.25	14.20	14.31	14.26	0.532
3	Sto. Domingo	23.12	47.3	22.87	22.95	23.02	23.10	0.312
11	Sto. Domingo	14.45	29.3	14.08	14.20	14.14	14.26	0.692
14	India	16.61	49.2	17.00	16.53	17.11	16.62	0.253
23	Java	21.05	48.8	21.21	20.93	21.34	21.07	0.269
16	Philippines	22.81	59.3	...	22.85	...	22.99	0.348
	Av.	...	40.5	...	...	...	...	0.447
Av., omitting No. 16		17.74	..	17.77	17.53	17.86	17.61	...
		High-Test Molasses						
6	Cuba	56.60	49.8	56.71	56.29	57.04	56.60	0.273
7	Cuba	42.91	50.7	42.46	42.74	42.71	43.00	0.268
8	Cuba	58.51	48.1	58.17	58.13	58.51	58.47	0.307
9	Cuba	58.71	48.5	58.49	58.37	58.83	58.70	0.351
12	Cuba	62.27	55.2	61.40	62.12	61.70	62.53	0.230
17	Cuba	41.63	51.7	41.06	41.48	41.34	41.74	0.253
5	Barbados	31.51	53.2	31.49	31.51	31.63	31.66	0.299
	Av.	50.31	51.0	49.97	50.09	50.25	50.39	0.273
		Refinery Blackstraps						
19		18.75	55.0	...	18.73	...	18.86	...
20		21.50	56.2	...	21.50	...	21.63	...
22		26.84	56.7	...	26.84	...	26.98	...
24		23.39	55.5	...	23.37	...	23.50	...
	Av.	22.62	55.8	...	22.61	...	22.74	...
		Refinery Filtered Sirups						
21		19.57	57.4	...	19.60	...	19.73	...
23		23.69	58.9	...	23.73	...	23.87	...
25		28.55	57.1	...	28.55	...	28.72	...
	Av.	23.94	57.8	...	23.96	...	24.11	...

The new method was next applied to the analysis of molasses and sirups from various sources, with the results shown in Table III. The third column in this table gives the percentage of total reducing sugars (dextrose plus levulose), and the fourth the percentage of dextrose in the reducing sugars. It is noted that in the raw sugar blackstraps, with the exception of No. 16, this percentage is below 50, and in some cases much lower; the average figure is 40.5. The average for the high-test molasses (partially inverted sirups) is much higher, 51.0, although in some individual cases it runs below 50. This would indicate that the acid inversion process in the factory tends to destroy some of the levulose, as would be expected. In order to prove this definitely, however, it would be necessary to determine dextrose and levulose in the sirup before and after it is inverted in the manufacturing process.

TABLE IV. COMPARISON BETWEEN MUNSON AND WALKER GRAVIMETRIC METHOD AND LANE AND EYNON VOLUMETRIC METHOD

No	Reducing Sugars as Invert Sugar: Method and table of Munson and Walker	Reducing Sugars as Invert Sugar: Method of Lane and Eynon
	%	%
	Raw Sugar Blackstraps	
27	19.90	19.74
28	16.39	15.68
29	23.22	22.52
30	17.59	17.24
31	12.17	12.09
33	17.59	17.24
34	19.48	19 07
35	15.61	15.31
39	18.72	18.72
40	19.23	19.25
41	18.29	18.13
46	18.87	18.83
47	22.21	20.78
48	20.13	19.74
	Av. 18.53	18.17
	High-Test Molasses	
32	30.07	29.48
36	32.75	32.86
37	55.64	55.00
38	46.36	46.30
42	50.00	48.58
43	49.08	49.50
44	49.31	49.30
45	66.30	65.20
49	53.50	55.80
50	31.64	31.78
51	37.80	36.74
52	55.29	55 50
53	39.16	38.64
54	51.23	50.46
55	46.78	45.93
56	33.75	32.94
57	36.26	37.20
	Av. 44.99	44.78

An idea of the proportion between dextrose and levulose may be gained also from Browne's "polarizing constant" (*2*), which is the ratio of $S - P$ to R, where S is the sucrose determined by the optical method with invertase, P the direct polarization, and R the total reducing sugars, usually expressed as invert sugar. The raw sugar blackstraps and high-test molasses listed in Table III, excepting No. 16, had been received by this laboratory for routine trade analyses, and the sucrose determinations were therefore made by the U. S. Treasury method and not by the invertase method. For this reason the polarizing constants shown in the last column of Table III are only approximate, but they are nevertheless useful for a comparison with the ratio of dextrose to total reducing sugars, given in column 3. A polarizing constant of about 0.3 denotes equal parts of dextrose and levulose; when the levulose is higher than the dextrose the polarizing constant rises above 0.3, and it decreases below 0.3 when the dextrose is higher than the levulose. The figures in the last column of the table show that most of the blackstraps have a polarizing constant above 0.3, with an average of 0.447, while in the high-test molasses the constant is in most cases below 0.3, with an average of 0.273, thus confirming the results obtained by the combined reduction method as to the ratio between dextrose and levulose.

The refinery blackstraps and filtered sirups were analyzed only by the combined reduction method. The blackstraps show a distinct excess of dextrose over levulose, and the filtered sirups a still greater one. This corroborates the general observation that levulose is removed in the refinery process, particularly by treatment with bone black.

Table V. Milligrams of Levulose Corresponding to Milligrams of Cupric Oxide or Copper, and Reducing Ratios *a*

For varying proportions of dextrose and levulose in presence of sucrose (0.4 gram of total sugars in 50 ml. of solution), by Munson and Walker method

CuO	Cu	Levulose	Reducing Ratio, *a*, for Varying Proportions between *D* and *L*									
	Milligrams		100 *D* 0 *L*	90 *D* 10 *L*	80 *D* 20 *L*	70 *D* 30 *L*	60 *D* 40 *L*	50 *D* 50 *L*	40 *D* 60 *L*	30 *D* 70 *L*	20 *D* 80 *L*	10 *D* 90 *L*
50	39.9	18.3	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.126	1.125	1.124
52	41.5	19.1	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.126	1.125	1.124
54	43.1	20.0	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.126	1.125	1.124
56	44.7	20.9	1.118	1.120	1.122	1.124	1.126	1.128	1.127	1.126	1.125	1.124
58	46.3	21.7	1.118	1.120	1.122	1.124	1.126	1.128	1.127	1.126	1.125	1.124
60	47.9	22.6	1.118	1.120	1.122	1.124	1.126	1.128	1.127	1.126	1.125	1.124
62	49.5	23.5	1.117	1.120	1.122	1.124	1.126	1.128	1.127	1.126	1.125	1.124
64	51.1	24.3	1.117	1.120	1.122	1.124	1.126	1.128	1.127	1.126	1.125	1.124
66	52.7	25.2	1.116	1.119	1.121	1.124	1.126	1.128	1.127	1.126	1.125	1.124
68	54.3	26.1	1.116	1.119	1.121	1.124	1.126	1.128	1.127	1.126	1.125	1.124
70	55.9	27.0	1.116	1.119	1.121	1.124	1.126	1.128	1.127	1.126	1.125	1.124
72	57.5	27.9	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.125	1.125	1.124
74	59.1	28.7	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.125	1.125	1.124
76	60.7	29.6	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.125	1.125	1.124
78	62.3	30.5	1.114	1.117	1.119	1.122	1.125	1.127	1.126	1.125	1.125	1.124
80	63.9	31.4	1.114	1.117	1.119	1.122	1.125	1.127	1.126	1.125	1.125	1.124
82	65.6	32.3	1.113	1.116	1.118	1.121	1.124	1.127	1.126	1.125	1.125	1.124
84	67.1	33.2	1.113	1.116	1.118	1.121	1.124	1.126	1.126	1.125	1.125	1.124
86	68.7	34.1	1.112	1.115	1.117	1.120	1.123	1.126	1.126	1.125	1.125	1.124
88	70.3	35.0	1.112	1.115	1.117	1.120	1.123	1.126	1.126	1.125	1.125	1.124
90	71.9	35.8	1.112	1.115	1.117	1.120	1.123	1.126	1.126	1.125	1.125	1.124
92	73.5	36.7	1.111	1.114	1.117	1.120	1.123	1.126	1.126	1.125	1.125	1.124
94	75.1	37.6	1.111	1.114	1.117	1.120	1.123	1.126	1.126	1.125	1.125	1.124
96	76.7	38.4	1.111	1.114	1.117	1.120	1.123	1.125	1.125	1.125	1.125	1.124
98	78.3	39.3	1.111	1.114	1.117	1.120	1.123	1.125	1.125	1.125	1.125	1.124
100	79.9	40.2	1.111	1.114	1.117	1.120	1.123	1.125	1.125	1.125	1.125	1.124
102	81.5	41.1	1.111	1.114	1.117	1.120	1.123	1.125	1.125	1.125	1.124	1.124
104	83.1	42.0	1.110	1.113	1.116	1.119	1.122	1.125	1.125	1.125	1.124	1.124
106	84.7	42.9	1.110	1.113	1.116	1.119	1.122	1.125	1.125	1.125	1.124	1.124
108	86.3	43.8	1.110	1.113	1.116	1.119	1.122	1.125	1.125	1.125	1.124	1.124
110	87.9	44.7	1.110	1.113	1.116	1.119	1.122	1.124	1.124	1.124	1.124	1.124
112	89.5	45.6	1.109	1.112	1.115	1.118	1.121	1.124	1.124	1.124	1.124	1.124
114	91.1	46.5	1.109	1.112	1.115	1.118	1.121	1.124	1.124	1.124	1.124	1.124
116	92.7	47.4	1.109	1.112	1.115	1.118	1.121	1.124	1.124	1.124	1.124	1.124
118	94.3	48.2	1.109	1.112	1.115	1.118	1.121	1.124	1.124	1.124	1.124	1.124
120	95.9	49.1	1.108	1.111	1.114	1.117	1.120	1.124	1.124	1.124	1.124	1.124
122	97.5	50.0	1.108	1.111	1.114	1.117	1.120	1.124	1.124	1.124	1.124	1.124
124	99.1	50.9	1.108	1.111	1.114	1.117	1.120	1.123	1.123	1.123	1.124	1.124
126	100.7	51.8	1.108	1.111	1.114	1.117	1.120	1.123	1.123	1.123	1.124	1.124
128	102.3	52.7	1.107	1.110	1.113	1.116	1.119	1.123	1.123	1.123	1.124	1.124
130	103.9	53.6	1.107	1.110	1.113	1.116	1.119	1.122	1.122	1.123	1.124	1.124
132	105.5	54.4	1.107	1.110	1.113	1.116	1.119	1.122	1.122	1.123	1.124	1.124
134	107.1	55.3	1.107	1.110	1.113	1.116	1.119	1.122	1.122	1.123	1.124	1.124
136	108.7	56.2	1.106	1.109	1.112	1.115	1.118	1.121	1.121	1.122	1.123	1.124
138	110.3	57.1	1.106	1.109	1.112	1.115	1.118	1.121	1.121	1.122	1.123	1.124
140	111.8	58.0	1.106	1.109	1.112	1.115	1.118	1.120	1.121	1.122	1.123	1.124
142	113.4	58.9	1.106	1.109	1.112	1.115	1.118	1.120	1.121	1.122	1.123	1.124
144	115.0	59.8	1.105	1.108	1.111	1.114	1.117	1.120	1.121	1.122	1.123	1.124
146	116.6	60.7	1.105	1.108	1.111	1.114	1.117	1.119	1.120	1.121	1.122	1.124
148	118.2	61.6	1.105	1.108	1.111	1.114	1.117	1.119	1.120	1.121	1.122	1.124
150	119.8	62.5	1.105	1.108	1.111	1.114	1.117	1.119	1.120	1.121	1.122	1.124
152	121.4	63.4	1.104	1.107	1.110	1.113	1.116	1.118	1.119	1.120	1.122	1.124
154	123.0	64.3	1.104	1.107	1.110	1.113	1.116	1.118	1.119	1.120	1.122	1.124
156	124.6	65.2	1.104	1.107	1.110	1.113	1.116	1.118	1.119	1.120	1.122	1.123
158	126.2	66.1	1.104	1.107	1.110	1.112	1.115	1.117	1.118	1.119	1.121	1.123
300	239.7	131.2	1.086	1.087	1.088	1.089	1.090	1.091	1.091	1.090	1.090	1.090
302	241.3	132.1	1.086	1.087	1.088	1.089	1.090	1.091	1.091	1.091	1.090	1.090
304	242.9	133.1	1.086	1.087	1.088	1.089	1.090	1.090	1.090	1.090	1.089	1.089
306	244.5	134.0	1.086	1.087	1.088	1.089	1.090	1.090	1.090	1.090	1.089	1.089
308	246.1	135.0	1.085	1.086	1.087	1.088	1.089	1.089	1.089	1.089	1.088	1.088
310	247.7	135.9	1.085	1.086	1.087	1.088	1.089	1.089	1.089	1.089	1.088	1.088
312	249.3	136.9	1.085	1.086	1.087	1.088	1.089	1.089	1.089	1.089	1.088	1.088
314	250.9	137.8	1.085	1.086	1.087	1.088	1.088	1.088	1.088	1.088	1.087	1.087
316	252.5	138.8	1.085	1.086	1.087	1.088	1.088	1.088	1.088	1.088	1.087	1.087
318	254.1	139.7	1.084	1.085	1.086	1.087	1.088	1.088	1.088	1.088	1.087	1.087
320	255.7	140.6	1.084	1.085	1.086	1.087	1.087	1.087	1.087	1.087	1.086	1.086
322	257.3	141.5	1.084	1.085	1.086	1.087	1.087	1.087	1.087	1.087	1.086	1.086
324	258.9	142.5	1.084	1.085	1.086	1.086	1.086	1.086	1.086	1.086	1.086	1.086
326	260.4	143.4	1.084	1.085	1.086	1.086	1.086	1.086	1.086	1.086	1.085	1.085
328	262.0	144.4	1.084	1.085	1.086	1.086	1.086	1.086	1.086	1.086	1.085	1.085
330	263.6	145.3	1.083	1.084	1.085	1.085	1.085	1.085	1.085	1.085	1.085	1.085
332	265.2	146.3	1.083	1.084	1.085	1.085	1.085	1.085	1.085	1.085	1.084	1.084
334	266.8	147.2	1.083	1.084	1.085	1.085	1.085	1.085	1.085	1.085	1.084	1.084
336	268.4	148.2	1.083	1.083	1.084	1.084	1.084	1.084	1.084	1.084	1.084	1.084
338	270.0	149.1	1.083	1.083	1.084	1.084	1.084	1.084	1.084	1.084	1.083	1.083
340	271.6	150.0	1.082	1.082	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083
342	273.2	151.0	1.082	1.082	1.083	1.083	1.083	1.083	1.083	1.083	1.083	1.083
344	274.8	151.9	1.082	1.082	1.083	1.083	1.083	1.083	1.083	1.083	1.082	1.082
346	276.4	152.9	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082
348	278.0	153.9	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082
350	279.6	154.8	1.081	1.081	1.082	1.082	1.082	1.082	1.082	1.082	1.081	1.081
352	281.2	155.7	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081
354	282.8	156.7	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081	1.081
356	284.4	157.6	1.081	1.081	1.081	1.080	1.080	1.080	1.080	1.080	1.080	1.080
358	286.0	158.6	1.081	1.081	1.080	1.080	1.080	1.080	1.080	1.080	1.080	1.080
360	287.6	159.5	1.081	1.081	1.080	1.080	1.080	1.080	1.080	1.080	1.080	1.080
362	289.2	160.5	1.080	1.080	1.080	1.080	1.079	1.079	1.079	1.079	1.079	1.079
364	290.8	161.4	1.080	1.080	1.080	1.080	1.079	1.079	1.079	1.079	1.079	1.079
366	292.4	162.4	1.080	1.080	1.080	1.079	1.079	1.079	1.079	1.079	1.079	1.079
368	294.0	163.3	1.080	1.080	1.079	1.079	1.078	1.078	1.078	1.078	1.078	1.078
370	295.6	164.3	1.080	1.080	1.079	1.079	1.078	1.078	1.078	1.078	1.078	1.078
372	297.2	165.2	1.079	1.079	1.079	1.078	1.077	1.077	1.077	1.078	1.078	1.078
374	298.8	166.2	1.079	1.079	1.078	1.077	1.077	1.077	1.077	1.077	1.077	1.077
376	300.4	167.1	1.079	1.079	1.078	1.078	1.077	1.077	1.077	1.077	1.077	1.077
378	302.0	168.1	1.079	1.079	1.078	1.077	1.077	1.076	1.076	1.077	1.077	1.077
380	303.6	169.0	1.079	1.079	1.078	1.077	1.076	1.076	1.076	1.076	1.076	1.076
382	305.2	170.0	1.078	1.078	1.077	1.076	1.076	1.076	1.076	1.076	1.075	1.075
384	306.8	170.9	1.078	1.078	1.077	1.076	1.076	1.075	1.075	1.075	1.075	1.075
386	308.4	171.9	1.078	1.078	1.077	1.076	1.076	1.075	1.075	1.075	1.075	1.075
388	310.0	172.8	1.078	1.078	1.077	1.076	1.076	1.075	1.075	1.075	1.074	1.074
390	311.6	173.8	1.078	1.078	1.077	1.076	1.075	1.074	1.074	1.074	1.074	1.074
392	313.2	174.7	1.078	1.078	1.077	1.076	1.075	1.074	1.074	1.074	1.074	1.074
394	314.8	175.7	1.077	1.077	1.077	1.076	1.075	1.074	1.074	1.074	1.073	1.073
396	316.4	176.6	1.077	1.077	1.076	1.075	1.074	1.073	1.073	1.073	1.073	1.073
398	318.0	177.6	1.077	1.077	1.076	1.075	1.074	1.073	1.073	1.073	1.073	1.073
400	319.6	178.6	1.077	1.077	1.076	1.075	1.074	1.073	1.073	1.073	1.072	1.072
402	321.2	179.5	1.077	1.076	1.075	1.074	1.073	1.072	1.072	1.072	1.072	1.072
404	322.8	180.5	1.076	1.076	1.075	1.074	1.073	1.072	1.072	1.072	1.072	1.072
406	324.4	181.5	1.076	1.075	1.074	1.073	1.072	1.071	1.071	1.071	1.071	1.071
408	326.0	182.4	1.076	1.075	1.074	1.073	1.072	1.071	1.071	1.071	1.071	1.071

160	127.8	67.0	1.103	1.106	1.109	1.112	1.115	1.117	1.118	1.119	1.121	1.122
162	129.4	67.9	1.103	1.106	1.109	1.112	1.115	1.116	1.118	1.119	1.120	1.122
164	131.0	68.8	1.103	1.106	1.109	1.112	1.115	1.116	1.118	1.119	1.120	1.122
166	132.6	69.7	1.103	1.106	1.109	1.112	1.115	1.116	1.118	1.119	1.120	1.121
168	134.2	70.6	1.102	1.105	1.108	1.111	1.113	1.115	1.117	1.119	1.120	1.121
170	135.8	71.5	1.102	1.105	1.108	1.111	1.113	1.115	1.117	1.118	1.119	1.120
172	137.4	72.4	1.102	1.105	1.108	1.111	1.113	1.115	1.117	1.118	1.119	1.120
174	139.0	73.3	1.102	1.105	1.107	1.110	1.112	1.114	1.116	1.117	1.118	1.119
176	140.6	74.2	1.101	1.104	1.107	1.110	1.112	1.114	1.116	1.117	1.118	1.119
178	141.2	75.1	1.101	1.104	1.107	1.110	1.112	1.114	1.116	1.117	1.118	1.119
180	143.8	76.1	1.101	1.104	1.106	1.109	1.111	1.113	1.115	1.116	1.117	1.118
182	145.4	77.0	1.101	1.104	1.106	1.109	1.111	1.113	1.115	1.116	1.117	1.118
184	146.0	77.9	1.100	1.103	1.105	1.108	1.110	1.112	1.114	1.115	1.116	1.117
186	147.6	78.8	1.100	1.103	1.105	1.108	1.110	1.112	1.114	1.115	1.116	1.117
188	149.2	79.7	1.100	1.103	1.105	1.108	1.110	1.112	1.114	1.115	1.116	1.117
190	151.8	80.6	1.100	1.102	1.104	1.106	1.108	1.111	1.113	1.114	1.115	1.116
192	153.4	81.5	1.099	1.102	1.104	1.106	1.108	1.111	1.113	1.114	1.115	1.116
194	155.0	82.4	1.099	1.102	1.104	1.106	1.108	1.111	1.112	1.113	1.114	1.115
196	156.6	83.3	1.099	1.102	1.104	1.106	1.108	1.110	1.112	1.113	1.114	1.115
198	158.2	84.2	1.099	1.102	1.104	1.106	1.108	1.110	1.111	1.112	1.113	1.114
200	159.8	85.1	1.098	1.101	1.103	1.106	1.108	1.110	1.111	1.112	1.113	1.114
202	161.4	86.0	1.098	1.100	1.102	1.104	1.106	1.109	1.110	1.111	1.112	1.113
204	163.0	86.9	1.098	1.100	1.102	1.104	1.106	1.109	1.110	1.111	1.112	1.113
206	164.6	87.8	1.098	1.100	1.102	1.104	1.106	1.108	1.110	1.111	1.112	1.113
208	166.2	88.7	1.098	1.100	1.102	1.104	1.106	1.108	1.109	1.110	1.111	1.112
210	167.8	89.7	1.097	1.099	1.101	1.103	1.105	1.108	1.109	1.110	1.111	1.112
212	169.4	90.6	1.097	1.099	1.101	1.103	1.105	1.107	1.108	1.109	1.110	1.111
214	171.0	91.5	1.097	1.099	1.101	1.103	1.105	1.107	1.108	1.109	1.110	1.111
216	172.6	92.4	1.097	1.098	1.100	1.102	1.104	1.106	1.107	1.108	1.109	1.110
218	174.2	93.3	1.096	1.098	1.100	1.102	1.104	1.106	1.107	1.108	1.109	1.110
220	175.8	94.3	1.096	1.098	1.100	1.102	1.104	1.106	1.107	1.108	1.109	1.110
222	177.4	95.2	1.096	1.097	1.099	1.101	1.103	1.105	1.106	1.107	1.108	1.109
224	179.0	96.1	1.096	1.097	1.099	1.101	1.103	1.105	1.106	1.107	1.108	1.109
226	180.6	97.0	1.095	1.097	1.099	1.101	1.103	1.105	1.106	1.107	1.108	1.108
228	182.2	97.9	1.095	1.097	1.099	1.101	1.103	1.104	1.105	1.106	1.107	1.108
230	183.8	98.8	1.095	1.097	1.099	1.101	1.103	1.104	1.105	1.106	1.107	1.107
232	185.3	99.7	1.095	1.097	1.099	1.101	1.103	1.104	1.105	1.106	1.107	1.107
234	186.9	100.6	1.095	1.097	1.099	1.101	1.102	1.103	1.104	1.105	1.106	1.106
236	188.5	101.5	1.094	1.096	1.098	1.100	1.102	1.103	1.104	1.105	1.106	1.106
238	190.1	102.4	1.094	1.096	1.098	1.100	1.101	1.102	1.103	1.104	1.105	1.105
240	191.7	103.4	1.094	1.096	1.098	1.100	1.101	1.102	1.103	1.104	1.105	1.105
242	193.3	104.3	1.094	1.096	1.098	1.100	1.101	1.102	1.103	1.104	1.104	1.104
244	194.9	105.2	1.093	1.095	1.097	1.099	1.100	1.101	1.102	1.103	1.104	1.104
246	196.5	106.1	1.093	1.095	1.097	1.099	1.100	1.101	1.102	1.103	1.104	1.104
248	198.1	107.0	1.093	1.095	1.097	1.099	1.100	1.101	1.102	1.103	1.104	1.103
250	199.7	108.0	1.093	1.095	1.097	1.098	1.099	1.100	1.101	1.102	1.103	1.103
252	201.3	108.9	1.092	1.094	1.096	1.098	1.099	1.100	1.100	1.101	1.102	1.102
254	202.9	109.8	1.092	1.094	1.096	1.098	1.099	1.100	1.100	1.101	1.102	1.102
256	204.5	110.8	1.092	1.094	1.096	1.097	1.098	1.099	1.099	1.100	1.101	1.101
258	206.1	111.7	1.092	1.094	1.096	1.097	1.098	1.099	1.099	1.100	1.101	1.101
260	207.7	112.7	1.091	1.093	1.095	1.096	1.097	1.098	1.098	1.099	1.100	1.100
262	209.3	113.6	1.091	1.093	1.095	1.096	1.097	1.098	1.098	1.099	1.100	1.100
264	210.9	114.5	1.091	1.093	1.095	1.096	1.097	1.098	1.099	1.099	1.099	1.099
266	212.5	115.5	1.091	1.092	1.094	1.095	1.096	1.097	1.098	1.099	1.099	1.099
268	214.1	116.4	1.090	1.092	1.094	1.095	1.096	1.097	1.097	1.098	1.098	1.098
270	215.7	117.3	1.090	1.092	1.094	1.095	1.096	1.097	1.097	1.098	1.098	1.098
272	217.3	118.2	1.090	1.092	1.093	1.094	1.095	1.096	1.096	1.097	1.097	1.097
274	218.9	119.1	1.090	1.092	1.093	1.094	1.095	1.096	1.096	1.097	1.097	1.097
276	220.5	120.0	1.089	1.091	1.092	1.093	1.094	1.095	1.095	1.096	1.096	1.096
278	222.1	121.0	1.089	1.091	1.092	1.093	1.094	1.095	1.095	1.096	1.096	1.096
280	223.7	121.9	1.089	1.091	1.092	1.093	1.094	1.095	1.095	1.095	1.095	1.095
282	225.3	122.9	1.089	1.090	1.091	1.092	1.093	1.094	1.094	1.095	1.095	1.095
284	226.9	123.8	1.088	1.090	1.091	1.092	1.093	1.094	1.094	1.094	1.094	1.094
286	228.5	124.8	1.088	1.090	1.091	1.092	1.093	1.094	1.094	1.094	1.094	1.094
288	230.1	125.7	1.088	1.089	1.090	1.091	1.092	1.093	1.093	1.093	1.093	1.093
290	231.7	126.6	1.088	1.089	1.090	1.091	1.092	1.093	1.093	1.093	1.093	1.093
292	233.3	127.5	1.087	1.089	1.090	1.091	1.092	1.093	1.093	1.093	1.092	1.092
294	234.9	128.5	1.087	1.088	1.089	1.090	1.091	1.092	1.092	1.092	1.092	1.092
296	236.5	129.4	1.087	1.088	1.089	1.090	1.091	1.092	1.092	1.092	1.091	1.091
298	238.1	130.3	1.087	1.088	1.089	1.090	1.091	1.091	1.091	1.091	1.091	1.091
410	327.6	183.4	1.076	1.075	1.074	1.073	1.072	1.071	1.071	1.071	1.071	1.071
412	329.2	184.4	1.076	1.075	1.074	1.073	1.072	1.070	1.070	1.070	1.070	1.070
414	330.8	185.3	1.075	1.074	1.073	1.072	1.071	1.070	1.070	1.070	1.070	1.070
416	332.3	186.3	1.075	1.074	1.073	1.072	1.071	1.070	1.070	1.070	1.070	1.070
418	333.9	187.3	1.075	1.074	1.072	1.071	1.070	1.069	1.069	1.069	1.069	1.069
420	335.5	188.2	1.075	1.074	1.072	1.071	1.070	1.069	1.069	1.069	1.069	1.069
422	337.1	189.2	1.075	1.074	1.072	1.071	1.070	1.069	1.069	1.069	1.069	1.069
424	338.7	190.2	1.074	1.073	1.071	1.070	1.069	1.068	1.068	1.068	1.068	1.068
426	340.3	191.1	1.074	1.073	1.071	1.070	1.069	1.068	1.068	1.068	1.068	1.068
428	341.9	192.1	1.074	1.073	1.071	1.070	1.069	1.068	1.068	1.068	1.067	1.067
430	343.5	193.1	1.074	1.073	1.071	1.069	1.068	1.067	1.067	1.067	1.067	1.067
432	345.1	194.0	1.074	1.073	1.071	1.069	1.068	1.067	1.067	1.066	1.066	1.066
434	346.7	195.0	1.073	1.072	1.070	1.069	1.068	1.067	1.067	1.066	1.066	1.066
436	348.3	196.0	1.073	1.072	1.070	1.068	1.067	1.066	1.066	1.066	1.066	1.066
438	349.9	196.9	1.073	1.072	1.070	1.068	1.067	1.066	1.066	1.066	1.065	1.065
440	351.5	197.9	1.073	1.072	1.070	1.068	1.067	1.066	1.066	1.066	1.065	1.065
442	353.1	198.9	1.073	1.071	1.069	1.067	1.066	1.065	1.065	1.065	1.064	1.064
444	354.7	199.9	1.072	1.070	1.069	1.067	1.066	1.065	1.065	1.065	1.064	1.064
446	356.3	200.8	1.072	1.070	1.069	1.067	1.065	1.064	1.064	1.064	1.063	1.063
448	357.9	201.8	1.072	1.070	1.069	1.067	1.065	1.064	1.064	1.064	1.063	1.063
450	359.5	202.8	1.072	1.070	1.069	1.067	1.065	1.064	1.064	1.064	1.063	1.063
452	361.1	203.7	1.072	1.070	1.068	1.066	1.064	1.063	1.063	1.063	1.062	1.062
454	362.7	204.7	1.072	1.070	1.068	1.066	1.064	1.063	1.063	1.063	1.062	1.062
456	364.3	205.7	1.071	1.069	1.067	1.065	1.064	1.063	1.063	1.062	1.061	1.061
458	365.9	206.7	1.071	1.069	1.067	1.065	1.063	1.062	1.062	1.062	1.061	1.061
460	367.5	207.6	1.071	1.069	1.067	1.065	1.063	1.062	1.062	1.061	1.060	1.060
462	369.1	208.6	1.071	1.069	1.067	1.065	1.063	1.062	1.062	1.061	1.060	1.060
464	370.7	209.6	1.071	1.069	1.067	1.065	1.063	1.061	1.061	1.060	1.060	1.060
466	372.3	210.6	1.070	1.068	1.066	1.064	1.062	1.061	1.061	1.060	1.059	1.059
468	373.9	211.5	1.070	1.068	1.066	1.064	1.062	1.060	1.060	1.060	1.059	1.059
470	375.5	212.5	1.070	1.068	1.066	1.064	1.062	1.060	1.060	1.059	1.058	1.058
472	377.1	213.5	1.070	1.068	1.066	1.064	1.062	1.060	1.060	1.059	1.058	1.058
474	378.7	214.5	1.070	1.067	1.065	1.063	1.061	1.059	1.059	1.058	1.057	1.057
476	380.3	215.4	1.069	1.067	1.065	1.063	1.061	1.059	1.059	1.058	1.057	1.057
478	381.9	216.4	1.069	1.067	1.065	1.063	1.061	1.059	1.058	1.057	1.056	1.056
480	383.5	217.4	1.069	1.066	1.064	1.062	1.060	1.058	1.058	1.057	1.056	1.056
482	385.1	218.4	1.069	1.066	1.064	1.062	1.060	1.058	1.058	1.057	1.056	1.055
484	386.7	219.3	1.069	1.066	1.064	1.062	1.060	1.058	1.058	1.057	1.056	1.055
486	388.3	220.3	1.068	1.065	1.063	1.061	1.059	1.057	1.057	1.056	1.055	1.055
488	389.9	221.3	1.068	1.065	1.063	1.061	1.059	1.057	1.056	1.055	1.054	1.054
490	391.5	222.3	1.068	1.065	1.063	1.061	1.059	1.057	1.056	1.055	1.054	1.054
492	393.1	223.2	1.068	1.065	1.063	1.060	1.058	1.056	1.056	1.055	1.054	1.054
494	394.7	224.2	1.068	1.065	1.063	1.060	1.058	1.056	1.055	1.054	1.053	1.053
496	396.3	225.2	1.068	1.065	1.063	1.060	1.058	1.056	1.055	1.054	1.053	1.053
498	397.9	226.2	1.067	1.064	1.061	1.059	1.057	1.055	1.055	1.054	1.053	1.053
500	399.5	227.1	1.067	1.064	1.061	1.059	1.057	1.055	1.054	1.053	1.052	1.052
502	401.1	228.1	1.067	1.064	1.062	1.059	1.056	1.054	1.054	1.053	1.052	1.052
504	402.7	229.1	1.067	1.064	1.062	1.059	1.056	1.054	1.054	1.053	1.052	1.051
506	404.3	230.1	1.067	1.064	1.062	1.059	1.056	1.054	1.054	1.053	1.052	1.051
508	405.8	231.0	1.066	1.063	1.061	1.058	1.055	1.053	1.053	1.052	1.051	1.051
510	407.4	232.0	1.066	1.063	1.061	1.058	1.055	1.053	1.053	1.052	1.051	1.051
512	409.0	233.0	1.066	1.063	1.061	1.058	1.055	1.053	1.053	1.052	1.051	1.050
514	410.6	234.0	1.066	1.063	1.060	1.057	1.054	1.052	1.052	1.051	1.050	1.050
516	412.2	235.0	1.066	1.063	1.060	1.057	1.054	1.052	1.052	1.051	1.050	1.050
518	413.8	236.0	1.065	1.062	1.059	1.056	1.054	1.052	1.052	1.051	1.050	1.050
520	415.4	237.0	1.065	1.062	1.059	1.056	1.053	1.051	1.051	1.050	1.049	1.049
522	417.0	237.9	1.065	1.062	1.059	1.056	1.053	1.051	1.051	1.050	1.049	1.049
524	418.6	238.9	1.065	1.062	1.059	1.056	1.053	1.050	1.050	1.050	1.049	1.049
526	420.2	239.9	1.065	1.062	1.059	1.056	1.053	1.050	1.050	1.050	1.049	1.049
528	421.8	240.9	1.064	1.061	1.058	1.055	1.052	1.050	1.050	1.050	1.049	1.049
530	423.4	241.9	1.064	1.061	1.058	1.055	1.052	1.050	1.050	1.049	1.048	1.048
532	425.0	242.9	1.064	1.061	1.058	1.055	1.052	1.049	1.049	1.049	1.048	1.048
534	426.6	243.9	1.064	1.061	1.058	1.055	1.052	1.049	1.049	1.049	1.048	1.048
536	428.2	244.9	1.064	1.060	1.057	1.054	1.051	1.048	1.048	1.048	1.048	1.048
538	429.8	245.9	1.064	1.060	1.057	1.054	1.051	1.048	1.048	1.048	1.047	1.047
540	431.4	246.9	1.063	1.060	1.057	1.054	1.051	1.048	1.048	1.048	1.047	1.047
542	433.0	247.9	1.063	1.059	1.056	1.053	1.050	1.047	1.047	1.047	1.047	1.047
544	434.6	248.9	1.063	1.059	1.056	1.053	1.050	1.047	1.047	1.047	1.046	1.046
546	436.2	249.9	1.063	1.059	1.056	1.053	1.050	1.047	1.047	1.047	1.046	1.046
548	438.8	250.9	1.063	1.059	1.055	1.052	1.049	1.046	1.046	1.046	1.046	1.046
550	439.4	251.9	1.062	1.059	1.055	1.052	1.049	1.046	1.046	1.046	1.046	1.046

The routine analyses referred to above included also determinations of reducing sugars by the gravimetric Munson and Walker method, the results being reported as invert sugar, on the basis of the original Munson and Walker tables. The figures obtained are shown in column 5 of Table III. For the purpose of direct comparison, the results of the volumetric determinations have been recalculated and expressed as invert sugar, on the basis of the original Munson and Walker tables. Owing to the pressure of routine work it was usually not possible to run the volumetric determinations at the same time as the gravimetric, and in some cases there was an interval of several weeks, during which time the samples may have undergone slight changes. The comparisons, therefore, do not permit of definite conclusions. Nevertheless, with the blackstraps the results of the volumetric method check in most cases with those of the gravimetric within the limits of error, but in some they are distinctly lower. The average tendency is towards lower results, reflecting the effect of the mineral impurities on the result of the gravimetric method. In the high-test molasses, however, the results of the volumetric method are in several instances distinctly higher than those of the gravimetric and the average tendency is also towards high values. It has been noticed that these high-test molasses are often very acid, and it may therefore be expected that inversion still goes on slowly during storage.

The general tendency of the gravimetric Munson and Walker method to give high results is well illustrated by comparison with the Lane and Eynon volumetric method. These analyses, shown in Table IV, were made with an entirely different series of molasses samples, and the two determinations were run simultaneously, so that the time factor does not enter.

With the blackstraps, the Lane and Eynon method gave lower results in all cases except two, but in these two the figures are not more than 0.02 per cent higher, well within the limit of error. The average Lane and Eynon result is 0.36 per cent lower, or 1.94 per cent on total reducing sugars. With the high-test molasses the average Lane and Eynon figure is only 0.21 per cent lower, or 0.47 per cent on the basis of total reducing sugars. These results are just as would be expected, since the high-test molasses have a much higher total sugar purity than the blackstraps, their ash content is much lower, and the copper precipitate should therefore carry down less mineral matter than in the case of blackstraps. If the results of the gravimetric method are calculated from the new Munson and Walker table of the writers, the figures of the Lane and Eynon method for the blackstraps average 0.45 per cent lower, or 2.42 per cent lower on the basis of the total reducing sugars; for the high-test molasses they average 0.48 per cent lower, or 1.06 per cent on the total reducing sugars.

If the Munson and Walker method is retained as an official method for the analysis of molasses, the copper in the precipitate should be determined by a convenient method, either volumetric or electrolytic. Much time could be saved, without sacrificing accuracy, by substituting the Lane and Eynon method for that of Munson and Walker.

Summary and Conclusions

The reducing effect of dextrose only, and of levulose only, in the presence of sucrose, on Fehling solution has been determined for the method of Munson and Walker, and the results are given in the form of a table. By combining this method for the determination of total reducing sugars with that of Jackson and Mathews for the determination of apparent levulose, the dextrose and the levulose can be calculated from the two equations. Check analyses gave satisfactory results. Application of the method to the analysis of various types of molasses and sirups has shown that in raw sugar blackstraps the levulose usually exceeds the dextrose; in inverted (high-test) molasses, however, the dextrose is generally higher than the levulose, part of the latter being destroyed during the manufacturing process. Refinery blackstraps contain a lower proportion of levulose than invert molasses, and filtered refinery sirups a still lower one. The gravimetric Munson and Walker method gives too high results for reducing sugars, no matter whether the precipitate is weighed as oxide or after reduction to metal, because of the mineral impurities carried down by the precipitate. It is suggested that either the copper be determined by a volumetric or electrolytic method, or that the Lane and Eynon method be substituted for the Munson and Walker method.

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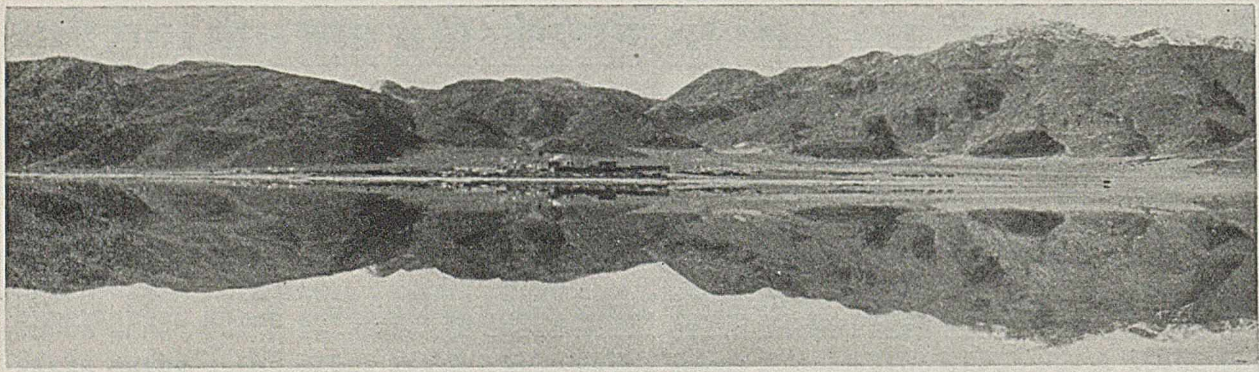

Plant of the American Potash and Chemical Corporation, Trona, Calif.

Estimation of Degree of Souring in Sugar-Cane Juice

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Because of variations in the normal acidity of cane from different sugar-cane varieties and from different fields, and also the differences in normal acidity due to the degree of topping, the total acidity shown by soured juices gives a poor indication of the excess acidity produced by the souring. The determination of the excess acidity formed in the cane after damage by freezing can be approximated from the final pH, the amount of the drop in pH, or by a simple distillation test. The comparative values for the excess acidity, pH, and pH drop obtained during the past season in Louisiana are given, and the distillation test is described. The use of excess acidity rather than total acidity values is recommended for the evaluation of deteriorated cane.

DETERIORATION of sugar cane following the severe freezes of the recent Louisiana harvest made it desirable for factory operators to have a method for evaluating the cane for milling. The common commercial practice was to determine total titrated acidity of the crusher juices of hand-mill samples. Operators realized that this basis was far from ideal, but it was the only practicable measuring stick they could use. Knowing that total acidity was not a very satisfactory criterion, preliminary experiments were carried out at the Houma Field Station in search of a better one. Fortunately, suitable material was available in connection with windrowing experiments, since tests were possible on sound cane, before deterioration started, and later with corresponding samples of soured cane. By sound cane is meant cane either before freezing or immediately after freezing before souring occurred.

It is now generally known that the acidity of juices from sound cane varies widely because of varietal characteristics, soil effects, fertilization, climate, and other factors. In a particular locality the normal acidity may vary from 1.5 to 3.0 cc., but for the entire sugar belt the range is more nearly 0.7- to 4.5-cc. acidity. This being the case, it is evident that total acidity cannot be a very satisfactory basis for the estimation of degree of deterioration following freezing. For example, of two lots of cane of 4.0-cc. acidity, one may be sound cane in which the high acidity is due to normal conditions of growth, while the other may be soured cane that originally had low acidity. If acidity is a measure of the condition of frozen cane, then only the acidity produced by the deterioration can properly be considered. For the purposes of this discussion, the acidity formed by souring will be called "excess acidity." It is not certain to what extent excess acidity is a measure of the quality of the cane from the viewpoint of factory operations, but it is certain to be a much more accurate basis than total acidity. At least, it is a true measure of the degree of souring. The question, however, as to whether souring is directly correlated with degree of gum formation will not be discussed at this time.

Excess Acidity versus pH

In spite of the considerable variation in the total acidity of normal cane juices from different varieties and fields, it has nevertheless been found that in a particular locality the variation in pH is very small, and even in the entire sugar belt the range is not large. For example, in a given locality the variation is likely to be about 0.2 pH, say from 5.30 to 5.50 pH, and for the whole Louisiana sugar-producing area the range is probably only from 5.2 to 5.6 pH. Because of the relatively constant pH of normal cane juices, pH values below 5.20 give an immediate indication of souring. The correlation of pH and the pH drop with excess acidity was extensively studied during the past season, and while the amount of information obtained may not permit the absolute estimation of excess acidity, it is sufficient for the purpose of estimating the approximate amount of excess acidity in grading the cane. As the measurement of pH is comparatively convenient and speedy, it is especially suited to control work.

The equipment used was a commercial glass-electrode pH electrometer, but the quinhydrone electrode, although slower to use, is otherwise satisfactory. The pH and electrometrically titrated acidity were determined immediately after the freeze and subsequently on duplicate samples of juice from windrowed and standing cane at different stages of souring. The principal studies were made on the varieties Co. 281 and Co. 290, but limited tests on all commercial varieties were included. The windrow tests were conducted in the Houma area. The data obtained were examined from two viewpoints, (1) the exactness with which the pH value indicated the degree of souring independent of the initial pH of the sound cane, and (2) the relation between the amount of the drop in pH and excess acidity. The excess acidity was the difference between the acidity of the sound cane juice and that of the corresponding soured samples after storage.

TABLE I. VALUES FOR pH AND pH DROP VERSUS EXCESS ACIDITY

Excess Acidity[a]	pH Value	Drop in pH
Cc.		
0.5	5.05–5.15	0.2–0.3
1.0	4.85–5.05	0.3–0.5
1.5	4.70–4.85	0.5–0.7
2.0	4.55–4.70	0.7–0.8
2.5	4.45–4.55	0.8–0.9
3.0	4.40–4.45	0.9–1.0
3.5	4.35–4.40	1.0–1.1
5.0	4.10–4.20	1.1–1.2
7.0	3.95–4.05	1.3–1.4

[a] Cc. of 0.1 *N* alkali for 10 cc. of juice.

It was found that when souring had proceeded to the extent of developing about 1.0-cc. excess acidity or more, the correlation between pH and excess acidity was a definite factor. When the souring was very slight, the pH was influenced by the initial pH of the sound cane and the degree of souring was uncertain unless the normal pH was known for comparison. For the range of 1.0- to 3.0-cc. excess acidity, which some operators believe are the limits within which deteriorated cane can possibly be handled reasonably well in the factory, the final pH determination gives a fair measure of the degree of souring. A comparison of pH and excess acidity is given in Table I. As more widespread information is accumulated in the future, it may be found that the comparative values will not agree exactly with those obtained in this preliminary study.

Excess Acidity versus pH Drop

If the initial pH of the sound cane is known, the drop in pH can be estimated from the pH value of the soured cane. This was the case in these experiments, but in the factory it is possible only when the average pH of the cane supply is known. The pH of the juice during the normal part of the season is likely to be uniform, unless the cane is from widely separated areas, and if a number of samples are tested during this period, the average pH established is likely to be close to the pH of the normal cane remaining in the fields. The drop below this value after a freeze may then be interpreted as excess acidity with somewhat greater accuracy than is possible from a single determination of the final pH value of the soured cane. This is especially true in the range of excess acidity below 1.0 cc. The relation of drop in pH to excess acidity (as found in these experiments) is also shown in Table I.

Excess Acidity by Distillation

Since most of the acidity formed by the souring is acetic acid, which is volatile with steam (while the normal acids of sugar-cane juice are nonvolatile), it is possible to estimate the excess acidity by a distillation method. A simple distillation setup of a 300-cc. flask connected with a condenser is all that is required. For complete distillation of the volatile acids the flask has to be equipped with a dropping funnel for the addition of water, or with a live steam jet. From the preliminary tests, however, it appears likely that complete distillation of the volatile acids is not needed to obtain a fair estimate of the excess acidity. The procedure suggested is to distill off 25 cc. from a 100-cc. juice sample and titrate the distillate in the usual manner with 0.1 *N* alkali, using phenolphthalein as indicator. The value thus obtained was found to be a good approximation of the excess acidity of 10 cc. of juice—that is, roughly 10 per cent of the total excess acidity in the 100-cc. sample distilled over in the first 25 cc. of condensate, which is equivalent to the excess acidity in 10 cc. of juice.

In the preliminary work the distillations were made on juices the excess acidity of which was known. The distillate was collected and titrated in 25-cc. portions until essentially complete distillation of the volatile acids was obtained. It was noted that the first 25 cc. of condensate indicated the amount of the excess acidity in the manner just described. The total volatile acids agreed with the known excess acidity when the degree of souring was relatively slight, especially under 1.0 cc. of excess acidity. When the souring was extreme not all the excess acidity could be recovered by distillation, and it is assumed that as the souring progresses there are possibly nonvolatile acids formed to some extent in addition to the acetic acid. That such may be the case is also indicated by some experiments where the drop in pH was measured after additions of 0.1 *N* acetic acid to sound cane juice. The pH obtained with acetic acid agreed with that from the same degree of souring up to roughly 2 cc. of excess acidity, but beyond that point the pH drop due to souring was greater than that found for the corresponding amounts of acetic acid, indicating the presence of acids stronger than acetic in the soured juice. These might be acids such as malic, oxalic, or tartaric which are stronger acids than acetic, are nonvolatile, and have been found in other fermentation products.

When souring is slight, the titration of the first 25 cc. of distillate from a 100-cc. sample of juice is a better measure of excess acidity than is the pH determination. Sound cane juice gives no titratable acids in the distillate until the sample is practically boiled dry, and then only a trace. So even a little acid in the first 25 cc. of condensate is a sure sign of souring and indicates approximately the amount of excess acidity. It is to be clearly understood that the values thus obtained by distillation are not absolute measures of excess acidity, yet they are satisfactory for practical purposes, and with standardization of equipment and method may become rather exact.

TABLE II. SECTIONING TESTS ON NORMAL AND SOURED CANE

	Initial Acidity Cc.	Total Acidity after Souring Cc.	Excess Acidity Cc.
Whole cane (normally topped)	2.21	3.50	1.29
Cane topped back one-third (average of bottom two-thirds)	1.58	2.69	1.11
Top third section	2.74	5.60	2.86
Middle third section	1.86	3.48	1.62
Bottom third section	1.30	1.90	0.60

On first consideration a distillation test of this kind may appear too cumbersome for routine factory control, but as it is possible to set up 10 or more of the simple distillation outfits in a rather compact manner, and, as the distillation required is brief, it is believed that one operator may be able to test a hundred or more samples per day. This method is better than the pH determination (1) because it does not require any assumption as to the original, normal pH or acidity of the juice—in short, it is specific for the volatile acids produced by souring; (2) because it gives a more accurate value for small amounts of souring, detecting even traces; and (3) because the cost of laboratory equipment is less. The pH procedure of estimating excess acidity has the advantage in speed and in space required for the equipment, and is considered just as accurate for amounts of excess acidity above 1.0 cc. Both methods can doubtless be improved as further studies are made, but even at the present stage of development either can be used to put the evaluation of frozen cane on the better basis of excess acidity rather than on that of total acidity.

Effect of Low Topping

The use of the excess acidity instead of the total acidity determination as a measure of souring is justified not only because of the variation in the normal acidity of the whole cane but also because of the practice of severely topping back cane which shows souring. This cutting back is sometimes essential in order to obtain juices of higher purity and to save the better part of deteriorated cane for milling, when it may not be possible to save the entire crop; but it further complicates the interpretation of total acidity as a measure of deterioration because of the much lower normal acidity of cane topped in this manner. When soured cane is topped back a third or more, the relatively low acidity of the milled portion may actually include an unsuspected and considerable proportion of excess acidity. The experience at factories where juice of moderate total acidity gave trouble in processing can possibly be explained on this basis. Taking as an example one of the sectioning tests made on Co. 281 windrowed after the first freeze (Table II), there should be noted (1) the difference between the normal acidity of the sections, (2) the contrast between the acidity of the normally topped whole cane and that of cane which has been topped back a third, (3) the moderate total acidity of the bottom two-thirds (2.69 cc.) when the total acidity of the normally topped cane was high (3.50 cc.), and (4) the high excess acidity in the bottom two-thirds in spite of the moderate total acidity.

Not all damaged cane sours over its entire length, as was the case with this particular test; the degree of damage probably is an important factor. It is, however, likely that much of the frozen cane ground during the past season, which had been severely topped back, was moderately high in excess acidity even when, on the basis of total acidity, it appeared satisfactory for processing.

An alternate explanation of poor factory operation with juices of moderate total acidity lies in the possibility that gum formation may proceed without the corresponding formation of excess acidity. It is not known at present to what extent the formation of gums and acids is correlated. Much more information is needed before the evaluation of frozen and soured cane can be put on an entirely fair and accurate basis. The estimation of excess acidity, however, should be a forward step, as it affords a better means of determining actual souring in cane.

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Determination of Alpha- and Beta-Carotenes

By Means of the Spectrophotometer and the Photoelectric Photometer

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BECAUSE of the relationship of carotene and vitamin A and the difference in vitamin A potency of α- and β-carotenes, the accurate quantitative determination of the carotenes is of considerable importance. Colorimetric methods (*1*, *8*) were used early for the determination of carotene and are still used extensively (*3*, *7*, *9*, *12*). Schertz (*10*) found the spectrophotometric method more accurate than the colorimetric method. Although, when proper precautions are taken, accurate results may be obtained with the colorimetric method, the spectrophotometric method has the additional advantage that no standard solution is needed for comparison. It is necessary only to determine the absorption coefficient for pure carotene in the solvent to be used at the wave-length setting for the particular instrument used. The solvent chosen must be one in which carotene obeys Beer's law. Shrewsbury and Kraybill (*11*) and Barnett (*2*) have shown that carotene dissolved in fat does not obey Beer's law.

In this paper are reported the values of the absorption coefficients for α- and β-carotenes dissolved in heptane at two wave-length settings for the Bausch & Lomb spectrophotometer with definite light source and slit width adjustments. A comparison was made of the accuracy of determination of α- and β-carotenes by the spectrophotometric and the photoelectric photometric methods.

Experimental

Alpha- and β-carotenes were prepared by the procedure of Miller (*5*). All solvents used were repurified. An impure mixture of the carotenes (secured from the S. M. A. Corporation, Cleveland, Ohio) was dissolved in light petroleum ether and separated by passing through a column of calcium hydroxide 10 cm. (4 inches) high and 7.5 cm. (3 inches) in diameter. The layers containing the α- and β-carotenes were separated and the carotenes eluted with a 2 per cent solution of methyl alcohol in petroleum ether. Final separation and purification were effected by again passing the carotenes through calcium hydroxide columns. After elution from the calcium hydroxide the carotenes were concentrated at a low temperature *in vacuo*, crystallized from petroleum ether, dried in a desiccator, and stored in evacuated ampules. The following constants were obtained:

	Melting Point Corrected ° C.	Hydrogen %	Carbon %
α-Carotene	178.5	10.38	89.23
β-Carotene	177.8	10.34	88.94

Theoretically carotene ($C_{40}H_{56}$) contains 9.93 per cent of hydrogen and 90.07 per cent of carbon.

Samples of the carotenes were analyzed for purity by the spectrophotoelectric method. The following results were obtained: α-carotene, 96.0 ± 1.0 per cent; β-carotene, 97.4 ± 1.0 per cent; impurities colorless.

Calculations of the concentration of the carotene solutions used in this study were based on the purity of the carotenes as shown by the above analyses.

In previous work (*4*, *11*) carotene determinations were made with the spectrophotometer by the method of Schertz (*10*) at wave length 435.8 mμ, using light from a 1000-watt incandescent bulb. It is difficult to read transmittancies under these conditions because of the low light sensitivity of the eye and the low intensity of an incandescent lamp in that region. In order to overcome this difficulty the absorption spectra of α- and β-carotenes were determined to obtain a suitable wave length that would afford a greater light intensity. The results are reproduced in Figure 1, which shows that α-carotene dissolved in heptane exhibits maximum absorption at 447.5 and 475 mμ and β-carotene at 455 and 480 mμ. These maximum absorption points agree closely in wave lengths with those reported by Miller, Mackinney, and Zscheile (*6*) for α- and β-carotenes dissolved in alcohol and ether. In the work that follows 450 and 475 mμ were selected as wave lengths for the determination of α-carotene and 455 and 480 mμ for β-carotene.

TECHNIC. A stock solution of the carotene was prepared by weighing out 10 to 15 mg. of the material on the microbalance. This was made to volume with purified heptane and the five to eight solutions to be examined were prepared by dilution. Heptane was used as a solvent in preference to petroleum ether because loss of solvent by evaporation could thus be reduced materially. The solutions were examined immediately after preparation with the spectrophotometer and photoelectric photometer. A 2-cm. cell was used with the spectrophotometer with the majority of solutions. However, when the depth of color was low the 10-cm. cell was employed. One- and 2-cm. rectangular cells were used with the photoelectric photometer. The depths of the cells were measured accurately and corrections were applied in the calculations of transmittancies.

Table I. α Values of α- and β-Carotenes at Various Concentrations

(Photoelectric photometer)

Carotene Concentration	α-Carotene		β-Carotene	
Mg./l.	$-\log T$	α	$-\log T$	α
0.4	0.079	196.8	0.080	199.6
0.5	0.098	196.4	0.100	199.4
0.6	0.118	196.1	0.120	199.1
0.7	0.137	195.6	0.140	198.8
0.8	0.156	195.3	0.160	198.7
0.9	0.175	194.9	0.179	198.4
1.0	0.194	194.5	0.198	198.2
1.1	0.214	194.1	0.218	198.0
1.2	0.232	193.7	0.238	197.7
1.3	0.251	193.3	0.258	197.5
1.4	0.270	192.7	0.277	197.2
1.5	0.289	192.4	0.297	197.0
1.6	0.307	192.0	0.315	196.7
1.7	0.326	191.5	0.334	196.4
1.8	0.344	191.2	0.353	196.1
1.9	0.362	190.7	0.372	195.9
2.0	0.381	190.3	0.392	195.6
2.1	0.399	189.8	0.411	195.4
2.2	0.416	189.3	0.431	195.1
2.3	0.434	188.9	0.448	194.8
2.4	0.452	188.4	0.467	194.5
2.5	0.470	188.0	0.486	194.2
2.6	0.488	187.5	0.504	194.0
2.7	0.505	187.0	0.523	193.7
2.8	0.522	186.5	0.542	193.4
2.9	0.539	185.9	0.560	193.0
3.0	0.556	185.4	0.578	192.8
3.1	0.573	184.8	0.596	192.4
3.2	0.590	184.3	0.615	192.1
3.3	0.606	183.7	0.633	191.8
3.4	0.623	183.2	0.651	191.4
3.5	0.639	182.6	0.669	191.1
3.6	0.656	182.1	0.687	190.7
3.7	0.672	181.6	0.704	190.4
3.8	0.688	181.1	0.721	189.7
3.9	0.704	180.5	0.740	189.7
4.0	0.720	180.0	0.757	189.3
4.1	0.736	179.5	0.776	188.9
4.2	0.751	178.8	0.792	188.6
4.3	0.767	178.3	0.809	188.2
4.4	0.782	177.7	0.826	187.8
4.5	0.797	177.2	0.843	187.4
4.6	0.813	176.7	0.860	187.0
4.7	0.827	176.0	0.877	186.6
4.8	0.842	175.5	0.894	186.2
4.9	0.857	174.9	0.910	185.8
5.0	0.872	174.3	0.927	185.4
5.1	0.886	173.7	0.944	185.0
5.2	0.900	173.1	0.960	184.6
5.3	0.914	172.4	0.976	184.2
5.4	0.928	171.8	0.993	183.8
5.5	0.942	171.3	1.009	183.5

Photoelectric Photometer

The photoelectric photometer used in this work was described by Withrow, Shrewsbury, and Kraybill (*13*).

The absorption curves obtained with the spectrophotometer were used as an aid in selecting the proper filter system for the carotenes (Figure 1). The specific absorption coefficients for the solutions examined were calculated according to the formula $\alpha = 1000t/cl$, where c is the concentration of carotene in milligrams per liter, t the $-\log$ of the transmittancy, T, and l the depth of the cell in centimeters. Specific absorption coefficients for carotene concentrations of successive 0.5 mg. per liter intervals were plotted (Figure 2). More usable data are presented in Table I which gives the $-\log$ of the transmittances and the α values for concentrations of from 0.4 to 5.5 mg. of carotene per liter.

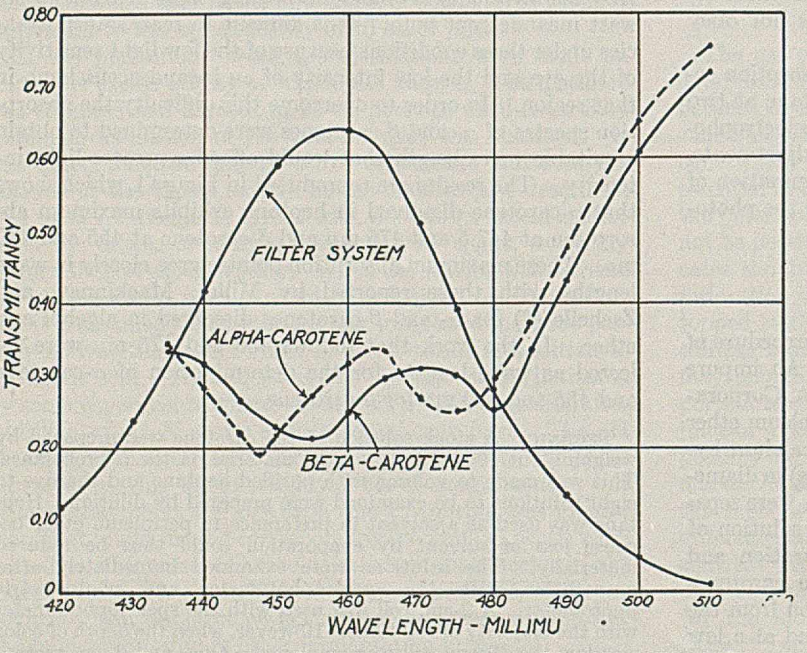

Figure 1. Transmission Curves of α- and β-Carotenes and Filter System of Photoelectric Photometer

Jena glass filter system = BG 12 and GG 5. 10-cm. (4-inch) depth, 5 per cent copper sulfate

An examination of Figure 2 and Table I shows that as the concentration increases the α values decrease. On account of the wide band of light used with the photoelectric photometer a straight-line relationship does not exist between carotene concentration and transmission as it does with the spectrophotometer. However, where extreme accuracy is not required the relationship is sufficiently linear between carotene concentrations of 0.5 and 2.5 mg. per liter to permit the use of the average α values. These are 192.2 for α-carotene and 196.8 for β-carotene. The use of these values will introduce an error of less than 2 per cent with β-carotene and less than 3 per cent with α-carotene.

Table I facilitates the calculation of the concentration of unknown solutions by furnishing the correct α value to be used for any given measured transmittancy ($-\log T$). Table II contains data checking the accuracy of determinations of β-carotene by means of the photoelectric photometer. These data were calculated by using the α values of Table I and were made several months after the original data had been obtained.

Solutions 1 to 11 were made from β-carotene from carrots separated and purified in the authors' own laboratory from an impure mixture of α- and β-carotenes (secured from the S. M. A. Corporation, Cleveland, Ohio). Solutions 12 to 15 were prepared from a sample of pure β-carotene from barley leaves furnished through the courtesy of H. H. Strain.

Inspection of Table II shows that β-carotene can be determined with a high degree of accuracy by means of the photoelectric photometer. The errors of most of the determinations were less than 1.0 per cent.

The use of the photoelectric photometer in the determination of carotene has the advantage that it is as accurate as the spectrophotometer and that the equipment is relatively cheaper. It is also rapid and not subject to personal errors such as are obtained in matching colors in the spectrophotometer with the human eye.

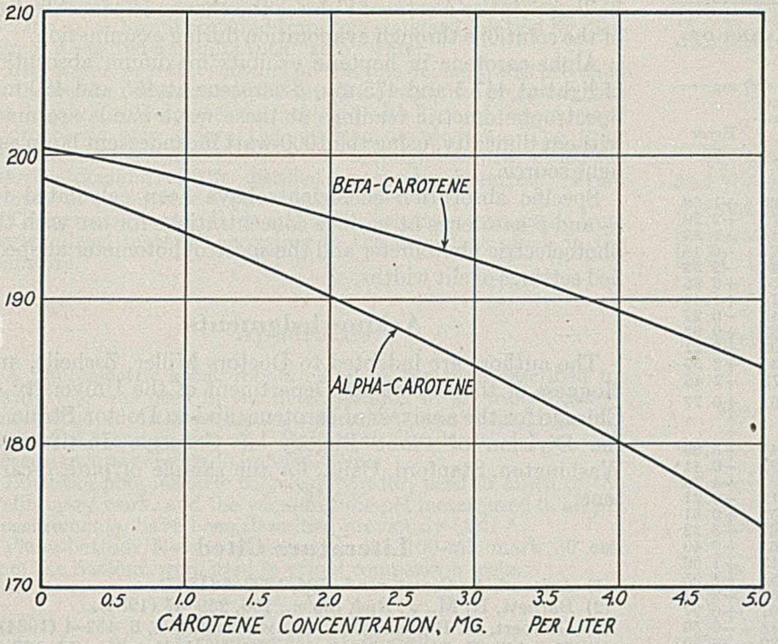

FIGURE 2. SPECIFIC ABSORPTION COEFFICIENTS OF α- AND β-CAROTENES AT DIFFERENT CONCENTRATIONS

Photoelectric photometer

TABLE II. ACCURACY OF PHOTOELECTRIC PHOTOMETER

(β-carotene)

Solution Number	Carotene Theoretical *Mg./l.*	Carotene Found *Mg./l.*	Error of Determination *Mg./l.*	Error %
1	0.442	0.439	−0.0030	−0.67
2	0.884	0.897	+0.0130	+1.47
3	1.326	1.333	+0.0070	+0.52
4	1.768	1.776	+0.0080	+0.45
5	2.210	2.227	+0.0170	+0.76
6	2.652	2.679	+0.0270	+1.01
			Av.	+0.59
7	0.4231	0.4190	−0.0041	−0.96
8	0.8462	0.8507	+0.0045	+0.53
9	1.2693	1.2526	−0.0167	−1.32
10	1.6924	1.6850	−0.0074	−0.43
11	2.1155	2.1193	+0.0038	+0.17
			Av.	−0.40
12[a]	0.6432	0.6377	−0.0055	−0.85
13[a]	0.9648	0.9582	−0.0066	−0.68
14[a]	1.2864	1.2707	−0.0157	−1.22
15[a]	1.6080	1.6005	−0.0075	−0.46
			Av.	−0.80

[a] Sample of pure β-carotene from barley leaves prepared by and furnished through the courtesy of H. H. Strain, Division of Plant Biology, Carnegie Institute of Washington, Stanford, Calif.

The Spectrophotometer

A Bausch & Lomb spectrophotometer with a 1000-watt projection lamp as light source was employed. This equipment permits the easy measurement of transmittancies in a 2-cm. cell of carotene solutions of concentrations between 0.5 and 3.0 mg. per liter at about 450 mμ and between 0.5 and 4.0 mg. per liter at about 480 mμ. Concentrations higher than these absorb so much light that matching is difficult or impossible and concentrations lower than these are too light in color to obtain accurate matches.

The spectroscope collimating slit and eyepiece slit were set on the third scale division when readings were made between wave lengths 400 and 460 mμ [slit width of entrance slit (collimator) 0.3 mm.; of exit slit (eye-piece) 0.9 mm.]. When readings were made at longer wave lengths the eye-piece slit was set on the third division and the collimating slit on the second division [slit width of entrance slit (collimator) 0.2 mm.; of exit slit (eye-piece) 0.9 mm.].

In the spectrophotometric work two observers made readings at both wave lengths on all the solutions. The average of the two sets of readings was used in the calculation of the specific absorption coefficients. Specific absorption coefficients (α values) were calculated for the solutions at two wave lengths according to the formula used above.

The following average specific absorption coefficients were found: α-carotene, 246.4 at 450 mμ, 223.6 at 475 mμ; β-carotene, 240.4 at 455 mμ, 210.0 at 480 mμ.

Figure 3 shows the results obtained when the logarithms of the transmittancies are plotted against carotene concentrations. A straight-line relationship holds which indicates that carotene in heptane obeys Beer's law.

The accuracy of determinations calculated from the specific absorption coefficients given above can be seen from an examination of Table III, which contains the results from a study of fifteen carotene solutions. It shows that the errors of determination were larger and not as constant as in the case of the photoelectric photometer. Although the average error was small, the variation between different samples was large. An average error of about 1.0 per cent was found.

Visual spectrophotometric determinations vary considerably because of the natural difficulty in matching colors. While this is usually not large enough to be of serious consequence, for practical purposes it increases the error above that found with instruments where the eye is not a factor.

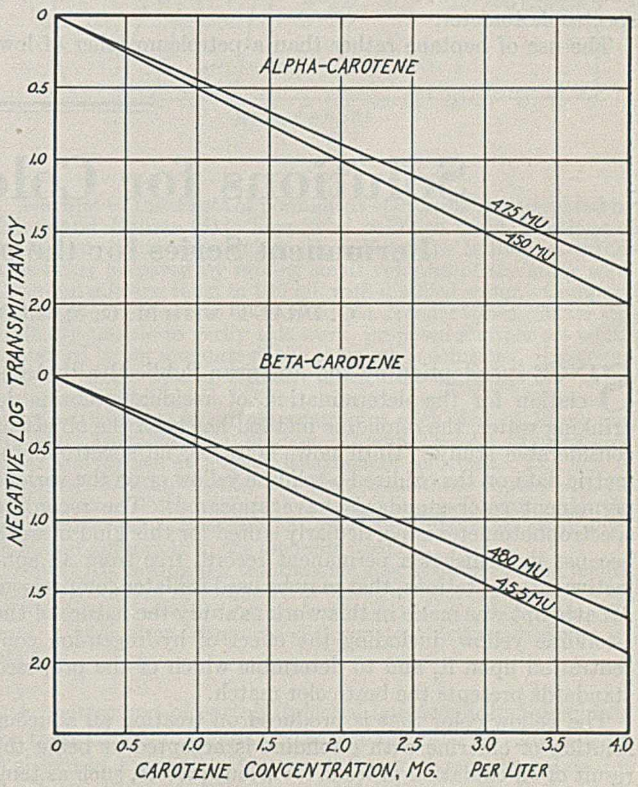

FIGURE 3. TRANSMITTANCIES OF α- AND β-CAROTENES AT WAVE LENGTHS OF MAXIMUM ABSORPTION

Measurements calculated on 2-cm. cell basis. Each curve is a composite of several determinations on solutions of similar concentration.

Table III. Determination of Carotenes by Means of Spectrophotometer

Solution Number	Wave Length 455 $m\mu$				Wave Length 480 $m\mu$		
	Carotene theoretical	Carotene found	Error of determination	Error	Carotene found	Error of determination	Error
	Mg./l.	*Mg./l.*	*Mg./l.*	%	*Mg./l.*	*Mg./l.*	%
			β-Carotene				
1	0.7569	0.7877	+0.0308	+4.06	0.7689	+0.0120	+1.58
2	0.8127	0.8231	+0.0104	+1.27	0.8306	+0.0179	+2.20
3	1.1354	1.1702	+0.0348	+3.06	1.1510	+0.0156	+1.37
4	1.1746	1.1723	−0.0023	−0.19	1.1724	−0.0022	−0.18
5	1.3441	1.2887	−0.0554	−4.12	1.3100	−0.0341	−2.53
6	1.5138	1.5485	+0.0347	+2.29	1.5497	+0.0359	+2.36
7	1.8925	1.9497	+0.0572	+3.02	1.9199	+0.0274	+1.44
8	1.9577	1.9580	+0.0003	+0.02	1.9532	−0.0045	−0.22
9	2.0318	2.0266	−0.0052	−0.25	2.0505	+0.0187	+0.92
10	2.2707	2.3384	+0.0677	+2.98	2.3210	+0.0503	+2.21
11	2.4381	2.4693	−0.0312	−1.27	2.5014	+0.0633	+2.59
12	3.1363	3.0848	−0.0515	−1.64	3.0591	−0.0772	−2.46
Av.	....	....	+0.0075	+0.769	....	+0.0102	+0.77
			α-Carotene				
1	0.4253	0.4298	+0.0045	+1.05	0.4006	−0.0247	−5.80
2	0.7623	0.7527	−0.0096	−1.25	0.7591	−0.0032	−0.41
3	0.8509	0.8859	+0.0350	+4.11	0.8102	−0.0407	−4.78
4	0.8814	0.8526	−0.0288	−3.26	0.8002	−0.0812	−9.21
5	1.0165	1.0009	−0.0156	−1.53	1.0217	+0.0052	+0.51
6	1.1386	1.1623	+0.0237	+2.08	1.1753	+0.0367	+3.22
7	1.2706	1.2713	+0.0007	+0.06	1.2643	−0.0063	−0.49
8	1.2764	1.3359	+0.0595	+4.66	1.2977	+0.0213	+1.66
9	1.3220	1.3117	−0.0103	−0.77	1.2565	−0.0655	−4.95
10	1.7628	1.7718	+0.0090	−0.51	1.7273	−0.0355	−2.01
11	2.1274	2.1754	+0.0480	+2.25	2.1481	+0.0207	+0.97
12	2.2034	2.2258	+0.0224	+1.01	2.1903	−0.0131	−0.59
13	2.5528	2.5871	+0.0343	+1.34	2.5398	−0.0130	−0.50
14	2.6440	2.6799	+0.0359	+1.35	2.6400	−0.0040	−0.15
15	2.8465	2.9018	+0.0553	+1.94	2.8893	+0.0428	+1.50
Av.	....	....	+0.0176	+0.83	....	+0.0107	−1.40

Conclusions

Data are presented on the determination of α- and β-carotenes by means of the photoelectric photometer and the spectrophotometer.

The carotenes can be determined with an accuracy of about 1 per cent with the photoelectric photometer or the spectrophotometer. The variation in the error is greater with the spectrophotometer.

The use of heptane rather than a petroleum ether of low boiling point as a solvent reduces the change in concentration of the solutions through evaporation during examination.

Alpha-carotene in heptane exhibits maximum absorption of light at 447.5 and 475 $m\mu$, β-carotene at 455 and 480 $m\mu$. Spectrophotometric readings at these wave bands are made without difficulty, using the 1000-watt incandescent lamp as a light source.

Specific absorption coefficients have been calculated for α- and β-carotenes at various concentrations for use with the photoelectric photometer and the spectrophotometer at specified settings of slit widths.

Acknowledgments

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Solutions for Colorimetric Standards

Permanent Series for the *o*-Tolidine Method for Chlorine

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SINCE its adoption by the American Public Health Association for the determination of residual chlorine in drinking water, the *o*-tolidine method has been the object of considerable study. Until now, however, no spectrophotometric data on the oxidized *o*-tolidine yellow or on the various permanent color standards have appeared. The recording spectrophotometer is particularly suited for this kind of work because it furnishes a permanent record, free from all subjective interpretations, that may be used for later comparison. An attempt was made in this work to study the nature of the *o*-tolidine yellow, including the effect of hydrogen-ion concentration upon it, and to determine which of the proposed standards presents the best color match.

The yellow color that is produced on treating an aqueous solution of chlorine with *o*-tolidine is accepted as being the result of an oxidation process. Various factors, such as temperature, time of contact between chlorine and reagent, presence or absence of bright light, and hydrogen-ion concentration, are known to affect the nature as well as the intensity of the color that is obtained. Of these factors, the proper control of the hydrogen-ion concentration has been least appreciated.

Reagents

The *o*-tolidine used was of Eastman Kodak grade. A 0.1 per cent solution in 10 per cent (by volume) hydrochloric acid was prepared according to the approved A. P. H. A. method (*2*). This solution is designated as the "standard" *o*-tolidine reagent. "Double-strength" reagent was prepared by using 20 per cent acid. All *o*-tolidine solutions were stored in the dark.

Standard chlorine water was obtained by diluting a stock solution which was prepared by the absorption of reagent grade gaseous chlorine in distilled water. The concentration of the solution (approximately 13 p. p. m.) was determined by titration with standard sodium thiosulfate (approximately 0.025 *N*). The disappearance of the blue starch color at the end point was made more distinct by transferring the solution being titrated to a 100-ml. Nessler tube and comparing with a suitable blank. The standard solution was kept in a black bottle, fitted to a microburet with glass connections, to facilitate the removal of measured volumes of solution with minimum loss of chlorine to the outside air. The separate solutions of the "temporary" standards (0.01 to 2.0 p. p. m.) were prepared from this standard solution by dilution of measured amounts with "zero" water.

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Zero water, or water showing no chlorine demand, was prepared by the method of Adams and Buswell (*1*), with the exception that the doubly distilled water was acidified with 3 ml. of concentrated hydrochloric acid before the chlorine overdosage. The prior acidification seemed to increase the thoroughness with which the chlorine demand of the distilled water was removed. Fresh samples of such water were made each day.

The permanent standards and buffer solutions were made from recrystallized material according to the directions given in the literature.

Apparatus

A photoelectric spectrophotometer, of the type described by Hardy (*6*), was used in the determination of all transmittancy data. The adjustment of this instrument was checked against lines of a mercury arc and Bureau of Standards glasses. All measurements were made in 5-cm. cells.

Both the photoelectric color comparator, used in much of the preliminary work, and the vacuum tube pH meter, used in all pH measurements, have been described previously (*8*).

Plane-bottom Nessler tubes, with the 100-ml. mark 30 cm. from the bottom, were used in visual comparison tests.

Experimental Work

McCrumb has shown (*7*) that *o*-tolidine in the oxidized form acts as a neutralization indicator, its hue changing from yellow to blue through the pH range 2.0 to 3.5. From this it is apparent that varying shades of *o*-tolidine yellow will be produced unless the final pH of the solution is constant or lies outside the range of color change. The A. P. H. A. method (*2*) specifies the use of 1 ml. of *o*-tolidine reagent (10 per cent hydrochloric acid by volume) per 100 ml. of water tested, this amount being assumed to provide a satisfactory pH value. Experiments show, however, that this amount of acid is hardly sufficient. Thus a sample of tap water having a pH of 7.67 was treated with 1 ml. of the standard reagent and the resultant solution had a pH of 2.24. Probably a more alkaline water, or one of greater hardness, would show a pH as high as 2.5 after treatment.

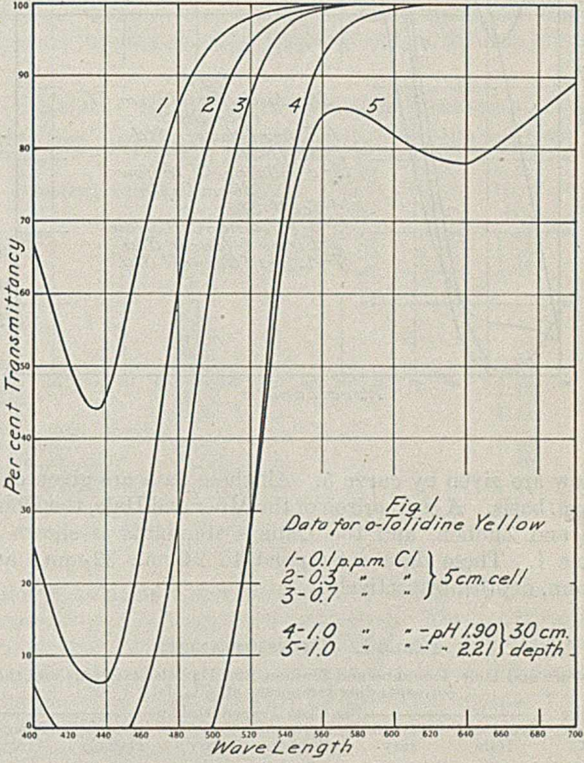
The result of this variation in final pH is shown in the transmittancy curves in Figure 1. The light absorption throughout the range of 560 to 700 mμ (curve 5) indicates the greenish yellow hue of the *o*-tolidine solution that results whenever the color is developed in the range of pH 2.0 to 2.5. The magnitude of the variation becomes far more evident when the data are calculated for a 30-cm. cell length, which corresponds to the depth of solution used in ordinary Nessler tube comparisons. The nature of the true *o*-tolidine yellow desired is shown by curve 4. It is apparent that a reproducible hue of the desired color is obtained only when the final pH of the solution is below 2.

The obvious solution to the problem is to use 2 ml. of the standard reagent or 1 ml. of the double-strength reagent, as suggested by McCrumb, per 100 ml. of test solution. In the large majority of cases this will ensure a final pH value that is below the region of color change.

With this factor in mind, the temporary standards were prepared and their transmittancy curves obtained. Recommendations regarding temperature, time of contact, and development of the color in the dark were observed, as given by the American Public Health Association (*2*). Fading during the time of measurement was very small, as the solution in the spectrophotometer was about 3 meters from the light source and the data were obtained within 15 minutes after the solution was prepared. The nature of the data is shown in curves 1, 2, and 3 of Figure 1. Two points in particular are to be observed: Each transmittancy curve shows a minimum at 436 mμ; and there is no absorption of light through the region 560 to 700 mμ. These items are of importance in the later discussion.

Permanent Standards

Because of the instability of the oxidized *o*-tolidine yellow and the difficulty of making up standards of known chlorine content, the estimation of unknown amounts necessitates the preparation of inorganic permanent standards, visually equivalent to the color produced by the chlorine–*o*-tolidine reaction.



The first of these sets of permanent standards was prepared by Ellms and Hauser (*5*). They used acidified stock solutions of potassium dichromate and cupric sulfate, the individual standards being prepared by mixing small volumes of the stock solutions and diluting them to 100 ml. with distilled water. Comparison with unknowns was made in 30-cm. Nessler tubes. Muer and Hale (*9*), unable to verify this work, proposed another set which contained larger amounts of the same stock solutions. However, they specified 24-cm. Nessler tubes, the necessity for which remained unexplained. Adams and Buswell (*1*) suggested a third set which is in virtual agreement with that of Ellms and Hauser. Donahue and Zimbon (*4*) and Daniels (*3*) prepared other sets for use with small thickness of solutions. The first of these uses 32-mm. depths, and the second three depths—13, 26, and 51 mm.—with a different standard for each depth. All the above permanent standards are made from the same stock solutions and differ only in the amounts used.

Scott (*10*), noting the troublesome specification of tube length and the variation in composition of the solutions, prepared a set of standards that could be used irrespective of tube length. He used a potassium chromate–dichromate mixture, buffered at pH 6.5.

A comparison of certain selected spectrophotometric data for these different standards, with their chlorine equivalents, is shown in Figure 2. Curves 4, 6, and 7 represent data for the Scott, Ellms and Hauser, and Adams and Buswell standards, respectively, for a chlorine concentration of 0.1 p. p. m. The corresponding transmittancy data for the *o*-tolidine

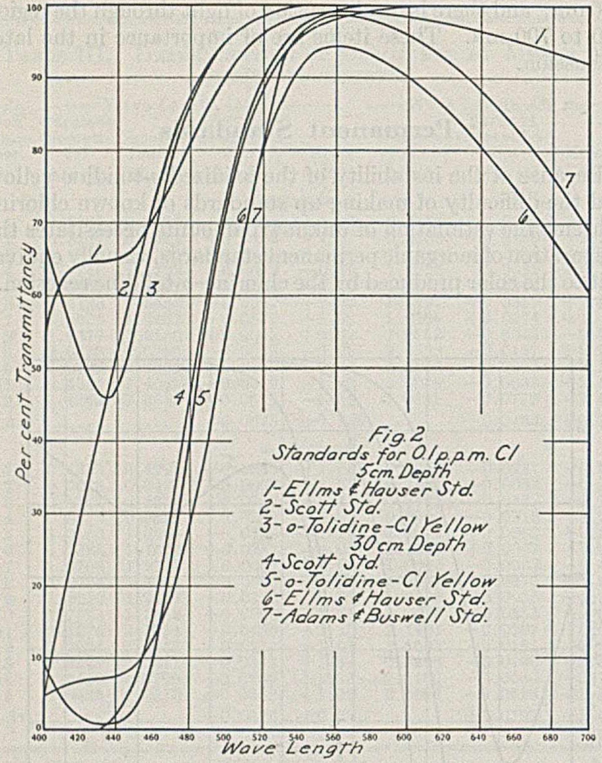


Fig. 2
Standards for 0.1 p.p.m. Cl
5 cm. Depth
1-Ellms & Hauser Std.
2-Scott Std.
3-o-Tolidine-Cl Yellow
30 cm. Depth
4-Scott Std.
5-o-Tolidine-Cl Yellow
6-Ellms & Hauser Std.
7-Adams & Buswell Std.

yellow are given by curve 5. All these data are given on a 30-cm. basis. A comparison of the Muer and Hale, the Donahue and Zimbon, and the Daniels standards is shown in Table I. These data correspond to 24-cm., 32-mm., and 51-mm. depths, respectively.

Table I. Transmittancies

(Muer and Hale, Donahue and Zimbon, and Daniels standards and the corresponding temporary standards)

Wave Length *Mμ*	Per Cent Transmittancy: Muer and Hale	Temporary	Donahue and Zimbon	Temporary	Daniels	Temporary
400	2.4	15.2	24.2	49.6	42.8	42.0
420	7.0	4.3	36.7	31.0	53.7	53.0
440	7.6	2.8	37.4	26.5	53.8	46.8
460	12.6	15.7	46.2	52.0	61.4	67.5
480	28.9	49.1	62.4	77.7	74.0	85.9
500	57.1	77.4	80.6	91.7	86.7	94.6
520	84.3	90.8	93.4	97.2	95.2	97.9
540	96.8	96.3	98.4	99.5	98.4	99.1
560	99.8	98.7	98.7	99.9	99.2	99.4
580	98.3	100.0	98.4	99.9	99.5	99.9
600	96.3	100.0	97.1	99.9	99.2	99.9
640	88.6	100.0	92.8	99.9	97.5	99.9
680	76.2	100.0	84.8	99.9	94.0	99.9
700	68.8	100.0	80.1	99.9	92.4	99.9

Comparison of the colorimetric data of the inorganic standards with their chlorine equivalents shows two striking differences. First, the permanent standards do not show the characteristic minimum at 436 mμ, which is peculiar to the *o*-tolidine yellow and would be difficult to duplicate. Fortunately, this difference occurs in the far blue where the sensitivity of the eye is very low. A second difference occurs in the region 600 to 700 mμ where all the permanent standards, with the exception of Scott's, show absorption due to the copper sulfate. It is apparent from the transmittancy curves that the chromate-dichromate mixtures of Scott present the best match, both in the form of the curve and in the agreement in the per cent transmittancy.

Curves 1, 2, and 3 of Figure 2 represent the transmittancy data of the Ellms and Hauser, the Scott, and the temporary standards, respectively, for 0.1 p. p. m. and a 5-cm. cell. Apart from the difference in the far blue, the agreement between the Scott and the temporary standard is good. The disagreement between the Ellms and Hauser and the temporary standard is marked, although probably not serious visually. From the agreement of the Scott and the temporary standards at both 5- and 30-cm. tube lengths, it is obvious that this set of permanent standards can be used irrespective of tube length.

A complete comparative study of the Scott standards and their chlorine equivalents revealed agreement in transmittancy curves throughout the range 0.1 to 2 p. p. m. Below 0.1 p. p. m. there were discrepancies, the Scott standards containing insufficient amounts of the chromate-dichromate stock solution. Because of these differences, a modification of the standards is proposed, as indicated in Table II.

Table II. Modified Scott Standards

Chlorine *P. p. m.*	Stock Solution: Present *Ml.*	Proposed *Ml.*
0.10	4.4	4.4
0.07	2.8	3.1
0.05	1.9	2.2
0.03	1.1	1.3
0.02	0.7	0.8
0.01	0.3	0.4

It is clear from the lack of relationship between the volumes of solution required to make up the permanent standards that the *o*-tolidine–chlorine yellow does not obey Beer's law.

Visual comparison of the various standards was made, but, because of the nature of the work, positive conclusions are very difficult. The authors were unable to differentiate between any of the standards and the corresponding *o*-tolidine yellow equivalent, when using the tube length for which these standards were designed. When comparisons were attempted at other tube lengths, it was very obvious that the permanent standards, with the exception of Scott's, did not present a colorimetric match. This interesting fact seems to be due to the peculiar balance between the absorption in the red and the blue regions at the tube length for which the standard was designed. It does not hold for comparisons at other tube lengths. The Scott standards, since they follow the *o*-tolidine absorption more closely, matched equally well at all tube lengths.

Conclusions

This spectrophotometric study of the *o*-tolidine method for chlorine shows (1) the colorimetric characteristics of the *o*-tolidine yellow, including the desirability of having the final pH below 2, and (2) the relation between the various permanent standards and their *o*-tolidine yellow equivalents. The Scott standards are considered the best, although the others are visually satisfactory, provided the specification regarding tube length is followed.

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Determination of Fluorine Spray Residue on Tomatoes

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THE aim of this paper is not to present a perfected method of analysis for fluorine in tomatoes but rather to describe some of the difficulties encountered in the application of the Willard and Winter titration method (*6*), using the Armstrong (*2*) modification to employ sodium alizarin sulfonate as indicator, and the chloroacetic acid buffer of Hoskins and Ferris (*5*). The merits of sulfuric and of perchloric acids for the distillation of fluorine are compared for pure fluorine solutions and for ashed samples of fluorine-bearing tomatoes, and a distillation procedure is suggested to utilize the merits of the two.

Solutions and Chemicals

SODIUM ALIZARIN SULFONATE SOLUTION. Dissolve 0.050 gram of sodium alizarin sulfonate in 100 ml. of water.

SODIUM FLUORIDE SOLUTIONS. 0.01 mg. of fluorine per ml. Weigh 2.2105 grams of C. P. sodium fluoride and make up to 1 liter. Prepare a standard by diluting 10.00 ml. of this solution to 1 liter.

THORIUM NITRATE SOLUTION. Dissolve 0.4579 gram of C. P. $Th(NO_3)_4 \cdot 12H_2O$ in water and make up to 1 liter.

CHLOROACETIC BUFFER (*5*), 0.24 *M*. Dissolve 22.7 grams of monochloroacetic acid to give 100 ml. of solution. Neutralize 50 ml. with 6 *N* sodium hydroxide, combine two portions, and make up to 1 liter.

MAGNESIUM OXIDE, C. P., low in fluorine.

SILVER PERCHLORATE SOLUTION (*1*). Adjust concentration so that 1 ml. is equivalent to 0.02 gram of sodium chloride.

Titration

To the sample to be titrated (not exceeding 12.5 ml. in volume) in a 50-ml. beaker are added 15 ml. of 95 per cent ethanol, 0.10 ± 0.01 ml. of 0.05 per cent sodium alizarin sulfonate, and water to make 27.5 ml. The color of the indicator is adjusted with 0.5 *N* sodium hydroxide and 0.5 *N* hydrochloric acid until it has a pure yellow color without excess of acid. Then 2.5 ml. of 0.24 *M* chloroacetic buffer are added and the solution is titrated with thorium nitrate solution using a 5-ml. microburet. It is assumed that the volume of 0.5 *N* hydrochloric acid or sodium hydroxide will not disturb the final volume more than about 1 ml. The end point is taken when the color matches that of a blank to which has been added exactly 0.05 ml. of the thorium nitrate solution. As the end point is approached the sample and standard are transferred to 50-cc. Nessler tubes in which more accurate matching of colors is possible than in the original beakers. The 50-ml. beakers are preferable initially, however, because of greater facility of mixing. The Nessler tubes should be illuminated from the bottom by a uniformly white surface receiving its light preferably from the blue sky, and never direct sunlight.

Because the red colored lake so produced is not stable, and appreciably intensifies in color after an hour or two, it has been found desirable to substitute for it a permanent color. This may be accomplished by matching the end-point color, above described, with an aqueous solution of cobalt nitrate and potassium chromate. The red and yellow colors from these two salts are easily adjusted to give a solution which has the same intensity and shade as the original thorium-alizarin sulfonate lake. Titrations of pure sodium fluoride solutions made in this manner are reproducible to about 0.01 ml. with the given concentrations.

As long as pure sodium fluoride is being titrated, the end points are satisfactory. The larger titrations show somewhat more vague color transitions, but no more than is compensated for by the greater volume of thorium nitrate solution to measure; hence the relative accuracy is about the same for titrations varying from 1 to 3 ml., which is the most satisfactory range. As many workers have reported, various ions can seriously interfere. The most common anions encountered are sulfate, perchlorate, carbonate, and chloride. The effect of these ions has been previously reported by tabulating limiting concentrations below which they do not seriously interfere. To clarify this matter, Table I shows the quantitative effect of these ions in various amounts under the standard titration conditions when titrating sodium fluoride solutions.

TABLE I. QUANTITATIVE EFFECT OF INTERFERING IONS

[Net (gross − 0.05) titrations for NaF using chloroacetic acid buffer (*5*) in presence of various ions. Total volume 30 ml., 50% in 95% C_2H_5OH]

Interfering Substance[a]	*Mg.*	0.00 Mg. F *Ml.*	0.02 Mg. F *Ml.*	0.05 Mg. F *Ml.*	0.10 Mg. F *Ml.*	0.15 Mg. F *Ml.*
None	....	0.00	0.20	0.69	1.46	2.19
H_2SO_4	0.10	0.02	0.23	0.76	1.56	..
	0.25	0.04	0.26	0.81	1.63	..
HCl	5.0	..	..	..	..	2.17
	10.0	..	..	..	..	2.15
$HClO_4$	10.0	..	..	..	..	2.19
	20.0	..	..	..	..	2.18
	30.0	..	..	..	..	2.18
$BaCl_2$	0.05	..	..	..	1.40	..
	0.10	..	..	..	1.37	..
H_2CO_3	20.0	..	..	..	1.47	..
	100.0	..	..	..	1.44	..
No buffer, 30-ml. volume	0.00	..	..	..	1.46	..
5 ml. extra H_2O	0.00	..	..	..	1.46	..
No buffer, 5 ml. extra H_2O	0.00	..	..	..	1.38	..

[a] Acids all added as the sodium salt.

Barium chloride is included, since an attempt to use it for the removal of sulfate might be considered. The last three items in the table illustrate the value of the buffer in greatly reducing the error arising from volumes of solution differing from the standard volume. This furnishes an argument for its use in addition to the claim of convenience and accuracy advanced by the originators.

Preparation of Sample for Distillation

In a 150-mm. porcelain evaporating dish are placed 100 grams of finely ground tomatoes, 1 gram of magnesium oxide of low fluorine content is thoroughly incorporated, and the mixture is slowly evaporated to dryness overnight on the water bath without stirring or other disturbance. It is then baked for 2 to 3 hours at 135° C. in an oven and finally transferred directly to the muffle furnace regulated at 500° C. The dishes at this point are provided with sheet-iron plates for covers, which are removed at the end of 2 minutes, when danger of loss of flying particles is over. Ashing is then allowed to proceed to a total time of 15 minutes, with some admission of air to burn the carbon. The dishes are then removed and cooled, and 50 ml. of water are added. The carbon is scraped loose from the sides of the dish and any lumps are crushed. Finally the whole is evaporated to dryness, heated for 30 minutes at 135° C., and returned to the muffle, again provided with the sheet-iron covers for the first 2 or 3 minutes to avoid loss by decrepitation. The covers are then removed and ashing is continued with some inlet of air until 15 minutes have elapsed, when the dishes are removed and allowed to cool.

This procedure has been found to give ash practically free of carbon with a total of only 30 minutes of ashing at 500° C. The ash, moreover, is easily handled in transferring it to the distilling flask. Chlorides, which in tomatoes vary from the natural content of about 0.05 per cent to a maximum in canned tomatoes of 1 per cent as sodium chloride, should then be precipitated without delay. For this purpose the ash is taken up as soon as cool in 50 ml. of hot water and silver perchlorate solution (*1*) is added dropwise. The point of neutralization of chloride has been reached when the brownish or yellowish color of silver oxide makes its appearance throughout the solution and is at least temporarily stable on stirring. If the dishes be allowed to stand for several hours after cooling, the carbon dioxide of the atmosphere will reduce the pH produced in the ash solution and no brown color will be produced by excess silver perchlorate. The end point must then be obtained by adding a few milliliters of 6 *N* sodium hydroxide prior to the silver perchlorate. The ash mixture is then dried on the water bath and thoroughly transferred to the distilling flask, first with a spatula and then with two 5-ml. portions of water, finally cleaning the dish of all traces of remaining ash with 5 ml. of 6 *N* acid of the kind to be used for the distillation. This distillation in the presence of the silver chloride has been found entirely satisfactory, not giving trouble by bumping, holding back fluorine, or releasing the chloride which it is desired to eliminate. Qualification of this last item must be made in the case of distillation at 160° to 165° C. with sulfuric acid, as the 250-ml. distillate then contains about 10 mg. of hydrochloric acid, which is preferably removed by adding about 1 ml. of the silver perchlorate solution to the distilling flask just before the addition of perchloric acid and start of the second distillation.

Distillation and Concentration of Distillate

When perchloric acid was used for the distillation, 24 ml. of the acid purified as described below were used, and the temperature was maintained at 135° to 138° C. Sulfuric acid distillations were made with 15 ml. of concentrated c. p. acid and the distillation temperature was held at 160° to 165° C., except in special experiments.

The Willard and Winter (*6*) distillation apparatus was used. It was found that the insertion into the water tube of a capillary tube of such dimensions that it allowed 4 ml. per minute to flow under a water head of 35 cm. with the stopcock completely open enabled the flow to be adjusted very precisely by raising or lowering the separatory funnel containing the water, so that it often distilled without change of temperature for relatively long periods.

Table II. Fractional Distillations

(2.5 mg. of F by H_2SO_4 at 135° to 138° C.)

No. of Fraction	Volume of Fraction	F in Fraction	Recovery	Remaining F Distilled into Fraction
	Ml.	*Mg.*	%	%
1	25	2.124	84.96	85.0
2	25	0.278	11.12	73.9
3	25	0.040	1.60	40.8
4	25	0.015	0.60	25.9
5	25	0.005	0.20	11.6
6	125	0.021[a]	0.84	..
	Total	2.483	99.32	

[a] Approximate, due to large correction for sulfate error.

The distillate was neutralized with 0.1 *N* sodium hydroxide to a faint pink color with the addition of one drop of phenolphthalein indicator, which does not interfere with the final titration. It was then concentrated to the volume required for titration on a hot plate, preferably with a blast of air blowing into the beaker to effect rapid evaporation without boiling.

Fractional Distillation

To study the manner in which fluorine distills, a fractional distillation was made by 25-ml. portions from a flask charge of 15 ml. of concentrated sulfuric acid and 25 ml. of sodium fluoride solution containing 0.1 mg. of fluorine per ml. Except on the first fraction, which was diluted fivefold before titration, 10-ml. portions of distillate were titrated. Table II shows the volume of fraction taken, the equivalent net titration of each fraction, the calculated percentage recovery for that fraction, and in the last column, the percentage of the fluorine remaining in the distilling flask at the beginning of a given fraction recovered in that fraction. It is this last column which is of interest. The values rapidly decrease as the volume distilled increases, indicating that it rapidly becomes more difficult to obtain a given percentage of recovery when the total amount of fluorine to be distilled is decreased. Data given include correction for sulfate error as discussed below. Dahle and Wichmann (*3*) found that sulfuric acid gives a logarithmic distillation recovery of fluorine; this is at variance with the authors' repeated experience as here illustrated. The cause of the discrepancy is not apparent.

Contamination during Distillation

In the fluorine analysis of tomato products it is desirable, in order to reduce the size of sample ashed, to concentrate the entire distillate into the final volume of not over 12.5 ml. Using sulfuric acid on distillation this becomes impossible as a variable amount of sulfate averaging approximately 3 mg. of sulfuric acid is contained in 250 ml. of distillate. From the interfering effect of sulfate as given in Table I it is seen, moreover, that an aliquot as small as 10 ml., which contains roughly 0.1 mg. of sulfate, would give a titration of about 107 per cent of the correct value when in the neighborhood of 0.10 mg. of fluorine, with greater error for smaller quantities of fluorine. These observations on sulfate error are in disagreement with published statements declaring sulfuric acid suitable for fluorine distillation, followed by thorium nitrate titration (*5*). When using perchloric acid under the given conditions of distillation approximately 7 mg. of perchloric acid are carried into the distillate. This quantity, as seen from Table I, will not interfere even when concentrated into one titration. However, c. p. 60 per cent perchloric acid as obtained in two different brands was found to give a blank titration which was not zero when 200 ml. of distillate were concentrated.

The use of rubber stoppers in conjunction with perchloric acid was found to contribute to this failure to obtain a zero blank, which was more nearly approached when glass stoppers were ground in to replace the rubber ones, including the thermometer–capillary tube inlet. The separatory funnel used for the introduction of acid into the flask was replaced by a glass stopper previous to the start of distillation. At the connection of the condenser, the glass tube was merely extended so that it discharged at a point within the water jacket, thus preventing condensate from leaching the cork used to fit the two together. With these precautions it was still found necessary to purify perchloric acid before use by distilling about 350 ml. at 140° C. from 60 ml. of 60 per cent perchloric acid or until experience showed it to yield a substantially zero blank.

Table III. Recovery of Fluorine

		Fluorine	Net Titration	Net Theoretica Titration
		Mg.	*Ml.*	*Ml.*
1	Direct titration	0.150	2.20	(2.20)
2	Distilled and titrated	0.150	2.22	2.20
3	Ashed sample distilled	0.022	0.41	0.32
4	Second 200 ml.	...	0.35	0.00
5	Third 200 ml. + 0.15 mg. F	...	2.48	2.20
6	Ashed sample distilled	0.10	1.76	1.74
7	Second 200 ml.	...	0.41	0.00
8	Third 200 ml.	...	0.12	0.00
9	Fourth 200 ml.	...	0.27	0.00
10	0.15 mg. F + 1 gram MgO	...	2.45	2.41
11	Second 200 ml.	...	0.09	0.00

All perchloric acid distillations were performed with 24 ml. of purified perchloric acid boiling at 140° C. In one case, 60 ml. of c. p. 60 per cent perchloric acid yielded net titrations on the first and second 250 ml. of purifying distillation of 0.08 ml. and 0.03 ml., the equivalents of roughly 0.005 and 0.002 mg. of fluorine, respectively. While the idea has not been proved, it is suspected that this titration is not due to fluorine, especially since either contaminating stoppers or the ash from a sample of tomatoes causes the titration to continue at a high and irregular level for an indefinite series of 200-ml. fractions. In the absence of organic contamination or of inorganic materials in more than fractional gram quantities, the distillation of pure sodium fluoride yields results which are equal to direct titration, or slightly higher when deviations are observed. Second distillates in such cases are small, indicating that perchloric acid achieves a nearly quantitative recovery of fluorine and does not introduce the above-described discrepancies when essentially pure sodium fluoride is distilled. These points are illustrated in Table III.

Lines 1 and 2 compare pure sodium fluoride on direct titration and after distillation, concentration, and titration. Lines 3, 4, and 5 are the titrations obtained on distilling a sample composed of 100 grams of tomatoes ashed at 500° C. with 1 gram of c. p. magnesium oxide and found by a double distillation, described below, to contain fluorine equivalent to the titration entered in the third column. This series indicates a greater than 100 per cent recovery on the first 200 ml., a second greater than 100 per cent recovery on the next 200 ml., and a greater than quantitative recovery when 0.15 mg. of fluorine as standard solution was added to the flask for the third 200 ml. Lines 6, 7, 8, and 9 show the series of titrations obtained on four successive 200-ml. distillates from a similarly ashed tomato sample. Here the apparent cumulative recovery amounts to 176 per cent of the known total fluorine content. The conclusion must be drawn that perchloric acid generates a substance which titrates like fluorine when distilling from these heavily salt-laden charges. The end points under these conditions are brownish in color, although reasonably definite. Lines 10 and 11 show results for the distillation of 0.15 mg. of fluorine which had been ashed with 1 gram of magnesium oxide in the absence of tomatoes. The first fraction fairly closely approximated the theoretical, and the titration found for the second fraction was considerably less than experienced when tomato ash was present. The conclusion is that magnesium oxide partly contributes to the effect, but that the tomato ash is the chief offender.

TABLE IV. SINGLE DISTILLATION FROM ASHED SAMPLE

(200 ml. with $HClO_4$ at 135° to 138° C. 0.07% = natural salt content of tomatoes used)

Sample No.	Added F	NaCl	Net Titration	Net Titration Minus Blank	Recovery
	Mg.	%	*Ml.*	*Ml.*	%
X	0.00	0.07	0.27	..	...
1	0.15	0.50	2.43	2.16	98.2
2	0.15	0.50	2.65	2.38	108.2
3	0.15	0.50	2.48	2.21	100.5
4	0.15	1.00	2.53	2.26	102.6
5	0.15	1.00	2.51	2.24	101.8
6	0.15	0.07	2.45	2.18	99.1
7	0.10	0.07	1.77	1.50	102.0
8	0.10	0.07	1.78	1.51	102.7
9	0.10	0.07	1.76	1.49	101.4
				Mean	102.4

Table IV gives the results of analyses of 100-gram samples of tomatoes with fluorine added as sodium fluoride, using a single distillation of 200 ml. with perchloric acid. Various amounts of salt were added. (The "blank" is the analysis of the tomatoes plus magnesium oxide without added fluorine. Both contributed fluorine to this blank, the magnesium oxide being found to contain 12.2 p. p. m. and the tomatoes 0.052 p. p. m of fluorine.)

Under these particular conditions the fluorine found averages about 102.4 per cent. These results would suggest the application of the method to the routine determination of fluorine in tomatoes, bearing in mind that the results depend on the compensation of incomplete distillation by the positive perchlorate error.

Double Distillation

In the effort to eliminate these errors a double distillation was tried, employing sulfuric acid for the first distillation because of its cost, purity, and suitability for high-temperature distillation. The first distillate, 300 ml., was concentrated as for titration, followed by distillation of 200 ml. with perchloric acid. In the case of the first sulfuric acid fraction, two 200-ml. fractions were taken on the perchloric acid distillation. Table V shows the essential features of this process, being the titrations found on distilling two 300-ml. fractions with sulfuric acid at 145° to 148° C., these fractions being redistilled with perchloric acid to volumes of 200 ml.

TABLE V. DOUBLE DISTILLATION

(100 grams of tomatoes ashed with 1 gram of MgO and 0.15 mg. of F as NaF)

	Net Titration
	Ml.
First 300 ml. by H_2SO_4 at 145–148° C.	
First 200 ml. by $HClO_4$, 135–138° C.	2.39
Second 200 ml. by $HClO_4$, 135–138° C.	0.01
Second 300 ml. by H_2SO_4 at 145–148° C.	
First 200 ml. by $HClO_4$, 135–138° C.	0.16
Total	2.56

Theoretical recovery = 0.15 mg. F plus blank = 2.52 ml.
Actual recovery = 2.56 ml. or 102%.

The cumulative recovery of fluorine is about 102 per cent for all fractions. What is more important, the second perchloric acid distillation of the first sulfuric acid fraction is now very small, indicating that the interfering action noted above with perchloric acid has here nearly disappeared. The interpretation of the titration of the second sulfuric acid fraction is difficult. It may be regarded either as fluorine which escaped distillation into the first fraction, or as being an interference effect similar to that exhibited by perchloric acid. The total recovery observed would suggest that this titration actually represents fluorine, but that a small interfering effect exists, accounting for the excess recovery. The idea of difficulty of recovery of fluorine receives some support from the demonstrated falling off in distillation rate previously shown in Table II, and is in agreement with the observation of Dahle and Wichmann (*4*) of the restraining effect of salts on the recovery.

A series of analyses was made on 100-gram samples of tomatoes containing amounts of added fluorine of 0.10 mg. and 0.15 mg. by the double distillation described. The sulfuric acid distillation temperature was 160° to 165° C. in the effort to force the fluorine into the first fraction, which was 300 ml. The natural fluorine content of this sample of tomatoes was found to be 0.096 p. p. m. Results are given in Table VI.

TABLE VI. DOUBLE DISTILLATION

(First 300 ml. by H_2SO_4 at 160–165° C. Second 200 ml. by $HClO_4$ at 135–138° C. Standard titration: 0.15 mg. of F = 2.19 ml. net; 0.10 mg. of F = 1.47 ml. net.)

Sample No.	Added F	NaCl	Net Titration	Net Titration minus Blank	Recovery
	Ml.	%	*Ml.*	*Ml.*	%
10	0.15	0.07	2.39	2.07	94.5
11	0.15	0.07	2.40	2.08	95.0
12	0.15	0.07	2.43	2.11	96.3
13	0.15	0.07	2.49	2.17	99.1
14	0.10	0.07	1.59	1.27	86.4
15	0.10	0.07	1.62	1.30	88.4
16	0.10	0.07	1.51	1.19	81.0
17	0.10	0.07	1.43	1.11	75.5
18[a]	0.00	0.07	0.18	..	..
19[b]	0.00	0.07	0.32	..	..

[a] 1 gram of MgO only ashed.
[b] 100 grams of tomatoes + 1 gram of MgO ashed.

The results show that the samples containing 0.15 mg. of added fluorine averaged about 96.2 per cent recovery. When 0.10 mg. of fluorine was involved the recoveries dropped inexplicably and became more erratic.

Summary

Suggestions have been made to facilitate the control of distillation of fluorine, and for the end point matching on the titration. Interfering ions are quantitatively compared.

The relative errors involved in the distillation of fluorine from ashed tomatoes by sulfuric acid and by perchloric acid are compared.

An efficient ashing procedure for the fluorine analysis of tomatoes using magnesium oxide is described.

A procedure which empirically gives an average recovery of 102.4 per cent, using a single perchloric acid distillation, is given.

Acknowledgment

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The Carotenoids in Forage

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For several years it has been known that vitamin A is an essential requirement for livestock. Since Steenbock (*10*) in 1919 reported a close correlation between yellow pigments and vitamin A, much attention has been directed towards a quantitative study of plant and animal pigments in relation to their vitamin A activity. Euler (*2*) limited the activity of yellow corn to the carotenes, $C_{40}H_{56}$. However, Kuhn and Grundman (*5*) isolated cryptoxanthin, $C_{40}H_{56}O$, which is also capable of serving as provitamin A. The zeaxanthin, $C_{40}H_{56}O_2$, a xanthophyll isolated chromatographically by Karrer (*4*), was found to be completely devoid of growth-promoting activity when fed to rats. Lutein, the xanthophyll found in alfalfa meal, is also without vitamin A activity.

The discovery of Borodin (*1*) in 1883 that the carotenoid pigments could be separated into alcohol-soluble and petroleum ether–soluble fractions has been the basis for most of the procedures that have been devised for the evaluation of carotene and other carotenoid pigments. As modern knowledge has shown that almost all the vitamin A potency of forage is due to its petroleum ether–phasic carotenoids, a rapid reliable spectrophotometric method for the estimation of these pigments would be a convenient index of its provitamin A content.

In 1913, Monteverde and Lumbimenko (*6*) reported a spectrocolorimetric method for the determination of the pigments of green leaves, and in the same year Willstätter and Stoll (*11*) presented a procedure for the evaluation of carotene and xanthophyll which has served as a starting point for nearly all subsequent modifications. The latter method consists essentially of acetone-extraction of plant tissue, saponification of chlorophylls and esters, separation of the carotenoids by means of petroleum ether and aqueous methanol, and the colorimetric determination of the pigments. A petroleum ether solution of carotene or an aqueous standard solution of potassium dichromate served as a colorimetric standard.

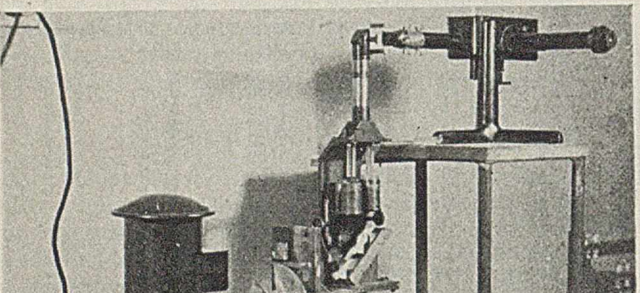

Figure 1. Photograph of Apparatus

In 1934, Guilbert (*3*) employed ethyl ether as an extraction solvent from which the pigments were transferred to petroleum ether. A standard solution of potassium dichromate (*8*) and Sprague's (*9*) dye standard were employed to evaluate the potency of carotene present.

In a recent paper Peterson, Hughes, and Freeman (*7*) reported a spectrophotometric method, which is a modification of the original Guilbert method, for the determination of carotene in forage. The main features of their method are as follows:

> The sample (1 to 5 grams) is digested for 30 minutes with a saturated solution of potassium hydroxide in ethanol. Petroleum ether (b. p. 40° to 60° C.) is used as an extraction solvent, the chlorophyllins, flavones, alkali, and xanthophylls being removed by washing first with water and then with 85 and 90 per cent methanol, respectively. The petroleum ether solution, containing the carotene, is brought to volume and the carotene concentration is determined spectrophotometrically by recording the optical density measurements at wave lengths 4550, 4700, and 4800 Å. By proper calculations involving the extinction coefficient for pure β-carotene in petroleum ether, concentration, and optical density reading it is possible to evaluate the potency of carotene present.

Of the various methods of assaying carotene—biological, chemical, colorimetric, and spectrophotometric—the latter has in recent years been accepted as the most satisfactory (Morton, 1935, and other workers).

In the investigation of several methods in this laboratory before and after the publication of the modified Guilbert method, it appeared desirable to devise an extraction and evaluation method of equal or greater accuracy with a higher degree of precision and applicability.

Numerous experiments were made to ascertain the most satisfactory procedure for the extraction as well as the actual determination of the carotene potency of commercial samples of alfalfa meal. As a result, it was observed that the use of purified technical heptane as an extraction solvent was preferable to petroleum ether, ethyl ether, normal benzine, or pyridine. (The heptane was prepared by removing the unsaturated hydrocarbons and other impurities by agitating thoroughly with concentrated sulfuric acid, sp. gr. 1.83, removing the spent acid and mineral sulfonates formed, neutralizing the remaining acid with caustic soda, drying with calcium chloride, and then collecting the fraction which distilled between 94° and 98° C.) The extraction method has been further shortened, since the chlorophyllins, flavones, alkali, and xanthophylls can be removed directly from the heptane portion by washing repeatedly with 90 per cent methanol, as the mutual solubility of the two solvents is practically nil.

The instrument employed for these investigations was a modified Bausch & Lomb visual spectrophotometer, equipped with a Duboscq colorimeter arrangement and a rotating sector as shown in Figure 1. In the process of standardizing the instrument (slit width 150 to 175 microns) with pure β-carotene,[1] it was thought desirable to compare the results with those recorded with the medium-sized quartz Bausch & Lomb spectrophotometer. Experiments conducted on the absorption curves of pure β-carotene as well as on the unsaponifiable portions of alfalfa meal and yellow corn with the latter instrument showed maximum absorption bands at 4500 Å. The discrepancy between the two instruments when determined by comparing the $E_{1\,\text{cm.}}^{1\,\%}$ at 4500 Å. for pure β-carotene in heptane was within the limits of ±3 per cent.

Experimental Method

Weigh accurately into a 250-ml. digestion flask 5 grams (more or less, depending on the relative potency) of dehydrated alfalfa meal. Add 75 ml. of 10 per cent ethanolic potassium hydroxide and reflux on a hot plate or steam bath for 30 minutes. Agitate occasionally in order to facilitate digestion. Cool the contents of the flask, add 100 ml. of purified technical heptane, shake thoroughly, allowing the suspended material to settle, and decant the liquid portion into a 500-ml. separatory funnel. Re-extract the residue with 50-ml. portions of heptane until the resultant solution is colorless (three extractions are usually sufficient). Combine the heptane extracts and wash free from chlorophyllins, flavones, alkali, and xanthophylls by shaking thoroughly with 90 per cent methanol (five washes are generally sufficient), and re-extract the first methanol portion with 50 ml. of heptane. Examine the last washing for free alkali by testing a few milliliters with phenolphthalein. Distill the heptane portion to a small volume under a vacuum in the presence of nitrogen gas. The concentrated carotene solution is then made to volume (50 ml.) with heptane and is ready for examination in the visual spectrophotometer. The intensity of absorption at 4500 Å. is determined by taking the average of several readings.

To determine the percentage of carotene in the sample of alfalfa meal, the $E_{1\,\text{cm.}}^{1\,\%}$ 4500 Å. (heptane) = 2380 (the extinction coefficient for pure β-carotene as determined by using the medium-sized quartz Bausch & Lomb spectrophotometer) is determined. By using the following equation it is possible to calculate the carotene for a 1 per cent solution:

$$(S \times F/R \times C) = \text{gamma of carotene for a } 1\% \text{ solution}$$

where

S = the screen factor
F = the conversion factor for pure β-carotene in heptane
R = the reading expressed in centimeters
C = the concentration

The results can be conveniently expressed as gamma of carotene per gram of alfalfa meal.

The samples of dehydrated alfalfa meal used for this investigation were obtained from the Nopco Experiment Station, Flemington, N. J. Duplicate examinations were carried out on each sample. In order to compare the results obtained with the method as recommended by this laboratory, the samples were also prepared for examination by the modified Guilbert method as outlined by Peterson, Hughes, and Freeman (*7*).

Samples of dehydrated alfalfa meal when prepared for spectrophotometric examination by the modified Guilbert method and by the method as recommended by this laboratory compared favorably as to their carotene contents when examined in the visual spectrophotometer (Table I). The latter extraction method is considerably more rapid and requires less care in order to obtain a higher degree of precision. Objections to the former method are the difficulties encountered during the washings with water and 85 and 90 per cent methanol and the use of a petroleum ether of low boiling point as the extraction solvent.

Table I. Carotene Content of Alfalfa Meal

Sample No.	Carotene by Modified Guilbert Method	Deviation	Carotene by New Method	Deviation	Differences between Deviations of Methods
	Gamma per gram		*Gamma per gram*		
A3R Alf. 3	72.1		73.9		
	71.4	0.7	73.6	0.3	+0.4
A3R Alf. 4	69.9		68.0		
	69.2	1.3	68.5	0.5	+0.8
A3R Alf. 8	67.3		69.0		
	68.9	1.6	69.6	0.6	+1.0
A3R Alf. 9	131.0		135.2		
	136.7	5.7	136.0	0.8	+4.9

The visual spectrophotometer is recommended as a convenient and rapid instrument for the quantitative evaluation of carotene. The results obtained with it are within ±3 per cent of those recorded with the medium-sized quartz spectrophotometer. The main disadvantage of the visual spectrophotometer as compared to the medium-sized quartz spectrophotometer is that a permanent record is not recorded for each determination. With the quartz spectrophotometer a photographic absorption plate is taken for each sample and affords a satisfactory permanent record.

Summary

A simple rapid spectrophotometric method is described for determining the carotene potency of alfalfa meal.

The results obtained on four samples of commercial dehydrated alfalfa meal with this method compare favorably with those obtained with the modified Guilbert method.

The visual spectrophotometer is described briefly and is recommended as an accurate, convenient instrument for routine evaluation of the carotene concentration of alfalfa meal.

A new absorption coefficient for pure β-carotene in heptane is reported.

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[1] S. M. A. Corporation, Cleveland Ohio, m. p. 184–184.5° C. corrected, optically inactive. On dissolving the β-carotene in chloroform and precipitating with methanol no change in melting point or absorption properties occurred.

Separation of Calcium as Sulfate by Precipitation in Concentrated Methanol Solution

Application to the Analysis of Magnesite and Technical Magnesium Oxide

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Calcium can be quantitatively precipitated as sulfate in 90 per cent methanol solution. In contrast to sulfate separation methods which depend upon conversion of both calcium and magnesium to sulfates followed by extraction of the magnesium sulfate with a solvent, in the method here described the calcium sulfate is formed in solution without attempting to convert all or even most of the magnesium to sulfate. The precipitated calcium sulfate is readily ignited and weighed as the anhydrous salt. By this method calcium can be accurately separated from a preponderant excess of magnesium and from small amounts of aluminum and iron, but not from other commonly associated elements such as strontium. The method is especially convenient for the rapid determination of calcium in magnesite and in technical grades of magnesium oxide. It is less satisfactory for the determination of high percentages of calcium, such as are found in limestone.

AN ACCURATE, practical method for the direct separation and determination of small amounts of calcium in the presence of large amounts of magnesium is much needed. Though the oxalate method gives satisfactory results when the calcium-magnesium ratio is favorable, it gives poor results when magnesium is greatly preponderant, on account of the incomplete precipitation of calcium as oxalate. The critical studies of Stolberg (*4*), Kallauner and Preller (*2*), and Rodt and Kindscher (*3*) have shown that methods based upon the difference in the solubility of calcium sulfate and magnesium sulfate in ethanol solutions, which have frequently been described in the literature, are not very satisfactory. The principal sources of error are the noticeable solubility of calcium sulfate in solvents of low ethanol content and the slight solubility of magnesium sulfate in solutions in which the ethanol concentration is high enough to precipitate the calcium quantitatively. To obviate this fundamental difficulty Stolberg (*4*) proposed the use of a mixed solvent composed of ten parts of ethanol and ninety parts of methanol. Stolberg's method was investigated critically by Kallauner and Preller, who proposed an improvement in the method, and by Rodt and Kindscher. Satisfactory results can apparently be obtained by the modified Stolberg method, but from a practical standpoint the procedure requires too much time.

Willard and Smith (*6*) first suggested the use of methanol alone for the separation of calcium from magnesium as sulfate, precipitation to be made from perchlorate solution, but no systematic experiments were apparently carried out. According to the preliminary experiments of the present investigation, methanol is decidedly superior to ethanol for the separation of calcium from magnesium by the sulfate method and is also superior to other organic solvents completely miscible with water, such as acetic acid or acetone. By using a methanol-water solution of high alcohol concentration, the solubility of calcium sulfate can be reduced low enough to give quantitative results while at the same time the solubilities of many other salts, notably magnesium sulfate, are not reduced nearly so much as in ethanol-water solutions in which calcium sulfate is sufficiently insoluble for quantitative determination. As finally evolved, the sulfate separation method here recommended differs from most preceding ones in being a precipitation method in which calcium sulfate is caused to form in solution without attempting to convert all or even most of the magnesium to sulfate. In this respect it is essentially different from those methods which depend upon the evaporation of the calcium and magnesium solution with sulfuric acid to bring about the conversion of both elements to sulfate, with subsequent separation of the sulfates by extraction with a solvent.

Methods of Precipitation Studied

The physical state of calcium sulfate precipitated in methanol solution is greatly influenced by the method of bringing the reacting solutions together. Though the order in which the reactants were mixed was found to have no effect on final completeness of precipitation, it had a decided influence on the time required for filtering and washing the precipitate (Table I).

TABLE I. EFFECT OF METHOD AND VOLUME ON TIME NEEDED FOR FILTRATION AND WASHING OF PRECIPITATE

(Solution containing 100 mg. of calcium)

Method of Precipitation	Final Volume of Solution	Number of Trials	Average Time
	Ml.		*Min.*
A[a]	100	3	10
	200	3	35
B[b]	100	3	70
	200	1	85
C[c]	100	2	40
	200	2	40
D[d]	100	2	80
	200	2	125

[a] Calcium solution + dilute sulfuric acid + methanol.
[b] Calcium solution + methanol + dilute sulfuric acid.
[c] Calcium solution + mixture of dilute sulfuric acid and methanol.
[d] Methanol + mixture of calcium solution and dilute sulfuric acid.

The final concentration of methanol in these experiments was 90 per cent, and a fixed amount of dilute sulfuric acid was used. The most favorable conditions are provided by method A. A modification of this method, to include slow evaporation of the calcium solution containing sulfuric acid to small volume before addition of the methanol, was found advantageous in reducing the time needed for filtering and washing large amounts of calcium sulfate, since the major part of the calcium is precipitated in large crystals before the addition of the nonaqueous solvent.

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General Procedure Adopted

The calcium is precipitated by one of the two following methods from a neutral chloride, nitrate, or perchlorate solution that is free from ammonium salts, barium, strontium, and lead, but may contain in addition to calcium and magnesium, small amounts of aluminum, iron, and manganese, and very small amounts of the alkalies.

I. Evaporate the solution to a volume of 4.5, 9.0, or 19 ml. or evaporate to dryness and dissolve in sufficient water to obtain the desired volume. Then add 0.5 or 1.0 ml. of 9 *N* sulfuric acid (1 volume of concentrated acid to 3 volumes of water) and precipitate the calcium sulfate by the slow addition of 45, 90, or 180 ml. of methanol in accordance with the volume of the aqueous solution, so that the final volume is 50, 100, or 200 ml. having a methanol concentration of 90 per cent. Stir constantly during addition of the methanol.

II. Add 1.0 or 2.0 ml. of 9 *N* sulfuric acid to the sample solution and evaporate until the volume is 5.0 ml. Then add 15 ml. of water and precipitate the calcium by the slow addition of 180 ml. of methanol while stirring constantly.

After precipitating by either method and allowing the solution to stand until precipitation is complete, filter through a weighed porcelain filter crucible, preferably a type A1 Koenig crucible. Wash the precipitate with 90 per cent methanol, first by decantation, then by stirring up the precipitate collected in the filter crucible with a stream of wash liquid and allowing the precipitate to remain in contact with each portion of wash liquid for a few minutes. Depending upon the quantity of calcium and other metals that are present, a total of 30 to 100 ml. will be required for washing. Dry the crucible and its contents for 30 to 45 minutes at 110° C., then ignite in an electric muffle for 30 to 45 minutes at 400° to 450° C., cool in a desiccator, and weigh as anhydrous calcium sulfate.

The choice of the method of precipitation is governed largely by the amount of calcium to be precipitated. With 5 mg. or less, method I and a total volume of 50 ml. should be used. With more than 5 but somewhat less than 100 mg., method I should be used with a total volume of 100 ml. When the quantity of calcium is about 100 mg. and foreign ions are present in low concentration, method I should be used with a total volume of 100 or 200 ml. On the other hand, when the amount of calcium is around 100 mg. and the concentration of foreign ions is high, or when the amount of calcium is considerably more than 100 mg., method II should be used. It is necessary to use a large volume of solution when the amount of calcium is high because calcium sulfate precipitated in methanol solution is very voluminous.

TABLE II. EFFECT OF COMPOSITION OF MEDIUM ON COMPLETENESS OF PRECIPITATION BY SULFURIC ACID IN METHANOL SOLUTION

CH_3OH	Total Volume of Solution	Ca Taken	Ca Found	Difference Error
% by volume	*Ml.*	*Gram*	*Gram*	*Gram*
70	50	0.0010	0.0005	−0.0005
80	50	0.0010	0.0010	±0.0000
90	50	0.0010	0.0010	±0.0000
70	100	0.0010	0.0000	−0.0010
80	100	0.0010	0.0008	−0.0002
90	100	0.0010	0.0010	±0.0000
70	100	0.1004	0.0988	−0.0016
80	100	0.1007	0.1003	−0.0004
90	100	0.1021	0.1018	−0.0003

The methanol should contain at least 99 per cent of the alcohol, but the most expensive grade of absolute methanol need not be used in this method.

The time of standing after precipitation is governed largely by the amounts of calcium and magnesium present, and by the total volume of solution used (see tables).

It is not possible to obtain quantitative results by weighing the precipitate in the air-dried state or after drying at 110°, since calcium sulfate precipitated in 90 per cent methanol solution is apparently an indefinite mixture of the dihydrate and hemihydrate. However, when ignited at the proper temperature it becomes inert anhydrous calcium sulfate that can be weighed without difficulty.

Conditions for Quantitative Precipitation

Complete precipitation of calcium as sulfate in methanol solution occurs only when the methanol concentration reaches about 90 per cent, as is shown by Table II. Except for changing the composition of the medium, these results were obtained by method I. In practice it is not desirable to precipitate the calcium in a solution containing more than 90 per cent methanol because aqueous sample and reagent solutions of inconveniently small volume are then required.

TABLE III. EFFECT OF TIME OF STANDING ON COMPLETENESS OF PRECIPITATION OF CALCIUM AS SULFATE

(In 90 per cent methanol solution)

Time of Standing	Mg Present	Ca Taken	Ca Found	Difference Error
Min.	*Gram*	*Gram*	*Gram*	*Gram*
30	None	0.0010	0.0010	±0.0000
30	None	0.0010	0.0010	±0.0000
60	None	0.0010	0.0010	±0.0000
60	None	0.0010	0.0010	±0.0000
15	None	0.0100	0.0100	±0.0000
30	None	0.0100	0.0099	−0.0001
60	None	0.0100	0.0101	+0.0001
90	None	0.0100	0.0099	−0.0001
30	0.0100	0.0010	0.0009	−0.0001
30	0.0250	0.0010	0.0009	−0.0001
30	0.0500	0.0010	0.0004	−0.0006
60	0.0500	0.0010	0.0006	−0.0004
120	0.0500	0.0010	0.0009	−0.0001
30	0.1000	0.0010	0.0003	−0.0007
180	0.1000	0.0010	0.0007	−0.0003
240	0.1000	0.0010	0.0008	−0.0002
60	0.1000	0.0010	0.0009	−0.0001[a]
120	0.1000	0.0010	0.0009	−0.0001[a]
180	0.1000	0.0010	0.0010	±0.0000[a]
240	0.1000	0.0010	0.0010	±0.0000[a]

[a] Precipitation made in a total volume of 50 ml. in these cases, the other precipitations being made in a volume of 100 ml.

At least twice the equivalent amount of sulfuric acid should be employed, and precipitation of calcium as sulfate is still quantitative when a very considerable excess of reagent is present—for example, precipitation of only 10 mg. of calcium in a 100-ml. volume was found to be complete when as much as 1 ml. of 96 per cent sulfuric acid was used. This amount of reagent is sufficient for any amount of calcium that can be conveniently handled by this method. However, a large excess of sulfuric acid should be avoided in the presence of ions other than calcium and magnesium, since sulfates insoluble in 90 per cent methanol may be coprecipitated with the calcium sulfate. Because of their tendency to increase the solubility of calcium sulfate, acids other than sulfuric cannot be present except in very low concentration.

When calcium is present alone precipitation is complete after a short period of standing, as is shown by the first set of results in Table III. It is necessary to wait more than an hour for complete precipitation only if the quantity of calcium amounts to but a few tenths of a milligram. On the other hand, as shown by the second set of results, when considerable magnesium is also present a much longer time is needed for the complete precipitation of small amounts of calcium. The effect of magnesium in retarding the quantitative precipitation of calcium sulfate is much less marked when large amounts of calcium are precipitated. It is desirable to restrict the total volume of solution as much as possible in order to obtain a more rapid quantitative precipitation of small amounts of calcium, especially when a large excess of magnesium is present. This is readily seen by comparing the last four results in Table III with the three preceding ones.

Test Analyses on Solutions

For the analytical experiments on pure calcium solutions and on solutions containing calcium and other metal ions, a highly purified sample of calcium carbonate, prepared by the reprecipitation of a reagent-grade salt, was used as the standard of reference. Standard solutions were prepared by dissolving accurately weighed quantities of this calcium carbonate in the necessary quantity of hydrochloric acid and diluting to definite volumes in calibrated flasks. The concentration of each solution in respect to calcium was checked by evaporating definite volumes with a slight excess of sulfuric acid in a platinum dish and weighing the residual calcium sulfate. The standard magnesium solutions were prepared from distilled metallic magnesium of high purity, and the standard solutions of the other metals were made from pure salts. Samples for the test analyses were prepared from accurately measured volumes of these standard solutions.

TABLE IV. DETERMINATIONS OF SMALL AMOUNTS OF CALCIUM IN PURE CALCIUM CHLORIDE SOLUTIONS

Final Volume of Solution	Time of Standing	Ca Taken	Ca Found	Difference Error
Ml.	*Min.*	*Gram*	*Gram*	*Gram*
50	60	0.0001	0.0000	−0.0001
50	240	0.0001	0.0001	±0.0000
50	60	0.0003	0.0002	−0.0001
50	240	0.0003	0.0002	−0.0001
50	60	0.0005	0.0005	±0.0000
50	240	0.0005	0.0005	±0.0000
100	30	0.0010	0.0010	±0.0000
100	30	0.0010	0.0010	±0.0000
100	60	0.0010	0.0010	±0.0000
100	60	0.0010	0.0010	±0.0000
100	30	0.0050	0.0050	±0.0000
100	30	0.0100	0.0099	−0.0001
100	30	0.0100	0.0100	±0.0000
100	60	0.0100	0.0098	−0.0002
100	90	0.0100	0.0099	−0.0001
200	30	0.0100	0.0099	−0.0001
200	30	0.0100	0.0099	−0.0001

As will be seen from Table IV, no difficulty was experienced in making accurate determinations of small amounts of calcium in the absence of other metal ions.

In Table V are shown results obtained on trial determinations of large amounts of calcium in pure calcium chloride solutions.

TABLE V. DETERMINATION OF LARGE AMOUNTS OF CALCIUM

(Lack of quantitative precipitation above a certain limit)

Method of Precipitation	Final Volume of Solution	Time of Standing	Ca Taken	Ca Found	Difference Error
	Ml.	*Min.*	*Gram*	*Gram*	*Gram*
I	100	30	0.1000	0.1001	+0.0001
I	100	30	0.1000	0.1001	+0.0001
I	100	60	0.1000	0.0999	−0.0001
I	100	60	0.1000	0.1000	±0.0000
I	200	30	0.0998	0.0998	±0.0000
I	200	30	0.1000	0.0998	−0.0002
I	200	60	0.1000	0.1000	±0.0000
II	200	30	0.0998	0.0997	−0.0001
II	200	45	0.0998	0.0996	−0.0002
I	200	45	0.1503	0.1500	−0.0003
I	200	75	0.1513	0.1509	−0.0004
I	100	30	0.2000	0.1994	−0.0006
I	200	30	0.2000	0.1991	−0.0009
I	200	60	0.2009	0.2004	−0.0005
II	200	30	0.2008	0.2005	−0.0003
II	200	30	0.2007	0.1996	−0.0011
II	200	60	0.1997	0.1984	−0.0013
I	200	45	0.3008	0.2992	−0.0016
I	200	75	0.2998	0.2982	−0.0016
II	200	30	0.3017	0.3006	−0.0011
II	200	60	0.4005	0.3986	−0.0019

Regardless of how the general procedure was applied, precipitation was incomplete above a certain limit, the results being often poor with 200 mg. of calcium and invariably so with as much as 300 or 400 mg. In part, at least, these low results can be ascribed to the solvent effect on the calcium sulfate of the ions remaining in solution after precipitation. Various attempts were made to eliminate this source of error—for example, precipitations were tried in acetate or perchlorate solutions in order to avoid the effect of chloride ion. The effect of greatly reducing the hydrogen-ion concentration was also tried, precipitation being made with alkyl ammonium sulfates instead of with sulfuric acid. Satisfactory results could not be obtained by any of these variations of the general method. However, the fact that precipitation is incomplete when the amount of calcium reaches about 200 mg. does not mean that this method cannot be applied in practice to the determination of moderate or even high percentages of calcium, since the whole difficulty can be avoided by properly restricting the weight of the original sample.

TABLE VI. DETERMINATION OF SMALL AMOUNTS OF CALCIUM IN THE PRESENCE OF A LARGE PROPORTION OF MAGNESIUM

Final Volume of Solution	Time of Standing	Mg Present	Ca Taken	Ca Found	Difference Error
Ml.	*Hours*	*Gram*	*Gram*	*Gram*	*Gram*
50	4	0.1000	0.0005	0.0000	−0.0005
50	8	0.1000	0.0005	0.0002	−0.0003
50	24	0.1000	0.0005	0.0005	±0.0000
50	1	0.1000	0.0010	0.0009	−0.0001
50	2	0.1000	0.0010	0.0009	−0.0001
50	3	0.1000	0.0010	0.0010	±0.0000
50	4	0.1000	0.0010	0.0010	±0.0000
50	9.5	0.2000	0.0010	0.0008	−0.0002
50	9.5	0.3000	0.0010	0.0005	−0.0005
50	9.5	0.4000	0.0010	0.0002	−0.0008
50	9.5	0.5000	0.0010	0.0002	−0.0008
50	24	0.5000	0.0010	0.0005	−0.0005
50	1	0.1000	0.0050	0.0050	±0.0000
50	2	0.1000	0.0050	0.0047	−0.0003
50	4	0.1000	0.0050	0.0053	+0.0003
50	4	0.2000	0.0050	0.0051	+0.0001
100	0.5	0.2000	0.0050	0.0048	−0.0002
100	0.5	0.3000	0.0050	0.0046	−0.0004
100	1	0.3000	0.0050	0.0047	−0.0003
50	1	0.1000	0.0100	0.0100	±0.0000
50	2	0.1000	0.0100	0.0100	±0.0000
50	4	0.1000	0.0100	0.0102	+0.0002
50	4	0.2000	0.0100	0.0103	+0.0003
100	0.5	0.1000	0.0100	0.0100	+0.0000
100	0.5	0.1000	0.0100	0.0098	−0.0002
100	0.5	0.1000	0.0100	0.0099	−0.0001
100	0.5	0.5000	0.0100	0.0097	−0.0003

The effect of a preponderant excess of magnesium on the quantitative precipitation of calcium is shown by Table VI. It is evident that complete precipitation of the calcium when the proportion of magnesium to calcium is as high as 200 to 1 takes place only after an inconveniently long period of standing, and that when the proportion is higher than this it is not possible to obtain quantitative results. On the other hand, when the proportion is 100 to 1, or less, precipitation of the calcium is complete after a conveniently short period of standing. In blank experiments in which 200 to 500 mg. of magnesium as chloride and 0.5 ml. of 9 N sulfuric acid were present in 50 ml. of 90 per cent methanol, no precipitation took place even after several hours' standing.

That no difficulty was experienced in the determination of large amounts of calcium in the presence of like amounts of magnesium is illustrated by Table VII. The results of experiments in which the magnesium was actually determined in the filtrate after the calcium determination are shown in Table VIII. In these experiments the calcium filtrates were evaporated to dryness on the steam bath, and, after dissolving the residues, the magnesium was precipitated as oxalate in 85 per cent acetic acid solution and weighed as oxide according to the method of Elving and Caley (*1*). The accuracy of this scheme of separation and determination can be judged from the results.

Small amounts of aluminum, iron, or manganese, in the form of salts soluble in 90 per cent methanol, do not interfere with the quantitative precipitation of calcium by this method. That no precipitation with sulfuric acid takes place when limited quantities of such salts are present alone was shown by appropriate blank experiments. For example, no

TABLE VII. DETERMINATION OF A LARGE AMOUNT OF CALCIUM IN THE PRESENCE OF AN EQUAL WEIGHT OF MAGNESIUM

Method of Precipitation	Final Volume of Solution	Mg Present	Ca Taken	Ca Found	Difference Error
	Ml.	*Gram*	*Gram*	*Gram*	*Gram*
I	100	0.1000	0.1000	0.1002	+0.0002
I	100	0.1000	0.1000	0.1000	±0.0000
I	100	0.1000	0.1000	0.1002	+0.0002
I	100	0.1000	0.1000	0.0999	−0.0001
I	100	0.1000	0.1000	0.1001	+0.0001
II	200	0.1000	0.0998	0.0994	−0.0004
II	200	0.1000	0.0998	0.0995	−0.0003

TABLE VIII. DETERMINATION OF CALCIUM AND MAGNESIUM IN THE SAME SOLUTION

Ca Taken	Ca Found	Difference Error	Mg Taken	Mg Found	Difference Error
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0100	0.0099	−0.0001	0.0101	0.0102	+0.0001
0.0100	0.0099	−0.0001	0.0101	0.0103	+0.0002
0.0100	0.0100	±0.0000	0.1002	0.0998	−0.0004
0.0100	0.0098	−0.0002	0.1002	0.1005	+0.0003
0.1000	0.0999	−0.0001	0.0101	0.0104	+0.0003
0.1000	0.1001	+0.0001	0.0101	0.0104	+0.0003
0.1000	0.1002	+0.0002	0.1002	0.1002	±0.0000
0.1000	0.1000	±0.0000	0.1002	0.1002	±0.0000

precipitation took place even after 48 hours' standing with 10 mg. of aluminum, manganese, or iron as chlorides in 10 ml. of 90 per cent methanol containing several drops of sulfuric acid. In analogous experiments with sodium and lithium chlorides the solutions remained clear as long as 7 hours. On the other hand, in similar experiments in which potassium was present as chloride, immediate precipitation resulted when the solution contained more than 4 mg. of potassium. With 2.5 mg. of potassium, precipitation began after 12 hours, but with 2 mg. of potassium no precipitation was observed.

In Table IX are shown results of quantitative experiments in which calcium was precipitated and determined in the presence of known amounts of individual foreign cations. Sodium and potassium interfere seriously, the interference of potassium being very marked, especially when the first method of precipitation is used. Fortunately, in the practical situations where this method is most applicable, as in the analysis of magnesite, the amount of acid-soluble sodium or potassium in a sample of moderate size is usually so small that no interference will result. When a large amount of soluble potassium is present in a sample, it is possible to avoid the difficulty by dissolving the sample in perchloric acid, removing the excess of perchloric acid, and extracting the residue with successive small portions of 90 per cent methanol. The calcium can then be precipitated from the combined extracts by means of sulfuric acid. Ammonium, like potassium, interferes seriously in this method because of the low solubility of its sulfate in methanol solution. Ammonium salts must therefore be removed. The usual nitric acid oxidation method is suitable, though all free nitric acid must be volatilized from the residual salts before proceeding to the determination of the calcium. That no interference results from the presence of lithium is illustrated by Table IX.

TABLE IX. PRECIPITATION OF CALCIUM IN THE PRESENCE OF VARIOUS METALS

Method of Precipitation	Solution Volume	Metal Present	Ca Taken	Ca Found	Difference Error
	Ml.	*Gram*	*Gram*	*Gram*	*Gram*
I	100	0.0500 Al	0.0100	0.0100	±0.0000
I	100	0.1000 Al	0.0100	0.0098	−0.0002
II	200	0.0100 Al	0.0998	0.0998	±0.0000
I	100	0.0100 Fe	0.0100	0.0100	±0.0000
I	100	0.1000 Fe	0.0100	0.0102	+0.0002
II	200	0.0250 Fe	0.0998	0.1000	+0.0002
II	200	0.0500 Fe	0.0998	0.0993	−0.0005
I	100	0.1000 Li	0.0100	0.0102	+0.0002
II	200	0.1000 Li	0.0998	0.0998	±0.0000
I	100	0.0050 Na	0.0100	0.0110	+0.0010
I	200	0.0050 Na	0.0100	0.0108	+0.0008
II	200	0.0050 Na	0.0998	0.1005	+0.0007
II	200	0.0100 Na	0.0998	0.1005	+0.0007
I	100	0.0050 K	0.0100	0.0112	+0.0012
I	200	0.0100 K	0.0100	0.0120	+0.0020
II	200	0.0050 K	0.0998	0.1000	+0.0002
II	200	0.0100 K	0.0998	0.1004	+0.0006

A rather satisfactory separation of calcium as sulfate can be made in the presence of small or moderate amounts of aluminum or iron. However, when the aluminum or iron is high in amount, incomplete precipitation of the calcium results. Prior removal of these elements by the usual methods is then necessary. If iron is present in excessive amount and the sample has been dissolved in perchloric acid, it is possible to eliminate most or all of the iron rapidly by evaporating the solution of the sample to dryness on the hot plate and heating the residue near the boiling point of perchloric acid until the free perchloric acid is removed. The iron perchlorate is decomposed and an insoluble residue of iron oxide remains behind, whereas calcium perchlorate remains undecomposed and may be dissolved out quantitatively from the residue.

TABLE X. DETERMINATION OF CALCIUM IN SYNTHETIC MIXTURES

	Sample A	Sample B	Sample C	Sample D
Al present, gram	0.0100	0.0100	0.0300	0.0300
Fe present, gram	0.0100	0.0100	0.0200	0.0200
Mg present, gram	0.1000	0.1000	0.0100	0.0100
Na present, gram	0.0020	0.0020	0.0050	0.0050
K present, gram	0.0020	0.0020	0.0050	0.0050
Ca present, gram	0.0998	0.0998	0.0998	0.0998
Ca found, gram	0.0999	0.0999	0.1001	0.1001
Difference, error, gram	+0.0001	+0.0001	+0.0003	+0.0003

The validity of this method of separation was demonstrated by suitable experiments. For example, two solutions, one containing 0.0199 gram of calcium and 0.050 gram of iron, the other containing 0.0199 gram of calcium and 0.100 gram of iron, were evaporated with perchloric acid, and after baking the residue, cooling, and treating with water, the insoluble iron oxide residues were filtered off with the aid of filter pulp and washed with water. On determining calcium in the filtrates, the calcium sulfate precipitates weighed 0.0674 and 0.0677 gram, respectively, as compared to the calculated 0.0677 gram. These calcium sulfate precipitates were dissolved and tested for iron by means of cupferron, but less than 0.05 mg. of iron was found in each case. On dissolving the iron residues and testing for calcium by means of picrolonic acid, no calcium could be detected. For the removal of interfering barium, strontium, or lead the nitric acid method of Willard and Goodspeed (*5*) is the most suitable to use in connection with this method for the determination of calcium.

In Table X are shown results obtained on synthetic samples in which various foreign ions were present in about the same proportions as in solutions of analytical samples of either limestone or dolomite. The second method of precipitation was used on all four samples, and the time allowed for precipitation was 35 minutes. The method is satisfactory for the direct determination of calcium in complex samples of this kind.

Test Analyses on Complex Materials

This method was further tested by applying it to mineral or rock samples of accurately known composition. The method seems to be especially satisfactory for the rapid determination of low percentages of calcium in complex materials that contain a high percentage of magnesium, low or moderate percentages of aluminum or iron, and very low percentages of potassium or sodium, such as, for example, natural or burned magnesite. In Table XI are shown the results obtained on the Bureau of Standards sample of burned magnesite (standard sample 104).

After a preliminary ignition in platinum, the weighed samples of this material were dissolved in a mixture of about 10 ml. of water and 10 ml. of 60 per cent perchloric acid in porcelain casseroles. The solutions were then evaporated nearly to dryness, and the covered casseroles were heated on the sand bath for 20 minutes at a temperature at which copious fumes of perchloric acid were evolved. After cooling, the residues were treated with water and the silica was filtered off and washed in the customary way. In the case of the first two samples in Table XI the iron was eliminated by evaporating the silica filtrates to dryness and decomposing the iron perchlorate, as described above; in the other samples the iron and accompanying elements were removed by precipitation with ammonia in dilute solution, the ammonium salts in the resulting filtrates being eliminated by evaporation with nitric acid. In all samples the calcium was precipitated by method I of the general procedure, the volumes of the solutions and the times of standing being varied as shown.

TABLE XI. DETERMINATION OF CALCIUM IN STANDARD BURNED MAGNESITE SAMPLE

Sample Taken *Gram*	Volume of Solution *Ml.*	Time of Standing *Hours*	CaO Found *%*
1.2279	100	1	3.32
0.9876	200	6.5	3.33
0.9661	100	1	3.39
1.1830	100	1	3.35
0.9861	200	1	3.31
1.2122	200	1	3.30
1.2684	100	2	3.30
1.3995	200	2	3.35
			Av. 3.33
Stated average, Bureau of Standards certificate			3.35

Both the individual results and the average agree well with the established percentage. Either method for the removal of the iron leads to the same results. Attempts to determine the calcium in this particular sample without prior removal of the iron did not yield satisfactory results by reason of the relatively high proportion of iron (7.07 per cent). However, when the percentage of iron is not quite so high good results can be obtained either without removing the iron or by removing most of it at the same time that the silica is eliminated. This was shown by a series of analyses, made in collaboration with another laboratory, of samples of technical magnesium oxide, both powdered and coarsely crystalline. The procedure finally developed for the determination of calcium in such materials is, because of its brevity and demonstrated usefulness, given here in detail.

To a 1.000-gram sample in a 250-ml. Pyrex beaker add 5 ml. of water and 10 ml. of 60 per cent perchloric acid, and then heat on the steam bath until solution is complete or only a small residue of silica remains. Fume off the excess of perchloric acid by placing the beaker on a high-temperature hot plate. If necessary remove the last traces of perchloric acid by heating the beaker wall with a flame. After cooling, dissolve the salts in about 20 ml. of water. Filter off the silica and wash with successive small portions of hot water. To save time in evaporation, the total volume of wash water should not exceed about 50 ml.

Catch the filtrate and washings in a 250-ml. beaker and evaporate to a volume of 9 ml. Then add 1 ml. of 9 *N* sulfuric acid and precipitate the calcium by adding very slowly from a pipet 90 ml. of methanol while stirring constantly. After allowing the mixture to stand at least 1 hour (several hours if the precipitate is small) filter off the calcium sulfate on a weighed porcelain filter crucible. Wash with successive small portions of 90 per cent methanol, using a total of about 50 ml. Dry and weigh the calcium sulfate as directed under the general procedure.

This procedure is not satisfactory when the iron in the sample exceeds about 3 per cent or the total potassium and sodium about 0.5 per cent. Accurate results for the calcium are not obtained when less than 0.5 per cent is present. Some comparative results on commercial samples, obtained independently by different operators, are shown in Table XII. The results obtained by method B, considered more or less standard on such material, correspond well with the results obtained in this laboratory by the methanol procedure. However, because it does not involve several separations and extended manipulation the latter procedure is probably more accurate in practice, and has the decided advantage of being much shorter.

TABLE XII. DETERMINATIONS OF CALCIUM OXIDE IN SAMPLES OF TECHNICAL MAGNESIUM OXIDE

Method and Laboratory	Sample I, %	Sample II, %	Sample III, %
A[a]	0.80	2.32	0.90
B[b]	0.82	2.25	0.91
C[c]	..	2.10	0.82

[a] Methanol precipitation procedure.

[b] A tedious but apparently accurate method that involved first converting the metals to sulfates and removing the major part of the magnesium sulfate by extraction with ethanol. After dissolving the residual salts, aluminum and iron were removed by ammonia precipitation, and calcium was determined in the filtrate by double precipitation as oxalate.

[c] After removing silica, aluminum, and iron by conventional methods, calcium and magnesium were precipitated together as phosphates. Then the mixed precipitate was dissolved in dilute sulfuric acid and calcium was precipitated as sulfate by addition of ethanol. This precipitate was dissolved and calcium was finally determined by the oxalate method.

Results obtained on the Bureau of Standards argillaceous limestone sample (standard sample 1a) and on the Bureau of Standards dolomite sample (standard sample 88) are shown in Table XIII. In these analyses silica was removed by means of perchloric acid, and the excess perchloric acid was eliminated by volatilization. Because of the small amounts present no attempt was made to remove the iron or aluminum, the filtrates from the silica separation being used directly for the preparation of the solution for the calcium determination. The calcium was precipitated in each sample by method II, the time of standing being varied as shown. That the results on the argillaceous limestone sample are as near as they are to the stated value is due in part to the fact that the strontium oxide in the sample (0.12 per cent) is here counted with the calcium oxide. A deduction of 0.09 per cent from each individual result and from the average should be made to give the percentages due to calcium alone. If this is done the results on the two samples deviate to about the same extent from the stated value, both being a trifle on the low side. On the whole, however, determinations of calcium in carbonate rock by this method are accurate enough for most purposes, and probably as good as those often obtained in practice by the oxalate method.

TABLE XIII. DETERMINATION OF CALCIUM IN STANDARD CARBONATE ROCK SAMPLES

Standard Sample	Sample Taken for Analysis *Gram*	Time of Standing *Hours*	CaO Found *%*
Argillaceous limestone	0.5985	0.5	41.23
	0.5397	0.5	41.28
	0.7182	1.0	41.25
	0.5140	1.0	41.28
			Av. 41.26
Stated average, Bureau of Standards certificate			41.32
Dolomite	0.9334	0.5	30.35
	0.6126	0.5	30.35
	0.8447	1.0	30.28
	0.4445	1.0	30.45
			Av. 30.36
Stated average, Bureau of Standards certificate			30.49

In the course of continuous experimentation with this method over a period of many months no unpleasant physiological effects resulted from working with methanol. Since the solvent contains 10 per cent of water, there appears to be no explosion hazard involved in evaporating filtrates from calcium determinations to dryness in cases where magnesium and alkali metals are in the form of perchlorates from treatment of the original sample with perchloric acid.

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Estimation of Ascorbic Acid in Citrus Juices

An Iodine Titration Method

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THIS iodine titration method for estimation of ascorbic acid was first described before the Food and Nutrition Section of the American Public Health Association in Pasadena, Calif., September 6, 1934, in a paper by A. J. Lorenz, R. W. Reynolds, and J. W. Stevens. Since that time the method has had extensive and satisfactory use by the California Fruit Growers Exchange in the estimation of the ascorbic acid content of citrus juices and various citrus juice products. It also has been used by Mack, Fellers, Maclinn, and Bean (*12*), and Roberts (*16*) in studies on citrus beverages and juices.

In the chemical estimation of ascorbic acid (vitamin C) in various biological materials the two reagents most commonly employed are 2,6-dichlorophenolindophenol and iodine. Titrations with the former reagent are made either in slightly acid solution as originally recommended by Tillmans, Hirsch, and Hirsch (*19*), or in relatively strong acid solution as described by Birch, Harris, and Ray (*2*). The iodine titration is restricted to use in relatively strong acid solution.

An important consideration in the chemical estimation of ascorbic acid is the specificity of the reagent employed. Many plant materials contain in addition to ascorbic acid various reducing substances such as glutathione and certain phenolic compounds which may titrate along with the vitamin. Since iodine is a strong oxidizing agent it may react with these interfering substances and hence the results obtained with the reagent may not be specific for vitamin C. The 2,6-dichlorophenolindophenol, on the other hand, is a relatively weak oxidizing agent and thus does not react so readily with these nonvitamin reducing substances. Because of the greater specificity of this reagent for vitamin C, many workers have preferred it to iodine.

Although the specificity of the method is of vital concern, certain other factors are important: standardization of the reagents employed, stability of the reagents, ease and rapidity of the titration procedure, sharpness of the end point, accuracy or reproducibility of the results, and, for extensive routine testing, the cost of the reagents.

The iodine method has certain advantages and except for its lack of specificity for vitamin C and the indefinite end point it would undoubtedly be used to a greater extent. Careful study of the various factors involved have shown that the most serious objections to its use may be largely eliminated. The interference of nonvitamin reducing substances may be lessened and the end point improved by proper adjustment of the acidity of the titration mixture by the addition of a strong mineral acid as disclosed by Tillmans, Hirsch, and Hirsch (*19*). The end point may be improved further by the use of a double back-titration, which gives better results than the back-titration employed by Tillmans and his associates. The following procedure was adopted for obtaining these improvements in the iodine method for citrus juices.

Method

Twenty milliliters of the natural-strength juice are transferred to a 250-ml. Erlenmeyer flask and 4 ml. of 12 *N* sulfuric acid are added. The added acid lowers the pH of the sample to about 0.02 to 0.08 by the hydrogen electrode. Freshly standardized 0.01 *N* iodine solution is then added until an excess of 1 or 2 ml. is present. Excess iodine may be detected by color change in the sample or by the addition of a drop of starch solution. The test solution is allowed to stand for about 0.5 minute for the reaction to go to completion. Standardized 0.01 *N* thiosulfate solution is now added to give an excess of about 1 ml., with 3 ml. of 0.5 per cent starch solution added as the indicator. A trial titration may be run to determine the amounts of iodine and thiosulfate solutions needed to obtain the desired excess values. Finally, more of the 0.01 *N* iodine solution is added slowly until the well-known starch-iodine end point is reached. The total volume of the iodine solution added minus the volume of thiosulfate solution used (on the iodine equivalent basis) equals the volume of iodine solution consumed by the reducing substances in the sample. One milliliter of 0.01 *N* iodine solution is equivalent to 0.88 mg. of ascorbic acid.

Preparation and Standardization of Reagents

Iodine Solution. An approximately 0.1 *N* stock solution is prepared by dissolving 25 grams of potassium iodide in as little distilled water as possible and then adding about 12.7 grams of resublimed iodine. After the iodine has dissolved, the solution is diluted to 1 liter with distilled water. The solution is protected from light by storing in a dark or wrapped bottle. From this stock solution the 0.01 *N* solution is prepared as needed for use in the ascorbic acid titration by diluting about 100 ml., together with 22.5 grams of potassium iodide, to 1 liter.

The normality of the dilute solution is checked, at the time of use, by titration of 20- or 25-ml. portions with standardized 0.01 *N* thiosulfate solutions, using starch solution as the indicator. The starch solution, about 3 ml., is not added until the titration is almost complete.

Starch Solution. The 0.5 per cent starch solution is prepared according to the procedure outlined by Treadwell and Hall (*20*). Five grams of powdered potato starch are triturated into a paste with a little water and poured slowly into a liter of boiling distilled water. Boiling is continued 1 or 2 minutes to obtain a nearly clear solution. The solution is cooled and allowed to stand several hours and is then filtered and transferred to 50-ml. bottles. After heating for about 2 hours in a steamer, or water bath, the bottles are closed with cork stoppers that have been dipped in hot paraffin. Starch solution prepared in this manner will give a good color reaction and retain its sensitivity for several months and is preferred to most of the soluble starch preparations. The solution may lose its sensitivity within a few days after the bottle is opened, usually because of mold growth.

Thiosulfate Solution. The convenience of the iodine titration method depends to a considerable extent upon the stability of the thiosulfate solution used as the standardizing agent, and consequently particular attention should be given to its preparation.

The deterioration of thiosulfate solutions has been attributed to a number of causes and several methods have been advanced for stabilizing the reagent. Kolthoff (*8*), Mayr (*13*), Schulek (*17*), Winkler (*21*), Hahn and Clos (*5*), Kolliker (*7*), and others are of the opinion that the deterioration of the reagent is due largely to the action of certain types of bacteria. Hahn and Windisch (*6*), Mayr and Kerschbaum (*14*), and Law (*9*) have pointed out the significance of carbon dioxide in the deterioration processes. Traces of copper may catalyze the decomposition of the solution as shown by Abel (*1*), Skrabal (*18*), and Hahn and Clos (*5*). Atmospheric oxidation and the catalytic effect of light are also recognized as factors.

The stability of the solution prepared by the procedure outlined below is probably due to the substantial exclusion of bacteria, carbon dioxide, and light as deterioration factors.

The approximately 0.1 *N* thiosulfate stock solution is prepared as follows:

The distilled water for the solution is placed in a Florence flask, or some other glass container that will stand boiling over a flame. A rubber stopper, with suitable connection for a buret and with soda-lime tube attached, is inserted loosely in the mouth of the flask. The flask is then placed over a gauze-covered flame and the water boiled for about 15 minutes. During this operation the soda lime should be protected from the steam. After boiling has stopped the thiosulfate crystals, 25 grams per liter of solution, are added and the stopper of the flask is pressed down firmly and secured. The connection for the buret should also be closed, so that any air drawn into the flask upon cooling will enter through the soda-lime tube, which should contain a cotton pad on either side of the soda lime. The thiosulfate crystals are dissolved by agitation and the solution is cooled. The buret, also fitted with a soda-lime tube, is attached and the solution is protected from light.

The thiosulfate solution is standardized essentially as described by Bray and Miller (*3*). The procedure is as follows:

A 0.1 *N* solution of potassium dichromate is prepared by dissolving 4.9035 grams of potassium dichromate, which has been recrystallized 2 or 3 times from water and dried for 48 hours at 110° C., in distilled water and diluting to 1 liter. Twenty-five milliliters of the dichromate solution are transferred to a 1-liter flask containing 2 grams of potassium iodide dissolved in 70 ml. of water, with 3.4 ml. of 6 *N* hydrochloric acid added for acidification. After standing in the dark for about 10 minutes, the solution is diluted to 500 to 600 ml. and titrated with the thiosulfate solution, with about 3 ml. of starch solution added as the indicator very near the end of the titration. The solution turns from blue to green in color at the end point. The normality of thiosulfate solution is calculated on the basis of the dichromate solution as exactly 0.1 *N*.

Other reliable methods of standardizing the thiosulfate solution are available. Before adopting a method at least two of the recognized methods should be employed in parallel. This comparison will enable the operator to prove the accuracy of the method preferred for continued use.

The thiosulfate solution is diluted to 0.01 *N* strength, preferably with freshly boiled and cooled water, for use in standardizing the iodine solution and in the ascorbic acid titration procedure. The 0.01 *N* solution deteriorates relatively fast and hence should be prepared fresh each day. The stock solution maintains its strength for several months.

Discussion

The iodine titration procedure outlined above differs from the ordinary iodine technic in two essential respects—namely, the high acidity under which the titration is carried out and the double back-titration.

Sufficient sulfuric acid must be added to lower the pH to about 0.02 to 0.08 to obtain a sharp end point. Lack of acid causes a sluggish titration and an indefinite end point. Furthermore, in the presence of the high acidity, iodine is more nearly specific for vitamin C. The amount of acid recommended is near the upper limit for obtaining a satisfactory titration.

The work of Fujita and Iwatake (*4*), Musulin and King (*15*), Mack and Tressler (*11*), Lorenz (*10*), and others on the use of metaphosphoric acid in the chemical estimation of vitamin C indicates that the acid might be a satisfactory substitute for sulfuric acid in the iodine method.

Sulfuric acid in excessive concentrations may liberate free iodine from the potassium iodide present in the iodine solution, but the quantity of acid recommended will not liberate sufficient iodine in 10 minutes to give a color with starch. The titration will, of course, be complete in considerably less time.

The procedure of adding an excess of iodine, then an excess of thiosulfate, followed by titration of the excess thiosulfate, was adopted to improve the end point. If the titration is carried out directly with iodine, the reaction proceeds too slowly near the end, giving irreproducible results. By adding an excess of iodine all substances capable of being oxidized by the reagent under the existing conditions are oxidized quickly and completely. The added thiosulfate then reacts quickly and quantitatively with the excess iodine. Excess thiosulfate is used, then back-titrated with more iodine to the end point because in titrating solutions containing large amounts of colored substances, such as orange juice or tomato juice, the end point can be detected better by the appearance of the blue color than by its disappearance. The addition of a few extra drops of iodine solution after the reading has been taken shows definitely that the end point has been passed, which is not possible when the end point is shown by the disappearance of color.

A large excess of iodine will result in a high titer, but this is not serious provided the excess does not exceed about 3 ml. The time the excess iodine is allowed to react is likewise not of particular importance if the reaction time does not exceed 3 minutes. The temperature of the solution is not important within the range of about 18° to 30° C.

The method must be used with caution in the estimation of ascorbic acid in canned juices. Higher than true values may be obtained, possibly because of the presence of ferrous iron and stannous tin. Misleading results may therefore be encountered in any canned juice when corrosion of the tin plate has occurred.

The essential oils of citrus fruits may interfere with the chemical estimation of vitamin C in juice products, causing slightly high results, but this source of error may usually be neglected.

The iodine method has the same limitation in the estimation of ascorbic acid in old oxidized products as the other chemical methods. Reversibly oxidized ascorbic acid, which is still biologically active, is not detected directly by the chemical methods. Various procedures have been offered for the application of chemical methods to the estimation of this form of the vitamin, but the methods are rather complicated for routine work and the uncertain evaluation of the results leaves much room for improvement in this direction.

The 2,6-dichlorophenolindophenol method and the improved iodine method give, on the average, nearly identical results with citrus juices. The iodine method is thus satisfactory for use in following the retention of vitamin C during the manufacture and storage of various citrus juice products. Its advantages are as follows: (1) It has a nonfading end point with a deep blue color that can be detected in the presence of any but the darkest colors. (2) Reproducibility of results is ensured by the definite nonfading end point. (3) Only common, inexpensive chemicals, available in almost any laboratory, are used. (4) The reagents employed can easily be standardized by well-known methods. (5) The reagents employed are relatively stable and can hence be made up in large quantities, thus saving much time.

The 2,6-dichlorophenolindophenol method, with one of the standard procedures, should be employed for vitamin C exploratory work. For more or less routine control work, however, where it has been shown by trial that the modified iodine method gives substantially the same results as the 2,6-dichlorophenolindophenol method, the advantages of the iodine method commend its use.

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Determination of Formic Acid

A Simplified Procedure

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FORMIC acid is determined ordinarily, in the presence of other acids, by oxidizing with a mercuric salt and then determining the quantity of carbon dioxide evolved or the weight of mercurous compound produced. Recently Weihe and Jacobs (*7*) proposed mercuric acetate solution as an oxidizing agent because of its superiority over insoluble mercuric oxide. The use of an oxidizing agent in solution has a number of advantages: (1) It allows the oxidation to be carried on slowly and smoothly, thus preventing loss of carbon dioxide due to failure of the system to absorb a large amount of gas suddenly evolved; (2) it allows a close control of the amount of oxidant added; and (3) it prevents admission of carbon dioxide from the air during addition of the oxidant.

The behavior of a number of materials such as acetone, glycerol, ethanol, methanol, oxalic acid, lactic acid, furfural, acetaldehyde, etc., was studied by Weihe and Jacobs, who found that these substances did not interfere appreciably with the determination of formic acid. The error in the determination of pure formic acid was about 0.25 per cent. However, the apparatus was relatively complicated, requiring a mercury pump to recirculate the gases evolved through barium hydroxide solution in a closed system. Therefore it was felt that the usefulness of this method could be increased greatly by simplification of the apparatus.

Various methods of absorption have been used in determining the carbon dioxide evolved from formic acid (*2*, *4*, *7*). However, the fritted-glass absorber, used successfully for the absorption of carbon dioxide by Thomas (*5*), Wells, May, and Senseman (*8*), and Waugh (*6*), has not been used previously in the determination of formic acid. Since the use of an oxidizing solution such as mercuric acetate allows the oxidation to take place slowly, it was felt that the fritted-glass absorber would be ideal for absorbing the carbon dioxide produced. Furthermore, the use of strong solutions and a large excess of absorbents could be avoided, since Wells, May, and Senseman have shown that under the conditions used less than a 10 per cent excess of 0.1 *N* sodium hydroxide solution was sufficient to absorb all the carbon dioxide evolved.

Description of Apparatus

The glass absorber, *A* (Figure 1), consisted essentially of a glass tube 70 cm. long having an inside diameter of 1.8 cm. and provided with a fine fritted-glass disk, *B*, sealed into the bottom. A tube of this length permitted the use of as much as 75 cc. of solution without danger of loss by entrainment. Bruce and Bent (*1*) described a method of making such disks, which was modified by Wells, May, and Senseman (*8*). The manufacture of fritted-glass disks has been patented (*3*).

Absorber *A* was inserted through a No. 11 rubber stopper, *C*, with an outlet tube, *D*. The absorber fitted tightly but was lubricated with glycerol, allowing ready movement through the stopper. The absorption tube was connected to the vacuum, *L*, at the upper end by a stopper and tube, *M*. The stopper, *C*, fitted a soft-glass titrating bottle, *K*, of about 300-cc. capacity. A second stopper, *N*, provided with two openings, was used to close the flask during the titration and exclude atmospheric carbon dioxide (Figure 2).

A bent glass tube, *R*, approximately 2 mm. in internal diameter and long enough to reach nearly to the bottom of flask *K*, was used to introduce the titrating acid under the surface of the solution, thereby reducing the possibility of losing carbon dioxide during the titration. The tube was connected to the flask by a short piece of moderately heavy rubber tubing. The horizontal section was about 10 cm. in length to assure free movement of the flask. To reduce danger of diffusion, the tube was constricted to about 0.5 mm. at the tip. The oxidation flask was a 200-cc. three-necked, round-bottomed Pyrex flask, *E*, fitted with a Friederich condenser, *F*, a dropping funnel, *G*, and a tube, *H*. Tube *H* was slightly constricted at the lower end and connected at the upper end to a long soda-lime tube, *I*. The reaction flask and absorber were connected by a rubber tube, *J*. A screw clamp, *Q*, was used to regulate the vacuum. A spring clamp was used at *P* to prevent the liquid from backing up into *H*.

Procedure

Introduce the sample, containing 50 to 100 mg. of formic acid, into flask *E*, dilute to 50 cc. with water, and add 5 cc. of *N* acetic

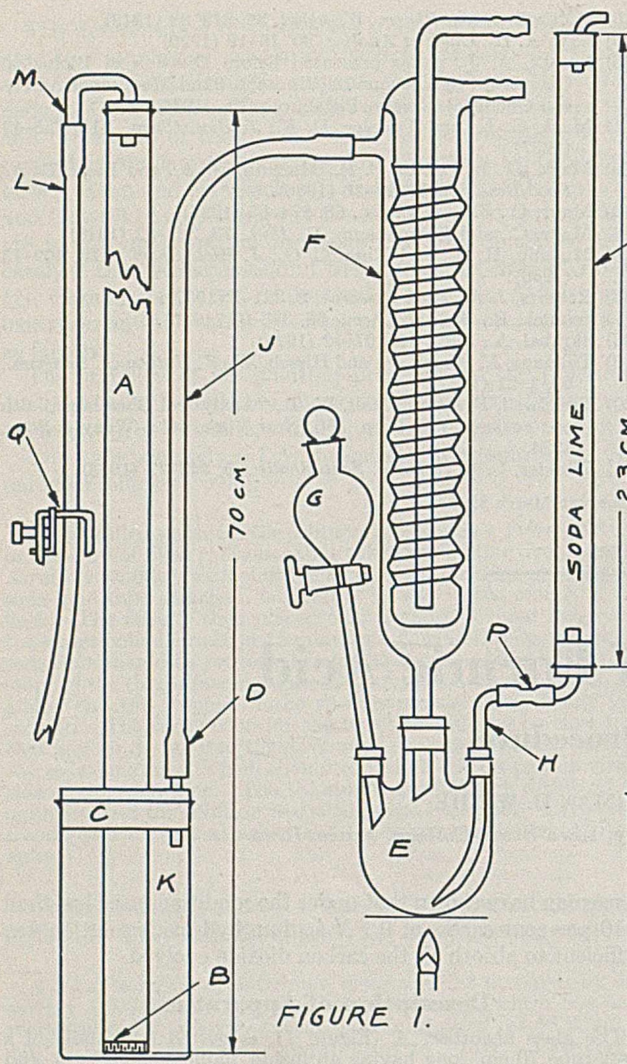

FIGURE 1.

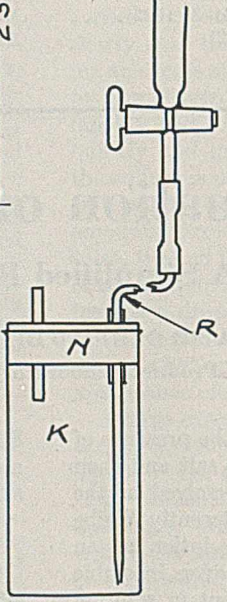

FIGURE 2.

acid. If necessary, a small particle of paraffin may be added to reduce foaming. Measure 20 cc. of mercuric acetate solution into the closed funnel, *G*. (The oxidizing solution, which was kept stoppered, was made by dissolving 100 grams of mercuric acetate in 1 liter of approximately 0.5 *N* acetic acid, and gently boiling for 1 hour to remove carbon dioxide.) With absorber *A* disconnected from the apparatus, connect the lower end of tube *J* directly to vacuum *L* and, by means of screw clamp *Q*, regulate the passage of air to about 200 to 250 cc. per minute.

Boil gently for 10 minutes to remove carbon dioxide, guarding against too vigorous boiling which may force the liquid back through tube *H* into the soda-lime tube, *I*. In the meantime place 4 drops of butyl alcohol in bottle *K* and follow by 50 cc. of approximately 0.1 *N* sodium hydroxide solution, which need not be previously standardized. Quickly connect bottle *K* to absorber *A* by means of stopper *C*. At the end of the 10-minute boiling period remove the flame, attach a spring clamp at *P*, disconnect the lower end of tube *J* from the vacuum line, connect it to bottle *K* at tube *D*, and attach vacuum line *L* to tube *M*. Replace the flame and remove the spring clamp at *P*. When gentle boiling begins, allow the oxidizing solution in funnel *G* to drop slowly, over a 5- to 10-minute period, into the reaction mixture.

After 20 minutes remove the flame, attach the spring clamp at *P*, remove the stopper from the top of absorber *A* and tube *J* from *D*. Raise absorber *A* through the stopper sufficiently to clear the final volume of solution, but not far enough to prevent washing. Let the absorbing solution drain from *A*. (This may be hastened by gentle suction at *D* or better by a slight pressure applied through a soda-lime tube at the top of *A*.) Wash the tube with three 40-cc. portions of carbon dioxide–free hot water, draining each completely. Remove stopper *C* and quickly wash the bottom end of absorber *A*, allowing the washings to drain into bottle *K*. Close *K* immediately with stopper *N*. Add 10 cc. of 15 per cent barium chloride solution by pipetting it through one of the openings in *N*. Then add several drops of phenolphthalein. (This should not be added before precipitation, as it has a tendency to be occluded in the precipitate.) Before titration of the excess alkali, the tube (*R*, Figure 2) should be full of the acid solution and free from air which has a tendency to be trapped in the rubber connection. Titrate with 0.1 *N* hydrochloric acid solution, swirling the solution vigorously during the titration.

Correct for any carbon dioxide from the reagents used or introduced from the air by making a blank determination in exactly the same manner on 50 cc. of the alkali used. The difference in acid used is proportional to the formic acid content of the sample. (One cubic centimeter of 0.1 *N* hydrochloric acid is equivalent to 0.0023 gram of formic acid.)

TABLE I. DETERMINATION OF CARBON DIOXIDE FROM SODIUM CARBONATE AND FROM OXIDATION OF FORMIC ACID

Material Used	Carbon Dioxide in Sample Calculated	Found	Difference	Error
	Gram	*Gram*	*Gram*	*%*
Sodium carbonate	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	
	0.0905	0.0908	0.0003	+0.33
Formic acid	0.0994	0.0999	0.0005	
	0.0994	0.0997	0.0003	
	0.0994	0.0999	0.0005	
	0.0994	0.0997	0.0003	+0.40 (av.)

Accuracy of Method

In Table I are recorded a number of results showing the efficiency of the absorption tube described using sodium carbonate solution and pure formic acid. In each case the end point was determined readily within 0.1 cc. and the error was found to be +0.33 per cent based on titration of the sodium carbonate solution. When pure formic acid was used, an error of +0.40 per cent was found.

Summary

A simplified and efficient procedure for the determination of formic acid is described, using a fritted-glass disk absorber to determine the carbon dioxide produced by the oxidation of the formic acid with mercuric acetate solution.

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Estimation of Boron by a Modified Flame Test

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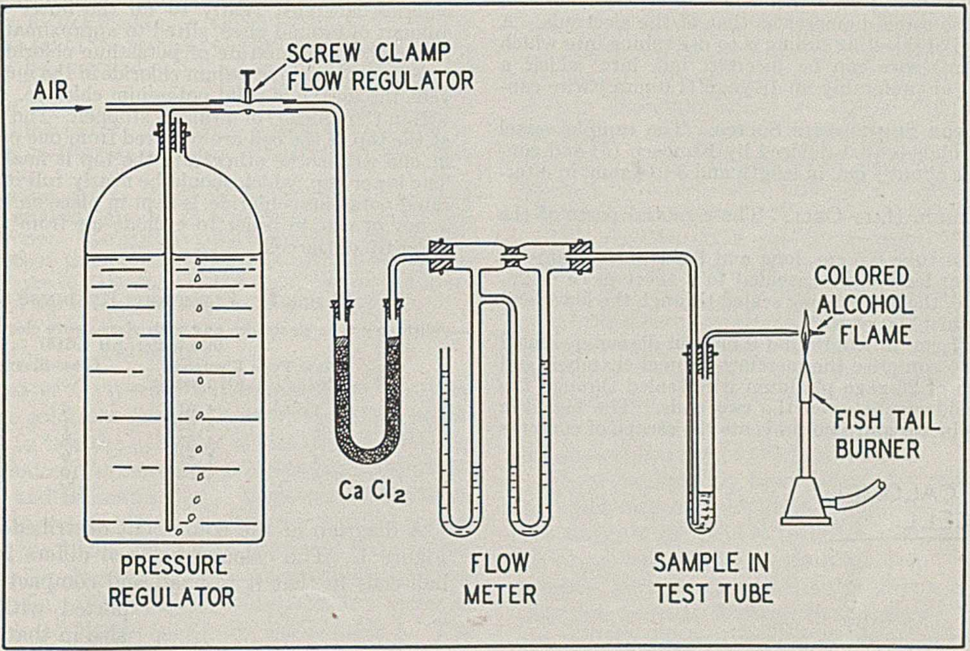
THE flame test, in which concentrated sulfuric acid and methyl alcohol produce a volatile boron compound, is commonly used for the detection of boron in some laboratories. The effects of the ratio of acid to alcohol, the temperature of the solution, and the amount of water present are presented by Stahl (*1*), who has devised a quantitative measurement of boron based on the intensity of the green coloring in the flame using a comparative standard. He claims an accuracy of 15 per cent.

Using the apparatus herein described, although the intensity of color in the flame diminishes at a marked rate when the amount of boron in the sample reaches 0.03 mg., the total time of duration of color is almost a straight-line function of the boron content up to about 0.1 mg. By successive dilution, a more concentrated sample of boron may be quickly analyzed, using this method.



The figure shows the apparatus used. Air passes at a rate of 150 cc. per minute through a calcium chloride drying tube and a flowmeter into the bottom of a test tube, where it bubbles through the 7 cc. of liquid containing the boron sample. A mixture of air, alcohol vapor, and methyl borate passes out the top of the test tube, through the nozzle, and through the thin part of a fan-shaped Bunsen flame, igniting and forming a small auxiliary flame at right angles to the other. It is this small flame that is colored distinctly green as long as an appreciable amount of methyl borate is present. The alcohol flame itself is blue-green, but the green imparted to the flame by the boron is enough different so that one has but little difficulty recognizing an end point. Observation of the flame at intervals of a few seconds is recommended rather than continuous observation. That point when the constant blue-green of the alcohol flame is noted at two successive observations is taken as the end point. After a few trials this point is readily determined.

To check the accuracy of the method and its ease of application, an apparatus was assembled and operated by an inexperienced observer. Two standard solutions were made up—one with 0.570 gram of boric acid, 2 grams of potassium hydroxide, and distilled water to make 1 liter, and the other by diluting 50 cc. of the first to 250 cc. One cubic centimeter of the first had an equivalent of 0.10 mg. of boron, and 1 cc. of the second, 0.02 mg. By placing a sample having the equivalent of 0.02 to 0.10 mg. of boron in a test tube, evaporating almost to dryness, adding a mixture of 6 cc. of methyl alcohol and 1 cc. of sulfuric acid, and placing the test tube in the apparatus, a green color was imparted to the flame. The duration of the color was proportional to the amount of borate present. The results shown in Table I were obtained by these tests, the times to the end points being recorded on a stop watch, the dial of which had been covered.

Table I. Estimation of Boron

Boron Present *Mg.*	Observed Duration of Flame *Sec.*	Average Duration of Flame *Sec.*
0.02	80, 82, 80, 75	79
0.04	170, 140, 135	148
0.06	265, 255	260
0.08	355, 275, 310, 330	318
0.10	390, 315, 340, 365, 360, 370, 410, 420, 365, 355, 360, 350, 325, 375, 330	362

The spread between the various tests is due in part to difficulty in holding the Bunsen flame in a single position. With a little practice an accuracy better than one significant figure may be obtained even for traces of boron, especially if the tests be carried out in a somewhat darkened room.

Difficultly soluble materials such as glasses are analyzed by fusing the sample in a nickel crucible with potassium carbonate, dissolving the fusion in distilled water, taking a suitable aliquot, and evaporating almost to dryness. The residue is acidified with sulfuric acid and then analyzed as outlined above. Even on glasses containing less than 1 per cent of boric oxide, checks of 10 per cent or better may be expected.

Acknowledgment

The authors wish to thank W. T. Hall for his helpful suggestions.

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A Simplified Quinhydrone Electrode

Application in Determining the H-Ion Concentration of Liquids and Semiplastic Solids

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THE modifications in the design of the quinhydrone electrode and calomel half-cell described herein have been made to simplify the work of preparing electrodes and conducting pH determinations, to increase the accuracy of tests, and to increase the portability of the equipment.

Apparatus and Procedure

ELECTRODE. The electrode consists of a platinum wire 10 cm. in length and approximately 0.6 to 0.65 mm. in diameter, or 22-gage (B and S), plated with gold.

SAMPLE TUBE FOR LIQUIDS. The sample vessel consists of a capillary Pyrex brand glass tube 7.5 cm. in length and 0.85 to 1.0 mm. in internal diameter, with a cup-shaped enlargement about 0.5 cm. in diameter at one end and with the other end flamed to about the same diameter as that of the electrode. A convenient method of selecting tubing is to use tubing into which a 20-gage (0.8-mm.) wire can be inserted but into which a 16-gage (1.3-mm.) or preferably an 18-gage (1.0-mm.) wire cannot be inserted.

SAMPLE TUBE FOR SEMIPLASTIC SOLIDS. The sample vessel for use with soft solids is that devised by Knudsen (*3*) and consists of a glass tube about 4 cm. in length and 3 to 4 mm. in internal diameter.

PORTABLE CALOMEL HALF-CELL. The essential parts of the cell are as follows:

A, an inner glass tube 6.5 cm. long and 3.5 mm. in diameter containing a copper lead-in wire welded to a short piece of 26-gage platinum wire, the latter being sealed through the lower end of the tube to conduct the current.

B, a glass tube 7 cm. in length and 9 mm. in diameter, sealed at the lower end to comprise the mercury-calomel chamber, and with a short piece of 26-gage platinum wire sealed through the wall at a point midway between the two ends. The sealed-in wire acts as a conductor and also prevents the escape of contents from the mercury-calomel chamber; it is the essentially new feature in this cell and makes it possible to ship or transport the cell without damage.

C, an outer glass tube 7.5 cm. in length and 1.75 cm. in diameter, to the lower end of which is sealed a tube 4 cm. in length and 7 mm. in diameter with a 1-mm. capillary which is flamed to about 0.65 mm. at the tip end.

A lower glass cap 3 cm. in length and of the proper size to fit on a No. 0 rubber stopper.

To assemble the cell, 0.25 cc. of pure mercury and a small amount of calomel are placed in tube *B*. Tube *A* is inserted within *B*, and sufficient amounts of crystalline potassium chloride and saturated solution of potassium chloride are added to *B* nearly to fill it. *A* is then fastened within *B* by means of a rubber stopper. A thick layer of crystalline potassium chloride is placed in *C* and a sufficient amount of a saturated solution of potassium chloride is added nearly to fill the outer chamber. A small amount of ground glass, sifted to approximately 0.75-mm. mesh, is added to the mixture of potassium chloride crystals and saturated solution of potassium chloride in the outer chamber, to prevent the escape of solid potassium chloride. Tube *B* is fastened within *C* by means of a rubber stopper. The two rubber stoppers at the top of the cell are so bored from one original stopper as to fit one within the other, and the top is finally sealed with wax. The lower cap, which should be nearly full of a solution of saturated potassium chloride, is kept in place on the cell when the cell is not in use, in order to exclude air from the capillary at the lower tip of the cell.

TABLE I. ELECTRODE READINGS OBTAINED

(With new type electrodes and with glass-sleeve electrodes in standard acetate buffer, pH 4.618)

New Type Electrode No.	pH reading	Glass-Sleeve Electrode No.	pH reading
1	4.61	6	4.61
2	4.62	7	4.61
3	4.62	8	4.63
4	4.61	9	4.63
5	4.60	10	4.61

A diagram of the equipment described above is shown in Figure 1. The calomel half-cell differs from other calomel half-cells in that it is small and compact and can be transported without damage, and also in that the electrical current is conducted from the mercury-calomel chamber to the solution of potassium chloride in the outer chamber by means of a platinum wire sealed in the wall of tube *B*, as shown in Figure 1. This sealed-in wire serves not only as a conductor, but also to retain the contents within tube *B*, a function which has been accomplished in other cells by the use of a stopcock or a plug of cotton, asbestos fiber, or agar.

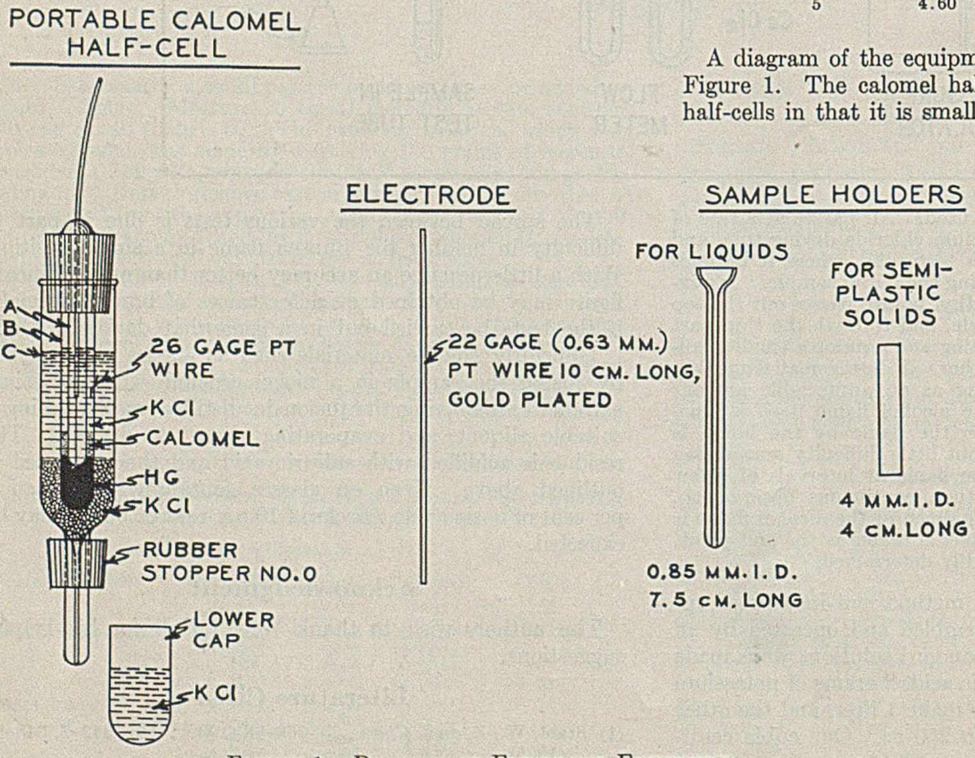

FIGURE 1. DIAGRAM OF ELECTRODE EQUIPMENT

Calomel cell, electrode, and sample vessels for pH determinations

DETERMINATION OF pH IN LIQUIDS. The capillary sample tube described above is rinsed with the test liquid by immersing the tip of the tube in the liquid and moving the tube upward and downward, the tube being held in a nearly horizontal position. Quinhydrone is applied to the electrode by any one of the three following methods: (1) A small amount of quinhydrone is mixed with the test liquid. (2) The electrode is wetted in the test liquid and dipped into quinhydrone crystals. (3) The electrode is wetted and dried alternately by dipping it into a saturated solution of quinhydrone in acetone, a layer of quinhydrone crystals thus being deposited on the surface.

The electrode, which is bent slightly so that it retains its final position within the tube, is inserted into the tube and the tip of the tube is immersed in the test liquid. The electrode is now moved upward and downward within the tube and capillary force causes the liquid to rise nearly to the top of the tube. The tip of the tube, with the lower end of the electrode at a point about 5 mm. above the lower end of the tube, is then immersed slightly below the surface of a solution of saturated potassium chloride which is contained in a small beaker, the lower tip of the calomel cell being also immersed in the same solution. With the lead-in wire of the calomel half-cell connected to the proper wire leading to the potentiometer, the other potentiometer wire is now connected to the top of the electrode and the voltage is read. The connections are made in the manner described by Watson (*8*). The complete circuit is as follows: potentiometer, wire to calomel cell, calomel cell, saturated solution of potassium chloride contained in a small beaker, capillary sample tube containing sample and electrode, and wire to potentiometer. The solution of potassium chloride in the beaker, in which both the tip of the calomel cell and the tip of the sample tube are immersed for making readings, must be removed and the beaker must be cleaned frequently.

After being used, the sample tubes are cleaned in soap solution and rinsed in distilled water. A 26-gage copper wire is used in cleaning the tubes and excess moisture is finally removed from the tubes by suction.

DETERMINATION OF pH IN SEMIPLASTIC SOLIDS. Two or 3 grams of test material are ground in a mortar with about 0.05 gram of quinhydrone. The sample tube is filled by tapping one end into the mixture in the mortar. The electrode is inserted into the sample in the tube to a depth of about 5 mm. above the lower end of the tube and the reading is made as described above.

Accuracy

A large number of comparative determinations has been made in the same solutions and test materials, over a period of several years, to test the accuracy of the new electrode as compared with that of the conventional glass-sleeve type designed by Cullen and Biilmann (*1*, *2*). Electrodes of the latter type were made by welding 22-gage platinum wires to copper wires and sealing the former into tubes of special glass known as No. 881 Corning Normal Tubing, then filling the glass sleeves with paraffin. Representative data from a series of tests with gold-plated electrodes are shown in Table I. The results have shown that the accuracy of the new type electrode is equal to that of the conventional type. In tests in various dairy food products, principally milk, whey, and cheese, duplicate readings correspond within 0.01 to 0.02 pH unit.

Long-continued use of the electrodes in testing milk and cheese samples has shown that cracks in the glass seals of glass-sleeve electrodes and failure to plate platinum electrodes with gold are frequently sources of error. This observation is in corroboration of results reported by Morgan and associates (*4*) and by Watson (*8*); the results indicate that while these factors may be negligible as sources of error in testing pure solutions, they become very important when organic materials of a complex nature are being tested. Watson (*8*) has previously shown that gold plating is essential in preventing and correcting poisoning of electrodes when samples of cheese are being tested. The data in Table II indicate the extent of the errors caused by cracks in the glass seals and by failure to plate platinum electrodes with gold.

TABLE II. ELECTRODE READINGS OBTAINED

(With new type electrodes and with glass-sleeve electrodes in daily use in testing samples of milk, whey, and cheese—test solution, standard acetate buffer, pH 4.618)

	Unplated Platinum			Gold-Plated Platinum		
Type of Electrode	No.	When prepared	After one month's use	No.	When prepared	After one month's use
New	1	4.61	4.60	9	4.61	4.61
	2	4.62	4.65	10	4.61	4.60
	3	4.63	4.64	11	4.62	4.63
	4	4.61	4.59	12	4.61	4.63
Glass-sleeve	5	4.58[a]	..	13	4.62	4.63
	6	4.61[a]	4.66	14	4.61	4.62
	7	4.62	4.59	15	4.63	4.61
	8	4.61	4.59	16	4.63	4.63

[a] Cracks developed in the glass seals in two of eight electrodes.

Discussion

The accuracy of the new electrode has been found to be within 0.01 to 0.02 pH unit. The percentage of defective electrodes, which is high among those of the conventional type, has been greatly reduced in the new type; such inaccuracies as result from cracks in the glass seal and the development of other defects incident to the use of the glass sleeve have been eliminated. The electrodes rarely become defective during use and when one is found to yield inaccurate values it is only necessary to replate it. The work of preparing electrodes is greatly reduced and breakage is entirely eliminated. Tests may be made in as little as 2 drops of liquid. The small size of the capillary has the further advantages that temperature equilibrium is attained almost instantly, a minimum amount of surface area of the sample is exposed to the air, and a large proportion of the surface of the electrode is in contact with the test material.

The modifications presented have resulted from work previously described in abstract form (*7*) in which the pH of cheese and other materials was obtained by inserting the quinhydrone-coated electrode into the test material and making the reading directly. Since no method has been found for removing the trace of quinhydrone which is deposited in the test material, the direct measurement by means other than with a glass electrode is considered inapplicable to food materials and has been abandoned.

There has recently been described a quinhydrone electrode and auxiliary equipment (*5*, *6*) for use in piercing tissues to the source of the fluid to be tested and for determining the pH of physiological fluid thus extracted. The equipment resembles that described herein in that a plain wire (36-gage) electrode is used; it differs in that its special application is in the withdrawal and testing of physiological fluids, while the equipment described above has general application in the testing of liquids and semiplastic materials.

Summary

Modifications of the quinhydrone electrode, sample vessel, and calomel half-cell are described, in which a plain gold-plated platinum wire is substituted for the conventional glass-sleeve electrode and in which a sealed-in platinum wire is substituted for a stopcock in the calomel half-cell. The application of the new electrode and portable half-cell in determining pH values of liquids and semiplastic materials is described.

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Determination of Carbon and Hydrogen

A Compact, Movable, and Easily Built Combustion Train

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DURING their research the authors needed a fairly rapid and reliable method for the analysis of compounds containing carbon and hydrogen, which would give consistent results with a moderate amount of training on the part of the operator and which did not have to be in constant use and adjustment.

The micromethod could be used successfully only if proper space and conditions were permanently available for the rather expensive microbalance and unwieldy combustion train (*6*). Moreover, unless a well-trained analyst is constantly engaged in microanalysis of carbon and hydrogen consistent results cannot be expected.

The macromethods which use samples of about 200 mg. are too slow, no more than one or two analyses being carried out in one day Although good results can be obtained more consistently than by the micromethod by a less trained operator, error is introduced because of the large amounts of oxygen or air used to burn so large a sample. An error in one analysis means that a whole day's work has been wasted.

Therefore a study was undertaken in order to develop an apparatus for the analysis of samples large enough to be conveniently weighed by the macrobalance but small enough to ensure rapid combustion. As 50 mg. can be weighed with an accuracy of 2 parts per thousand on a macroanalytical balance, this sample was chosen as the lower limit in size. After a careful study the upper limit of about 125 mg. was taken, as the largest sample which can be burned completely in a combustion train within 2 hours, and about 70 mg. was decided upon as a convenient sample.

Systems for the combustion of samples of such magnitude have been reported (*1–5*), but all have some disadvantage which renders them of little value for the authors' purpose. (1) It is assumed that a permanent place, usually a long desk, in the laboratory can be devoted exclusively to the analysis, whereas in view of limited space the authors needed a compact train which could be lifted and placed under the table without dismantling the apparatus. (2) These methods have the common error of neglecting to measure the volume of the gas used. The importance of this factor has been fully appreciated in microanalysis but not in macroanalysis. The authors found that when the time and bubble rate were controlled, they could not attain the reproducibility that could be realized by actually using a measured quantity of oxygen.

Requirements of Apparatus

In order to overcome these difficulties an apparatus was built which had the following specifications.

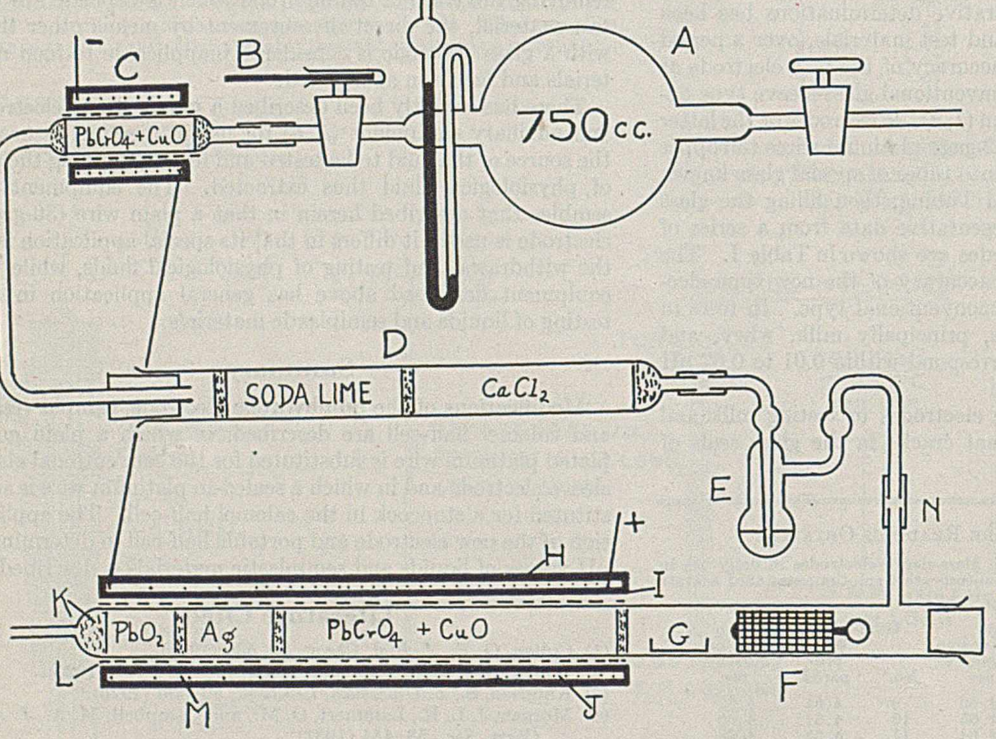

FIGURE 1. DIAGRAM OF APPARATUS

A. Gasometer
B. Stopcock lever
C. Preheater
D. Scrubber
E. Bubble counter
F. Copper oxide spiral
G. Platinum boat
H. Aluminum-painted asbestos
I. Inner asbestos insulation
J. Heating coil
K. Asbestos plug
L. Iron or Nichrome gauze
M. Heating coil widely spaced
N. Connection (at right angle to page)

COMPACTNESS. Figures 1 and 2 indicate how a compact and movable apparatus was secured. A single straight tube replaces the usual series of absorption tubes as scrubber for the elimination of water and carbon dioxide after the oxygen has passed through the preheater. By leading the train back and forth, the apparatus is made to occupy a space equal to the length of the combustion tube. When the tubes for absorption of carbon dioxide and water have been removed and stored in a desiccator, the whole apparatus can be lifted with one hand and conveniently stored without disturbing any of the setup, other than to disconnect it from the oxygen tank.

REPRODUCIBILITY OF RESULTS. On careful study, it was found that, if a slight modification of the Pregl "universal filling" (*6*) were used, practically any substance usually encoun-

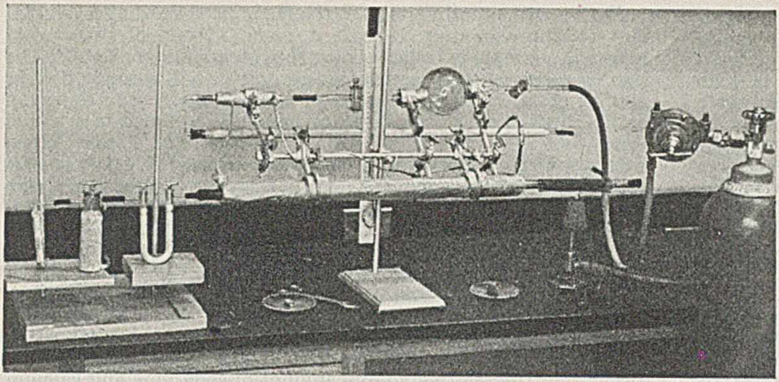

Figure 2. Photograph of Apparatus

tered could be completely burned. It was then observed that, on regulating the bubble counter and controlling the time, there could be as much as 100 per cent difference in the volume of oxygen used in two successive combustions, results were not consistent, and only an individual who had worked for some time with the apparatus could obtain reproducible results. It was decided, therefore, to include a gas-measuring device in the outfit. The Mariotte flask (*6*) was discarded because it is unwieldy, has no place in a movable apparatus, and reduces the pressure in the train so that it has a tendency, unless carefully controlled, to drag over incompletely burned vapors. These disadvantages were overcome by using a light gasometer, as shown in Figure 1, which may be placed behind the combustion train to drive the gas through under slight pressure. This same gasometer may be used in the Dumas nitrogen determination to measure the amount of carbon dioxide used.

Low Cost. The entire apparatus can be built from material usually found in the laboratory. Pyrex tubing may be used throughout. Earlier experimenters avoided Pyrex tubing as having too low a softening point, probably because of the tendency of an inexperienced operator to overheat the tube with gas flames. The authors have seen numerous cases where even the hardest glass has been badly distorted because of superheating, and if the Pyrex tube is heated directly by a roaring flame during the combustion the glass will easily distort under the internal pressure. If, however, the tube is encased in a short length of iron gauze and a moderate blue flame is used, the tube will last indefinitely. A temperature of 550° C. is adequate to burn most organic substances in a stream of oxygen and in the presence of lead chromate and copper oxide. When the apparatus is to be used by students, a harder glass should be used or the flame replaced by a small independent heating unit, 8 cm. in length, set at 550° C., which may be slid back and forth. This unit is easily built as described below.

More expensive combustion tubes of silica, Bohemian glass, hard Corning glass, and Supremax glass have been used, and have an advantage in their resistance to superheating and in that the combustion may be carried out more rapidly at a higher temperature (650° C.).

The authors are still using a Pyrex tube which has been in continuous service for several months. This tube, at 550° C., has expanded under the internal pressure to fit the surrounding wire gauze snugly, without impairing its efficiency.

This combustion train is recommended especially for the organic chemist, who can usually obtain more than 50 mg. of material for analysis and who wishes a method which will give consistent results without special effort. It is also recommended for students or as a teaching device for organic analysis where space is limited, only macrobalances are available, and consistent results are sought by the less skilled analyst. The apparatus does not lose its accuracy if not in continuous use. It can be built, when materials are available, in 1 or 2 days.

The authors attempted to analyze samples as small as 2 to 3 mg. with this apparatus, using a microbalance and microabsorption tubes. Although preliminary results were encouraging, it was decided, in order to cut down on the amount of oxygen used and make the apparatus even more compact, to use the usual sized combustion tube and build the coils to its size. This tube and coils could then be used interchangeably with the semimacrocombustion tube and its coils. (Since the preparation of the original manuscript, the authors have received the coöperation of the Empire Laboratory Supplies Company, New York, N. Y., in the preparation of a compact and efficient instrument for the determination of carbon and hydrogen on both micro- and macrosamples. The details and results of this investigation will be reported later.)

Building the Combustion Train

Heating Coils. The electric heater for the combustion tube is prepared as follows: A strip of iron or Nichrome gauze, 65 × 8 cm., is cut from a roll of ordinary laboratory gauze, and is bent around a long cylindrical piece of wood or glass tube, by gently tapping with a mallet, to form a cylinder 65 cm. long and of such diameter (approximately 2 cm.) that a tube of 16-mm. internal bore can be easily slipped in or out. The cylinder is made firm by binding at several places with soft iron wire. A strip of asbestos, slightly larger than the wire gauze and 0.6 cm. thick is soaked in water to make it soft and workable, and is pressed around the iron gauze cylinder to cover it completely. Smaller strips may be used, but all the gauze must be covered.

The asbestos is kept in place by the heating coil which is wound in the following manner: A single turn of soft iron wire is fastened around one end of the asbestos-covered cylinder, and to it is attached one end of a 6.5-meter (20-foot) Nichrome wire (B. and S. gage No. 22). A small piece of Nichrome wire is allowed to extend for purposes of electrical contact. The wire is then wound tightly around the cylinder with about 1 cm. between successive turns, until all but the last 12.5 cm. (5 inches) has been covered. The last turn is anchored with a turn of iron wire. Electric current is now sent through the whole length of the wire to dry and fix the asbestos in place. A thick paste is made of powdered asbestos (sells as asbestos cement for 5 cents per pound) and water. The cylinder is suspended by a tube going through the center and, except for the 12.5 cm. (5 inches) not covered with Nichrome wire, is evenly covered with asbestos paste to a thickness of about 2 cm. The current is sent through the whole length at short intervals, until the asbestos has dried to a semihard mass.

When dry, the asbestos covering is coated with several layers of aluminum paint (the kind used to silver radiators), which are dried by passing the electric current through the Nichrome coil. Some of the paint is absorbed in the asbestos and acts as a binder, making a hard surface. If a harder coating is desired, a small amount of any standard furnace cement may be added to the mixture of powdered asbestos and water. This gives a remarkably tough and light-weight coat. The aluminum paint prevents radiation from the coil, increasing the efficiency of the outfit and making it more comfortable for the operator.

In order to adjust the temperature in the cylinder, one contact is passed back and forth along the unused Nichrome wire. A temperature of approximately 550° C. is desirable with Pyrex glass and 650° C. with harder glass. Higher temperatures tend to fuse the lead chromate into the glass and considerably lower temperatures make for incomplete combustion. If a suitable pyrometer is not available, a sufficiently accurate adjustment may be made by sliding the contact along the wire until a red glow is seen along the center of the cylinder. Sufficient time (1 hour) must be allowed for the temperature to come to equilibrium. The contact is then moved so that the resistance is gradually increased until at about 525° C. the color definitely disappears. However, when a filled tube is inserted the temperature will rise markedly, for radiation is less than from the open tube. A Pyrex tube closed at one end by a rubber stopper may be inserted and suction or pressure applied at the other end; if the Pyrex tube softens and distorts under pressure the temperature is too high. When the filled combustion tube is inserted and allowed to come to equilibrium, the temperature should be high enough so that when the tube is withdrawn the lead chromate has turned from yellow to deep orange.

When a suitable resistance has thus been decided upon, the Nichrome wire in excess of that needed for resistance is cut away and the remainder is used to make heating coils for the preheater and the lead peroxide. To keep the part of the cylinder not covered with Nichrome wire, at 200° C., so that the lead peroxide does not decompose because of too high a temperature or absorb moisture because of too low a temperature, the Nichrome wire is wound over it with turns about 3.75 cm. (1.5 inches) apart. The end is anchored with a turn of soft iron wire (these turns of iron wire need not be removed) after the coil is finished. This part of the cylinder is covered with powdered asbestos paste and dried and silvered as before. Its temperature is readily determined by means of an ordinary thermometer. A temperature variation of less than 5° (195° to 200° C.) is easily obtained but, if unsatisfactory or not uniform, the powdered asbestos covering can easily be removed with a sharp instrument, and the turns rearranged and again covered with asbestos and aluminum paint to give the desired uniformity to the very end. The Nichrome wire, necessary as a resistance, is cut off, leaving a small length to act as contact. A preheating unit is made around a little cylinder of iron-wire gauze covered with asbestos, 16 cm. in length and 1.4 cm. in diameter, with turns of Nichrome wire spaced 1 cm. apart, coated with asbestos cement and aluminum paint as before. Any unused Nichrome wire may be used as a fixed resistance in series with the preheater and the main heating coil, thus maintaining the temperature all along the line as desired. A total of about 6 meters (18 feet) of Nichrome wire is necessary.

Combustion Tube. The combustion tube consists of ordinary Pyrex tubing 16 mm. in internal bore and 85 cm. long, sealed at one end to 3 cm. of tubing 3 mm. in internal bore and at the side, about 4 cm. from the other end, to a tube of similar bore. A tube of the same dimensions but of hard Corning glass is used for higher temperatures. This tube is filled, essentially in accordance with the Pregl universal filling. An asbestos plug is followed by 10 cm. of lead peroxide sealed in place by a second asbestos plug. The remainder of the tube is cleaned from any lead peroxide adhering to the side.

Silver foil is cleaned by immersing it in a solution of sodium bicarbonate in an aluminum container or in the presence of a piece of aluminum foil. The silver foil is washed with water, dried, cut up into narrow strips, and packed tightly into the tube for 10 cm., along the temperature gradient from the copper oxide–lead chromate mixture to the lead peroxide. It is secured with an asbestos plug, and the tube, for the length of the rest of the heating unit (36 cm.) is filled with the usual mixture of lead chromate and copper oxide. This is secured with an asbestos plug. One variation is to line the tube with 35 cm. of thin copper gauze, rolled to fit snugly inside the tube, before filling it with the mixture of lead chromate and copper oxide. On subsequently passing oxygen through the heated tube, the copper gauze is oxidized to copper oxide, leaving a thin film of copper oxide on the walls of the tube to protect it against the hot lead chromate.

Gasometer, Preheater, and Scrubber. A 750-cc. glass bulb is sealed at opposite ends to two stopcocks as in Figure 1. The pressure is read by a mercury manometer sealed to the apparatus. It is apparent that when the manometer reading, ΔP, is 25 cm. in a container of volume V (750 cm.) the gasometer can deliver a volume, ΔV, of 247 cc. at atmospheric pressure, P.

$$\Delta V = \frac{\Delta P}{P} \times V = \frac{25}{76} \times 750 = 247 \text{ cc.}$$

Each centimeter difference in the manometer reading is equivalent to approximately 10 cc. A 5-cm. margin of pressure is allowed to remain in order to keep the rate of flow constant in the bubble counter. In practice this gasometer will actually deliver 200 cc. of gas. To facilitate regulation of the rate of flow, the end of the hollow Pyrex stopcock handle is softened in a flame, drawn out with the aid of a pair of tweezers, and scraped down with a wire gauze to admit a long piece of wood or glass, to give leverage for delicate control. Once the rate of flow is set, the gasometer may be filled from the oxygen tank as often as necessary without changing the position of the regulating stopcock during delivery.

The gasometer is connected directly to the preheater, which acts to burn any organic particles in the gas. The gas is then freed of carbon dioxide and then water by passing it through a straight tube, of the same internal diameter as the combustion tube, filled half with soda lime and half with calcium chloride. Because of the relatively large amount of soda lime and calcium chloride used, this charge need not be renewed for long periods of time. The narrow end of this tube is attached by rubber tubing to a bubble counter whose inlet tube is at a 90° angle with the outlet tube. The outlet tube is then connected by a rubber tube directly to the side arm of the combustion tube. Wherever glass tubing is connected by means of rubber tubing, the glass ends must touch each other. The pressure-resistant rubber tubing is boiled in 10 per cent alkali, washed, and dried before use, but need not be impregnated with wax as for microanalysis.

The whole setup is mounted on one short ring stand by means of an iron rod, two rings, and several clamps (Figure 2).

The Combustion. A copper oxide spiral, 8 cm. long, made by winding copper gauze around a thick copper wire shaped at the end in the form of a handle, and heating in a stream of oxygen in the combustion train, is placed behind the boat containing the weighed sample. The tube to be heated by the flame must be encased in a short length of iron gauze and care must be taken, when the combustion tube is made of ordinary Pyrex, not to heat the glass tube directly or to use a roaring flame. The gauze should be heated to a dull red heat by a silent blue flame. A platinum boat may be conveniently made by folding about 1 to 2 grams of thin platinum sheeting or foil into the required shape and fusing the joints by heating the boat to redness and striking with the aid of screwdriver and hammer. Soda lime (2 per cent moisture) and calcium chloride (both 8-mesh) are used in the Nesbitt tube and the Schwartz tube, respectively (Figure 2).

One-half to one hour before the sample for analysis is to be introduced, the soda-lime and calcium chloride absorption tubes are attached and the coils are heated. At this time and all during the combustion, oxygen is sent through the apparatus at the rate of 3.5 cc. per minute. The bubble rate for the particular counter used is adjusted to deliver this volume. The absorption tubes are removed, allowed to remain in a desiccator for 15 minutes, and then weighed. Whenever the absorption tubes are not on the train, the outlet of the combustion tube is attached to a calcium chloride and soda-lime tube to keep moisture and carbon dioxide from the filling. The absorption tubes are returned to the train, the boat with about 70 mg. of sample is introduced, and the copper oxide spiral is put about 1 to 2 cm. behind the boat.

The Bunsen flame is brought slowly towards the boat, starting at the beginning of the copper oxide coil, the speed depending on the nature of the material. The material should be slowly distilled into the combustion chamber. After 15 minutes the flame should be under the boat, where it should be kept from 10 to 15 minutes or until the boat is clear of material, and then brought, gradually, up to the heating coil to clear the tube of material. This procedure is repeated twice. At the end of about 40 minutes, the flame is turned off and the washing is continued for an additional 45 minutes. The time of combustion varies with the substance from about 1.5 to 2.25 hours. In all cases, exactly 500 cc. of oxygen are used for the combustion and the washing. If less time is used, the rate of flow is decreased. The absorption tubes are now removed, placed in a desiccator, and weighed at the end of 15 minutes. During this time a second weighed sample is introduced, after the original boat has been removed, and a second set of absorption tubes is attached, beginning a second combustion. In this manner, four combustions and sometimes five can be carried out in one day.

Table I

Substance	Formula	Sample	CO_2 Found	H_2O Found	C Found	H Found	C Calcd.	H Calcd.
		Gram	*Gram*	*Gram*	%	%	%	%
Benzoic acid	$C_6H_5{\cdot}COOH$	0.0760	0.1915	0.0335	68.68	4.89	68.85	4.91
		0.0763	0.1930	0.0335	69.00	4.87		
1-Cystine	$[SCH_2CH(NH_2)$--	0.0760	0.0835	0.0360	29.96	5.26	30.00	5.00
	$COOH]_2$	0.0715	0.0781	0.0315	29.81	4.89		
Nitrophthalic acid	$NO_2C_6H_3(COOH)_2$	0.0710	0.1184	0.0175	45.47	2.62	45.49	2.37
		0.0757	0.1270	0.0183	45.75	2.68		
2,6-Dichlorobenzoquinone-imidochloride	$O:C_6H_2(Cl_2):NCl$	0.0694	0.0887	0.0081[a]	34.86	1.30	34.22	0.95
		0.0716	0.0916	0.0076	34.88	1.18		
o-Stilbene carbonic acid	$C_6H_5{\cdot}CH:CH{\cdot}$-	0.0707	0.2075	0.0313	80.04	4.92	80.35	5.35
	$C_6H_4{\cdot}COOH$	0.0707	0.2070	0.0310	79.88	4.88		

[a] Error in weighing so small an amount at least 2 per cent.

Results

The results presented in Table I consist of consecutive runs on substances containing different groups with varying degrees of ease of combustibility and unusual properties, to illustrate the effectiveness of the filling. Benzoic acid sublimes readily and must be approached slowly. Nitrophthalic acid explodes and must be heated gradually. 2,6-Dichlorobenzoquinone-imido-chloride is slow in burning and the flame must be kept under the boat for from 20 to 30 minutes. The amino, nitro, mercapto, and halogeno groups are included as representative of compounds encountered.

Summary

A compact, easily built combustion train for the determination of carbon and hydrogen in samples of organic compounds weighing from 50 to 125 mg. is described. The apparatus is mounted on one short ring stand, takes up little desk space, and can be easily moved to a convenient place without dismantling, when not in use.

The amount of gas used is measured by the introduction of a new type of gasometer. This makes results more consistent. Heating is done electrically throughout (the boat may also be heated by a flame).

Pyrex glass may be used permanently for the combustion tube, when special care is taken and the temperature is kept at about 550° C. It is recommended that, when available, harder glass be substituted and a temperature of 650° C. be used for more rapid combustion.

Directions are given for constructing the heating coils from materials readily available. A single heating coil is used to heat the combustion tube at different temperatures, as needed at different parts of the tube.

An application of this setup, with some modification, to the analysis of microsamples will be reported later.

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An Improved Constant-Pressure Valve

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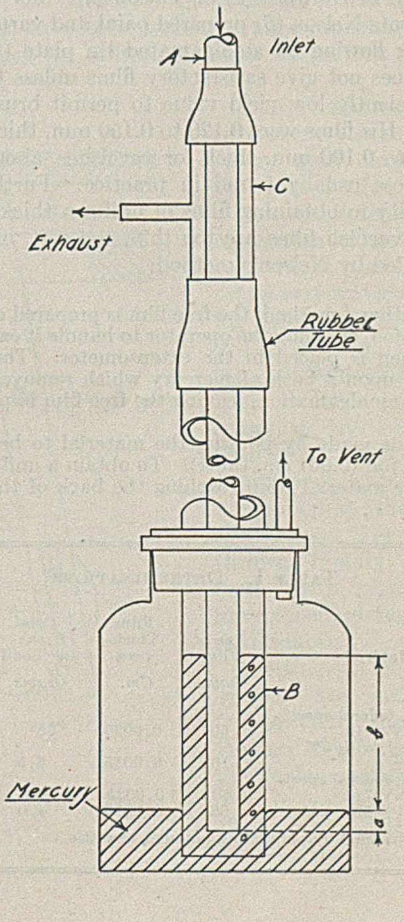
DURING the course of some recent experiments, it became necessary to remove a condensable gas, containing small amounts of noncondensables, from a generating system maintained at any desired constant pressure. It was necessary to liquefy as much of the condensable material as possible and remove the noncondensables while maintaining the generator in continuous operation. To permit the use of a vacuum pump for removing the noncondensables and yet maintain a constant pressure in the generator, a constant-pressure valve was needed and a mercury valve seemed to be a possible solution. However, no known form was found which would fill the above requirements.

The ordinary check valve (*6*) having a narrow inlet tube dipping below the surface of mercury in a larger tube, as well as the various U-shaped modifications of this type, was unsuitable because constant pressure on the fore part of the system can be maintained only if the back pressure is constant. Likewise, the Stock valve (*7*) using glass floats with ground ends to seal the tube even in its recent forms (*1*, *3*, *5*) suffers from the same defect. The recently developed check valve (*2*, *4*, *8*) using a thin layer of mercury on a porous plate has the same limitations. While a leveling bottle may be used to overcome these difficulties to some extent, such a device robs the valve of its simple automatic character.

A valve has been devised, however, which meets the above requirements of permitting gas removal at a constant pressure independent of the back pressure on the exhaust line. The valve permits gas take-off at pressures above or below atmospheric as desired, and serves also as a safety manometer to prevent excessive pressure in the system. Because of its applicability to various uses, particularly in vacuum distillations at constant pressure, a brief description of the valve appears desirable.

The construction and operation of the valve will be evident from the accompanying sketch. The gas enters through the inlet tube, *A*, whenever its pressure exceeds that represented by the height of mercury, *a*, and bubbles up through the mercury in the tube, *B*. The height of mercury, *b*, will depend on the back pressure of the exhaust line. By raising or lowering the tip of tube *A*, the take-off pressure may be varied at will. In case of blocking of the exhaust, both mercury levels *a* and *b* will drop below the end of tube *B* and the gas will escape into the large container which is open to the air or to a vent. In order to



minimize the fluctuations in the take-off pressure, tube *B* should be as small as is possible without permitting entrainment of the mercury in the exhaust gas. (If desirable, a plug of cotton or glass wool may be inserted in tube *C* below the exhaust to prevent passage of entrained mercury.) The surface of the mercury in the outer container should be large, so that its level will not vary appreciably with changes in level *b*.

For a moderate gas stream, standard Pyrex glass tubing having the following outside diameters was used satisfactorily: *A*, 7 mm.; *B*, 15 mm.; *C*, 10 mm. A 500-cc. Erlenmeyer flask or ordinary bottle may serve as the container.

Obviously, the dimensions may be varied as necessary, glass inner seals may be used in place of the rubber connections, and liquids other than mercury may be used if desired. In some applications where permanent seals between the glass tubes are necessary, a leveling bottle connected to the outer reservoir may prove advantageous in permitting operation under various pressure conditions.

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Preparing Fragile Paint and Varnish Films

For Determination of Tensile Strength, Elongation, and Permanent Set

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SEVERAL physical properties of paint and varnish films, such as toughness and elasticity, have usually been determined only indirectly. Reduction with kauri, exposure and weathering tests, etc., are not always suitable for evaluating such properties. Preparation of the free film in a form which permits handling makes possible a direct examination of its properties. Two methods of preparing free films—stripping from the foundation (*3*) or dissolving the foundation with acid (*1*) yield films which may be tested in extensiometers such as that of Gardner (*2*) or Tesson (*4*). For stress-strain measurements Nelson (*3*) prepared paint and varnish films by spraying or flowing on amalgamated tin plate (stating that brushing does not give satisfactory films unless the material has a sufficiently low yield value to permit brush marks to flow out). His films were 0.120 to 0.150 mm. thick for paints and 0.090 to 0.100 mm. thick for varnishes, about ten times the thickness usually found in practice. Furthermore, he had difficulty in obtaining films of uniform thickness. Most paint and varnish films are too thin, too soft, or too brittle to be handled by Nelson's method.

In the authors' method, the free film is prepared on a thin tin-foil foundation, enabling the operator to handle it easily until the test specimen is placed in the extensometer. There the test piece floats upon a bath of mercury which removes the tin-foil backing by amalgamation, leaving the free film in place for testing.

The film is made by pouring the material to be tested on a sheet of tin foil (0.001 cm. thick). To obtain a uniform film and to keep any material from reaching the back of the foil, which would later prevent the amalgamation of the tin, the coated foil is hung from a 3.2-mm. (0.125-inch) horizontally fixed metal rod to which it is attached with paper clips. A similar rod is attached to the bottom of the foil and left free, thus keeping the panel vertical and smooth. After drying, the test piece is cut so that its long axis is at right angles to the direction of flow of the material. In any other direction there will usually be an appreciable variation in film thickness. A template in the form of the test piece is helpful in cutting the specimen and marking it for elongation measurements. Two holes, 40 mm. apart, are drilled in it and carbon black is rubbed gently over the holes to get the elongation marks on the film.

The apparatus for testing is a horizontal extensometer. The test piece floats upon mercury in a shallow dish (5 mm. deep, 40 mm. wide, 250 mm. long). The ends of the test piece are gripped by folded emery paper held in position with paper clips. One grip is attached to a stationary support by a thin rubber band. The other is attached by a strong thread passing over a pulley to a light pan. The top of the pulley is on a level with the surface of the mercury. About half an hour is sufficient for amalgamation and then weights can be applied and measurements made. The progress of the amalgamation is usually visible.

Table I. Determinations

Material	Age of Film	Film Thickness	Total Breaking Load	Maximum Elongation	Permanent Set
	Days	*Cm.*	*Grams*	%	%
Spar varnish, federal specification TT-V-121a	60	0.0020	35	17	..
Raw linseed oil, with 5% liquid driers	10	0.0015	6.5	20	19
Floor varnish, federal specification TT-V-71	68	0.0025	74+	0	0
Vehicle of flat ceiling paint[a]	68	0.0015	4.0	30	30

[a] Vehicle obtained by permitting pigment to settle.

Some determinations by this method are given in Table I.

Discussion

Characteristics of paint and varnish films, the influence of age, humidity, and temperature, or the effect of new ingredients or a new procedure of production can be studied by this method. It offers a means for evaluating tough and elastic films, such as those called for by federal specification TT-P-51a and others.

This method can be used where the kauri reduction test is inapplicable because of incompatibility of the kauri solution and the vehicle of the material to be tested.

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A Reciprocating Laboratory Shaker

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LABORATORY agitating devices may be divided into two main classifications: rotating devices and reciprocating devices.

In rotating devices, the container may be rotated about its own axis, about a line parallel to its axis, or about a line not parallel to the axis of the container—e. g., a line perpendicular to the axis of the container, giving an end-over-end motion. In all of these, as the container revolves about a horizontal axis, the liquid surface rises with the container and falls or slides back under the force of gravity, producing a tumbling motion. In rotating devices, the speed and radius of rotation are limited by the fact that when the centrifugal force on the liquid becomes equal to the force of gravity the liquid will remain at the wall of the container and rotate with it.

Reciprocating devices impart a much more violent agitation to the liquid in the container. The sudden reversals of momentum throw the liquid up the sides of the container, first one way, then the other. A type commonly encountered in chemical laboratories consists of a box with flasks held in place by spring steel strips. The box is driven by a crank and rocker arrangement.

Construction of a Reciprocating-Type Agitator

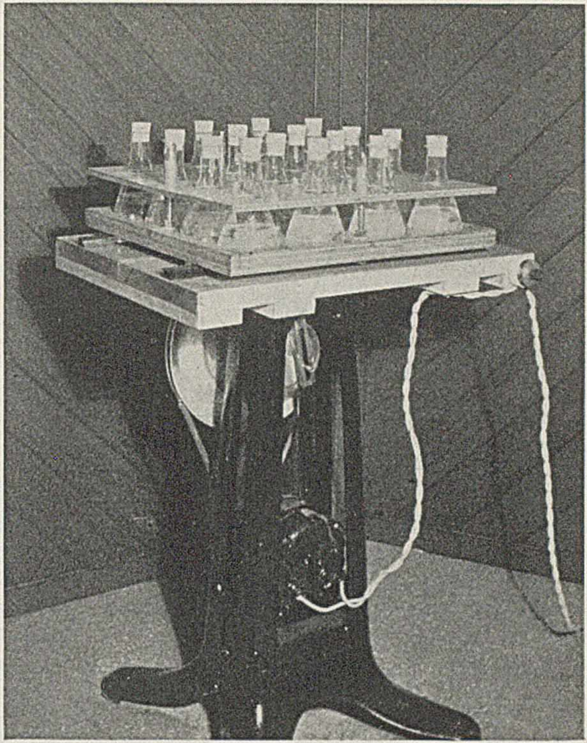

FIGURE 1. AGITATING MACHINE

During the course of investigations conducted at the M. I. T. Textile Laboratory on the electrical conductivity of cotton, it was desired to wash samples of cotton in distilled water to remove electrolytic salts. Owing to the natural waxes present on untreated cotton fibers, it is exceedingly difficult to wet them out in pure water without the addition of surface-active ingredients. Since the addition of such materials might defeat the purpose of the research, it was found necessary to design an agitator which, by purely mechanical means, would displace the entrapped air in the cotton and permit wetting out.

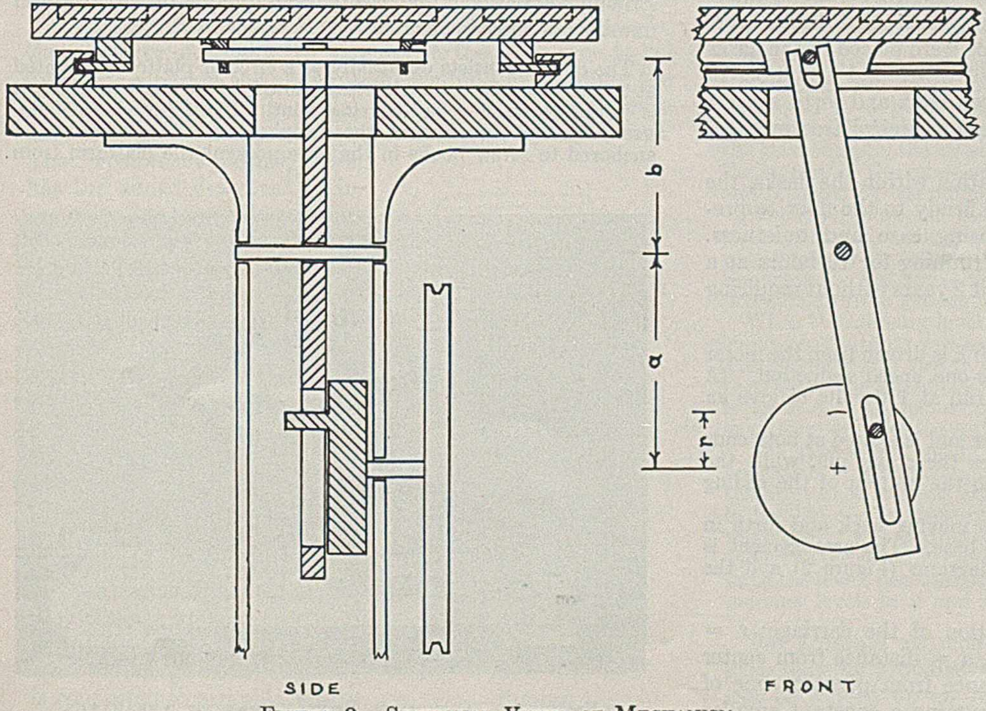

FIGURE 2. SECTIONAL VIEWS OF MECHANISM

The combined ideas of several members of the laboratory staff, together with the genius of a staff mechanic, finally resulted in the conversion of an abandoned cast-iron base and motor into a very serviceable agitating machine (Figure 1).

The machine carries sixteen 300-ml. Erlenmeyer flasks which are set into recesses in the carriage and then held firmly in place by a plywood board drilled to accommodate the necks of the flasks. The carriage is thrown rapidly back and forth by a crank-and-lever mechanism giving a quick-return motion.

Wetting-out of the cotton samples was complete in a few seconds, owing to the violence of the agitation, and the washing action was complete in less than 15 minutes. The agitator has also been used in special fabric-wash-

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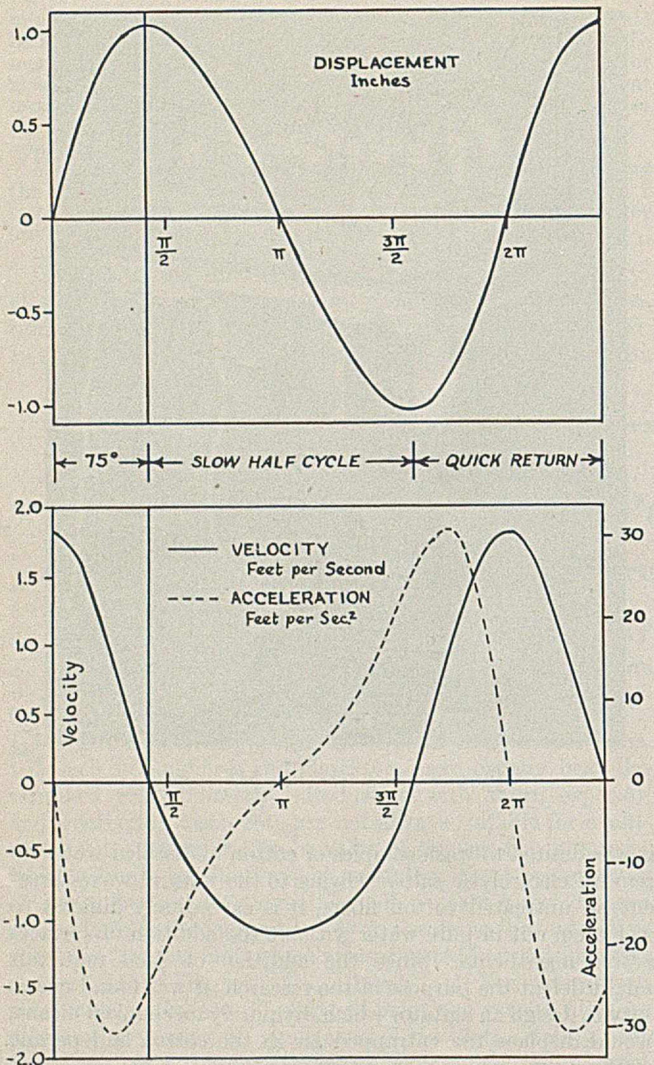

FIGURE 3

ing tests. Here, four 2-liter round-bottomed flasks were clamped into place, and the fabrics were placed in the flasks together with the desired amount of water and a number of rubber balls. The balls were thrown back and forth against the fabric, greatly augmenting the mechanical treatment of the goods.

Despite the violence of the agitation within the flasks, the machine, after having been bolted firmly to the floor to prevent "walking," ran with surprising ease and quietness. Upon occasions, it has been kept running for 10 hours at a time, and it has been in use for about 2 years without requiring mechanical attention.

DETAILS OF MECHANISM. The crank is driven from the motor through two pulleys giving a six-to-one speed reduction. (A 220-volt 0.1-horsepower motor was run at 110 volts to give an actual crank speed of 160 r. p. m.)

The lever is pivoted near its center and is slotted at both ends (Figure 2). One end accommodates the crank pin, while the other end engages a pin attached to the bottom of the sliding carriage.

The carriage rests on brass strips moving back and forth in slotted steel strips attached to the base. The arrangement is fairly evident from the sectional diagrams (Figure 2) and the photograph (Figure 1).

Three constants affect the motion of the carriage: r = radius of crank (to center of pin), a = distance from center of crank to pivot, and b = distance from pivot to line of motion of undercarriage pin. Assuming a constant angular velocity in the crank, the displacement (from center position), velocity, and acceleration of the carriage have been computed for a complete cycle, using the values: $a = 10$ cm. (4 inches), $b = 10$ cm. (4 inches), and $r = 2.5$ cm. (1 inch).

The maximum displacement occurs in this case when the crank has turned only 75° from the zero position (pin at top). The motion of the carriage to the right then takes 210°, while the return motion takes 150° (Figure 3). It is interesting to note that, while the slow half-cycle shows uniform acceleration changes, both the positive and negative peak accelerations are crowded into the quick-return half. These sharp acceleration peaks probably account for much of the efficiency of agitation of the mechanism.

The quick-return action could be augmented by decreasing the ratio of a to r. Thus, when $a = 2r$, the maximum displacement occurs at 60°. The two acceleration peaks are then greatly emphasized and occur in the short 120° portion of the cycle. The slow half-cycle takes exactly twice as long (240° rotation).

The machine is oiled at several points to reduce friction losses: crank face and pin, pivot of lever, pin on undercarriage, and the slide supporting the carriage.

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An Efficient Bottle-Shaking Apparatus

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THE apparatus described in this article was designed for use in an adsorption investigation in which a number of samples were to be shaken for a considerable length of time. The construction is simple and inexpensive, and the shaker has given excellent service in continuous use over long periods. Although designed originally for use with six 125-ml. Erlenmeyer flasks, it may easily be adapted to other types and numbers of containers.

The device consists essentially of a circular platform mounted at an angle of 15° upon a vertical motor-driven shaft to which it is joined through a ball-bearing joint. Three (or more, if desired) springs attached at the periphery of the platform and anchored to screw hooks in the base prevent the platform from

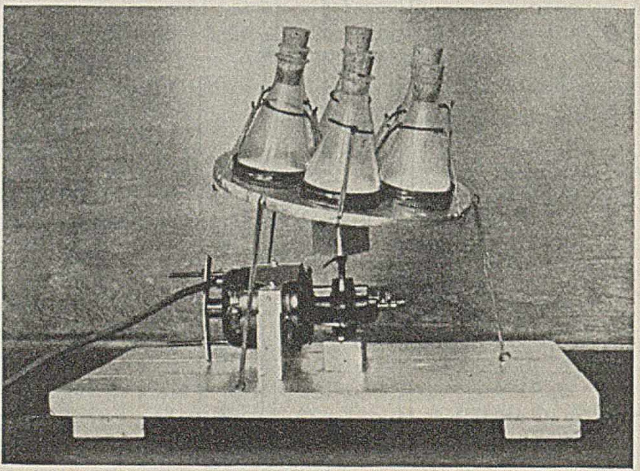

FIGURE 1. EFFICIENT BOTTLE-SHAKING APPARATUS

rotating, yet allow it to tip in every direction as the drive shaft rotates (Figures 1 and 2). The contents of containers or bottles mounted on the platform are shaken very effectively by this eccentric action.

Details of construction are shown in the illustrations. The motor used by the author is a Motorola phonograph attachment equipped with a built-in reducing gear and a vertical shaft. Other types of phonograph motors should be as satisfactory, and can generally be obtained on the second-hand market. The speed of the drive shaft should be about 100 to 200 r. p. m. for good results.

The ball bearing by which the platform is joined to the drive shaft is made from a steel chest caster with ball-bearing swivel joint. This type has a flat steel plate for fastening to furniture by wood screws. The wheel is removed and the frame cut down and drilled so that it can be bolted securely to a wooden block. The block is attached to the drive shaft as shown in Figure 2.

The flat plate of the caster is fastened to the platform with screws. The platform is 22.5 cm. (9 inches) in diameter and 1.25 cm. (0.5 inch) thick. A circular disk of wood, 7.5 cm. (3 inches) in diameter and 1.9 cm. (0.75 inch) thick, is mounted in the center of the platform. Six screw eyes in this block are used for fastening the flasks to the platform.

The metal cups in which the flasks are set are Kerr Mason jar rims. A ring made of No. 16 B. & S. wire, with two hooks soldered at diametrically opposite points, is slipped over the neck of a flask and anchored to screw hooks in the platform by means of several rubber bands.

The three springs which anchor the platform to the base may consist of several long rubber bands each, or of long coil springs. These springs must not be so powerful as to prevent motion of the shaker platform, and must be of equal strength.

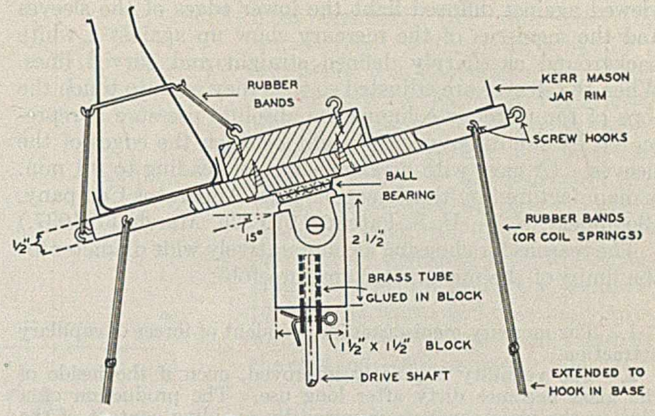

Figure 2. Details of Shaking Apparatus

The base on which the whole apparatus is mounted is of heavy lumber.

Careful selection of the motor is of vital importance to the success of this machine. A motor with good bearings, easily lubricated, and capable of running a long time without overheating is the ideal type. A rheostat may be used for a speed control.

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An Improved Mercury U-Gage

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THE most widely used manometer for the measurement of moderately low pressures—for example, in vacuum distillations—is a U-shaped glass tube with one end sealed and filled with mercury. Its usefulness is based mainly on its simple direct indication of the absolute pressure which can easily be read at any moment.

It has, however, some objectionable features—for example, the necessity of boiling the mercury in the glass tube to remove the air from the closed reference limb when filling the gage and the ease with which air gets into the reference limb after short service, rendering it useless for accurate work. The customary construction has the added drawback of inaccuracy due to capillary action on the meniscus of the mercury.

The modified gage described here has been designed to overcome these difficulties while preserving the desirable features of the U-gage, and is essentially a modification of the manometer recommended by von Rechenberg (*4*). Referring to Figure 1, *A* and *B* are the limbs of a U-tube, each having a diameter of 16 mm. Tube *A*, the indicating limb, is connected to the vacuum line in the customary manner. Tube *B*, the reference limb, however, instead of being sealed at the top, is connected to a capillary tube, *C*, which in turn is joined to a wide tube, *D*, at the bottom. *D* is also connected to the vacuum line.

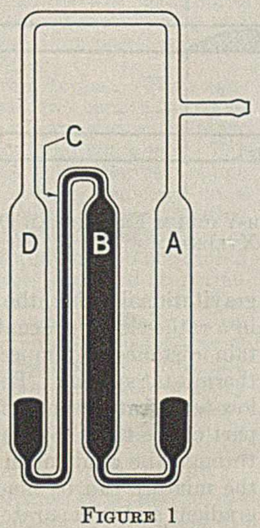

Figure 1

This connection of both the indicating and the reference limbs to the same vacuum line forms the fundamental difference from the ordinary U-tube manometer which has a closed reference limb. It greatly facilitates filling the gage and maintaining it in perfect working condition.

To get the gage ready for operation, mercury is poured through the side tube until *A* and *B* are about two-thirds full. It is then connected to a good vacuum pump and exhausted. By inclining it backward almost to a horizontal position and by tapping the glass sharply, the air adhering to the glass walls is brought to the surface of the reference as well as of the indicating column, and removed by the pump.

When no more air bubbles are visible under the reduced pressure at which the gage is to be used, it is tilted to the left until mercury flows over the top of *B* through *C* into *D*, thus removing the last traces of air from *B* and forming a seal which prevents air from getting into it again.

When the mercury level in *A* approaches the bottom, the gage is put back into its vertical position and the vacuum is released. The mercury will rise in *C* and *B* until the two columns flow together at the top of the bend, filling *B* and *C* completely. The levels in *A* and *D* should be about 20 mm. above the bottom, so as to form an effective seal.

The gage is now ready for use and may be connected to the apparatus in which the pressure is to be measured. As soon as the pressure is reduced to a value corresponding to the difference in heights of the mercury columns in *A* and *B* (or *C* and *D*), the mercury will separate at the top of the bend, between *B* and *C*, and as the pressure diminishes each part will recede in *B* and *C* until the levels become constant. The difference in height of the mercury levels in *A* and *B* indicates the absolute pressure.

For accurate and convenient reading of the pressure the gage may be provided with blackened metal sleeves which can be moved up and down over limbs *A* and *B*. When viewed against diffused light the lower edges of the sleeves and the meniscus of the mercury show up against a white background as sharply defined straight and curved lines. When the sleeves are adjusted so that they seem to touch the tops of the mercury columns the absolute pressure is represented by the difference in height between the edges of the sleeves. (A gage with arrangements for reading to 0.1 mm. is manufactured by the Scientific Glass Apparatus Company, Bloomfield, N. J., U. S. Patent 2,075,326, March 30, 1937.)

The reasons for choosing a comparatively wide diameter for the limbs of the manometer are threefold:

1. The mercury meniscus is independent of forces of capillary attraction.
2. The visibility is greatly improved, even if the inside of the glass becomes dirty after long use. The production of a film on the glass can be minimized by avoiding contact of the mercury with rubber, by using clean mercury free from other metals (*2*), and by trapping dust and mist by an appropriate filter.
3. Air, which after long use or by too sudden release of vacuum may get into the reference limb, will collect at the top of the bend in C. If the air bubble has a diameter of 0.2 mm., a size clearly visible to the naked eye, its volume would be 0.42 cu. mm. at 7.6 mm. of mercury (0.01 atmosphere) and 4.2 cu. mm. at 0.76 mm. of mercury (0.001 atmosphere). As the cross section of B is 200 sq. mm., the height of the air layer would be 0.0021 mm. at 7.6 mm. of mercury, and 0.0210 mm. at 0.76 mm.

The error caused in the reading would be 0.03 and 2.8 per cent, respectively. Even such small errors can be avoided by driving the air out of C in the following manner:

The gage is tilted to the right until the mercury level in D approaches the bottom, and is connected with the vacuum line while in this position. When the gage is evacuated, it is tilted to the left until the mercury flows over the top bend of C, pushing the air out into D. When the level in A approaches the bottom, the gage is put back in its vertical position.

For correct reading it is necessary to have the gage in a perfectly vertical position. Other precautions to be observed, especially for pressures of 2 mm. and less, have been discussed repeatedly in the literature (*1*, *3*).

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High-Vacuum Fractional Distillation without Gravitational Reflux

G. von ELBE and B. B. SCOTT, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

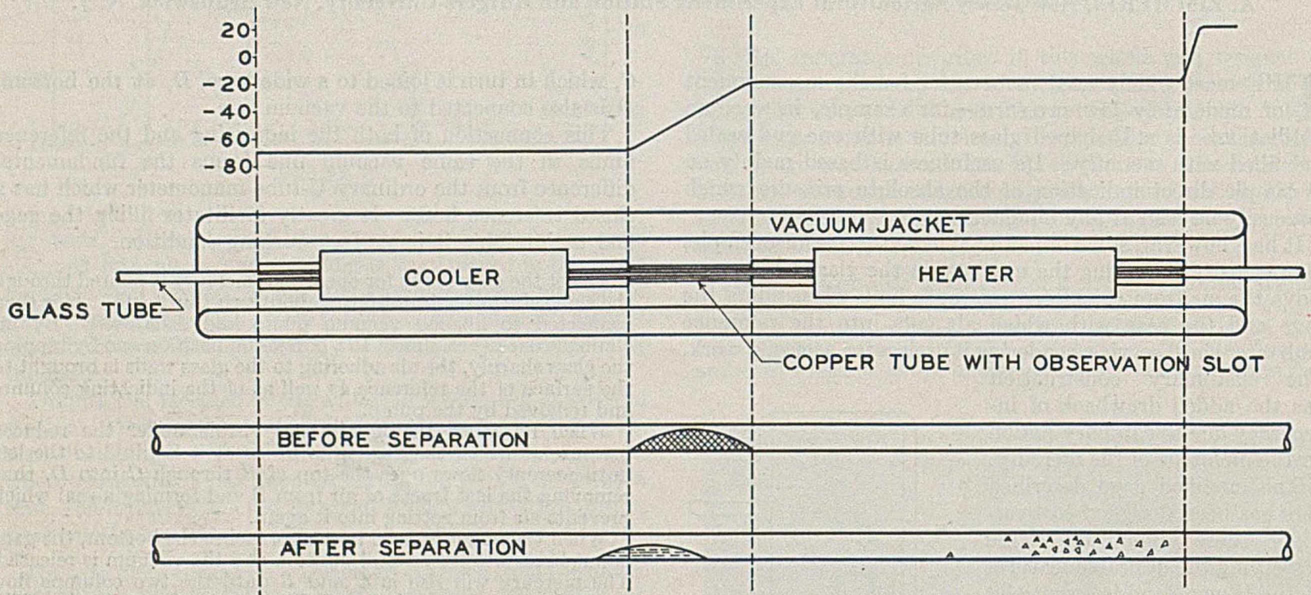

Figure 1. Schematic Representation of an Apparatus for High-Vacuum Fractional Distillation as Used for Separation of *p*- and *m*-Xylenes

The usual method of fractional distillation involving gravitational reflux cannot be applied to the separation of mixtures of substances of low vapor pressure, since, to maintain a reasonably fast reflux rate, the vapor pressure of the components must, in general, exceed 1 mm. Furthermore, this method is not applicable to liquid volumes smaller than a few milliliters, since the holdup losses then become a significant fraction of the total input. With the following apparently not previously described method, which is free from gravitational reflux, the mixture to be fractionated is placed in a rather long, evacuated glass tube, along which for a certain distance a temperature gradient is maintained by a thermostat system. The mixture tends to accumulate at the low-temperature end of the gradient, which is the coldest part of the tube; by pulling the latter slowly and uniformly through the gradient in the direction toward the warm end, the mixture can be made to distill continuously within the gradient and to separate more or less completely into its com-

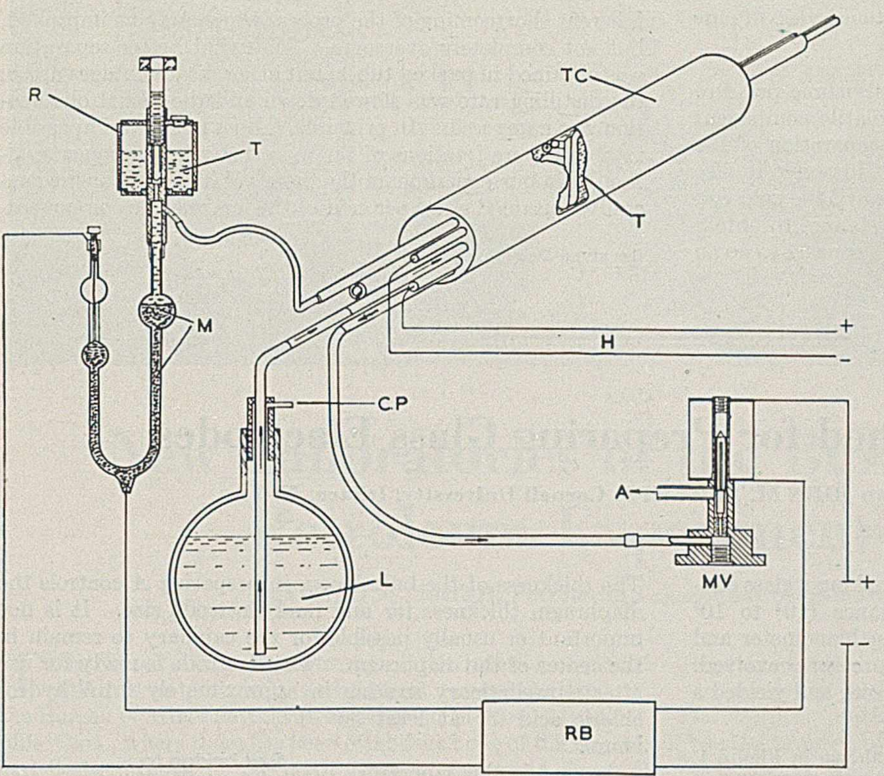

FIGURE 2. THERMOSTATIC CONTROL FOR HEATER AND COOLER

R, reservoir and regulating valve for toluene, *T*, by which the temperature of heater or cooler, *TC*, may be controlled. *H*, heating circuit. A constant pressure above atmospheric is maintained at *CP*. Liquid nitrogen, *L*, flows as shown by arrows on actuation of magnetic valve, *MV*, by mercury thermostat, *M*, permitting outlet of liquid nitrogen to atmosphere at *A*.

ponents, since the more volatile component distills faster than the less volatile. The volume of distillable substance to be used in this process can be kept very small, of the order of 10^{-3} cc., and distilling temperatures corresponding to vapor pressures much below 1 mm. may be chosen.

The design of the apparatus is shown schematically in Figure 1, as used for separation of *p*- and *m*-xylenes.

The straight glass tube in which distillation takes place passed through the axial bore of two cylindrical thermostats, the heater and the cooler, and through a copper tube connecting heater and cooler. Use of a tube 4 mm. in internal diameter ensured a fairly large surface-to-volume ratio without danger of clogging, using samples up to 0.1 cc. Larger diameters were found to decrease the efficiency and ease of operation of the process. The lengths of the tubes were between 1.5 and 2 meters. The temperature gradient shown above the apparatus was maintained along the copper tube, which was 22.5 cm. (9 inches) long and had an observation slot. A transparent vacuum jacket was used to minimize heat transfer to the surroundings.

The thermostats were made entirely from copper. Their construction is shown in Figure 2. Each had two copper spirals in the inner annular spaces, one containing a heating wire, the other allowing the passage of cold air from a liquid air container. The residual annular space was filled with toluene, the thermal volume change of which operated a mercury U-tube connected to a vacuum-tube relay which was used to control either a heating current or a magnetic valve which regulated the flow of cold air, as shown in Figure 2. The temperature fluctuations did not exceed 0.1° C. Thermocouples (not shown) were arranged to permit temperature measurements at any point along the gradient. The distilling tube was clamped at one end to an electrically driven carriage which moved on rails at a uniform rate, adjustable from a few millimeters per hour to several centimeters. Provision was made, furthermore, to keep the tube constantly rotating around its axis to ensure temperature equalization over any cross section. A photograph of the entire apparatus is shown in Figure 3.

A typical case studied was the separation of *p*- and *m*-xylenes. Their boiling points at atmospheric pressure are almost identical, 139° and 138° C., respectively. *p*-Xylene melts at 13.2°, and below this temperature its vapor pressure is lower than that of *m*-xylene, which melts at −51°. With the heater at temperatures below 13.2°, it was possible to follow the separation by visual observation of the crystals emerging from the liquid mixtures. Satisfactory distilling rates within the gradient were obtained if the temperature at the warm end was kept anywhere between 0° and −25°, and at the cold end −50° or lower.

The sample, 0.1 to 0.01 cc., was contained in a small glass tube which was placed in the distilling tube, which was then evacuated to $< 10^{-6}$ mm. of mercury and sealed. The sample tube was then broken by thermal expansion by applying a small flame momentarily. At the beginning of the process, the volatile material was allowed to condense in the coldest zone of the tube, within the cooler. The tube was then pulled, initially, at a rate such that the substance remained within the gradient. Separation soon occurred, *p*-xylene crystals concentrating at the warm end, as shown in the tube at the bottom of Figure 1. The pulling speed was then slowly raised until the crystals left the gradient and entered the heater zone, which was 35 cm. (14 inches) long. The process was continued without further adjustment until a stationary state was reached in which the bulk of the *p*-xylene was located within the heater and the *m*-xylene, with some *p*-xylene, was distributed along the gradient. The *m*-xylene cannot be pulled from the gradient because of its faster distilling rate. With a heater temperature of about −15°, and the cooler at about −70°, the pulling speed was approximately 6 cm. per hour.

The pure *p*-xylene was removed by sealing off the tube at the proper place or by reducing the temperature of both heater and cooler sufficiently so that the vapor pressures became practically zero, and then pulling that part of the tube containing the *p*-xylene out of the heater and allowing it to come to room temperature, at the same time passing dry filtered air through from the cooler end. Thus the evaporating *p*-xylene was blown out and collected in a liquid air trap. The purity of the *p*-xylene separated in this way was high. The residual mixture was again

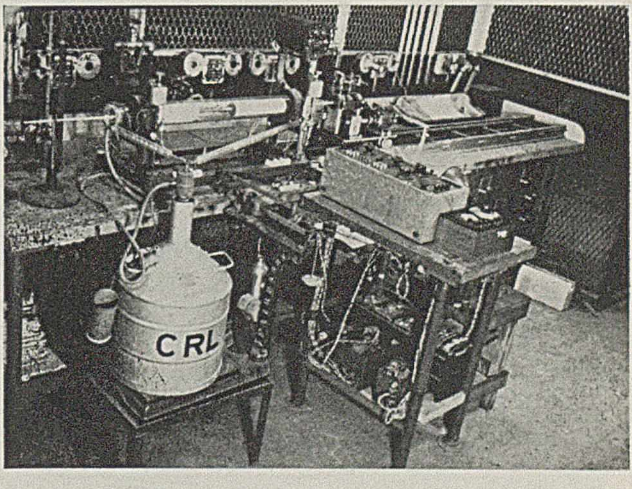

FIGURE 3. PHOTOGRAPH OF APPARATUS

Distilling tube passes through cooler and heater (left and right, respectively, within vacuum jacket) and is attached to carriage on guard rails (extreme right). In front, accessories for thermostatic control (liquid air flow regulated by magnetic valve) and thermocouple readings.

subjected to the same procedure, and an additional yield of pure *p*-xylene was obtained.

Within the distilling tube there exists a dynamic pressure gradient which tends to keep the more volatile component away from the warm end and thus favors separation of the less volatile material in the pure state. However, it also facilitates the intermixing of the vapors toward the cold end and is, therefore, the probable cause of the failure to obtain complete separation in one operation. This appears to be an inherent shortcoming of the process which may be improved, but not completely overcome. Somewhat better separation was obtained in packed tubes, but other disadvantages arose; the distilling rate was slowed down and the visual observation was hampered. In principle, it does not seem impossible to obtain pure fractions of the more volatile components, although in our experiments the more volatile component generally contained a few per cent of the less volatile component.

RECEIVED December 18, 1937.

A Simple Method for Preparing Glass Electrodes

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WHILE investigating the problem of making a glass electrode with a sufficiently low resistance (10^4 to 10^5 ohms) to permit its use with an ordinary galvanometer and potentiometer (*1*), the following procedure was evolved. This method was found to be easy to carry out, and yielded a sturdy product of high sensitivity.

Using 9-mm. Corning 015 glass, the parts shown in Figure 1, *A*, *B*, *C*, are prepared. *A* is formed by breaking off about half of a thin bulb blown on a section of 2- to 3-mm. tubing drawn from the 9-mm. stock. *B* is a short piece of 9-mm. tubing with an attached spindle to serve as a handle, and *C* is a section of the original tubing 10 to 12 cm. long.

To prepare the electrode, *B* is heated to softening at the open end and attached lightly to *A*, following which *C* is heated and sealed to *B*, over *A*, as shown in *D* and *E*. The seal is then heated uniformly and gently blown out to give *F*. The excess glass is cut off by a hot wire at the positions indicated by the dotted lines in *F*.

If the electrode is sufficiently sensitive, a spot of interference figures 9 to 16 sq. mm. in area will appear in the diaphragm.

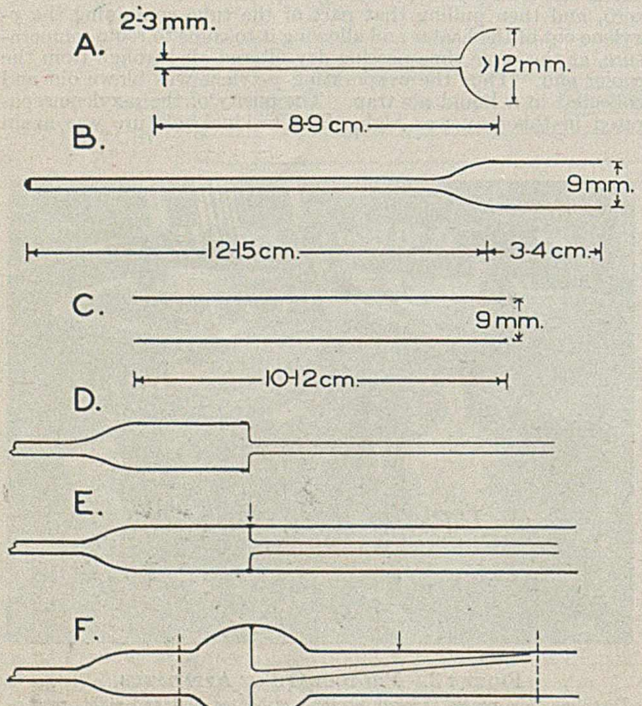

FIGURE 1. PREPARATION OF ELECTRODE

The thickness of the bulb blown in preparing *A* controls the diaphragm thickness for any final electrode size. It is not important or usually possible for the capillary to remain in the center of the diaphragm. The electrode is ready for use after a preliminary soaking in approximately 0.1 *N* hydrochloric acid for at least 36 hours.

As used in this laboratory, the electrode is rinsed with distilled water, superficially dried with filter paper, and filled to the level indicated by the arrow in *F* with a saturated solution of quinhydrone in approximately 0.1 *N* hydrochloric acid. A bare platinum wire is then inserted to make electrical contact. A convenient assembly is shown in Figure 2. The asymmetry potential which always develops across the diaphragm is determined on a solution of known pH value.

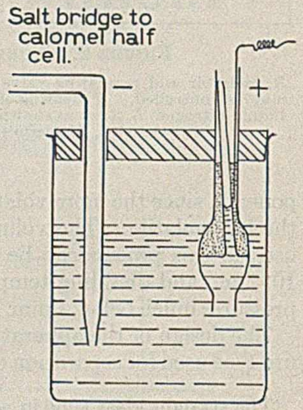

FIGURE 2. ELECTRODE ASSEMBLY

The precision obtained with this electrode used in conjunction with a Leeds & Northrup enclosed lamp and scale galvanometer and a potentiometer reading to 0.1 millivolt is better than 1 millivolt or 0.02 pH unit.

The advantages of this electrode are its mechanical stability, sensitivity (permitting its use with apparatus usually available), and ease of manufacture.

Obviously, this type of construction can be modified to suit individual requirements.

Summary

A simple procedure for making a very sensitive, durable glass electrode is given. Accurate measurements may be made with this electrode using a portable galvanometer with a sensitivity of the order of 40 megohms and an ordinary galvanometer.

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RECEIVED February 28, 1938.

Modern Laboratories

New Laboratories of the Bureau of Mines Petroleum Experiment Station

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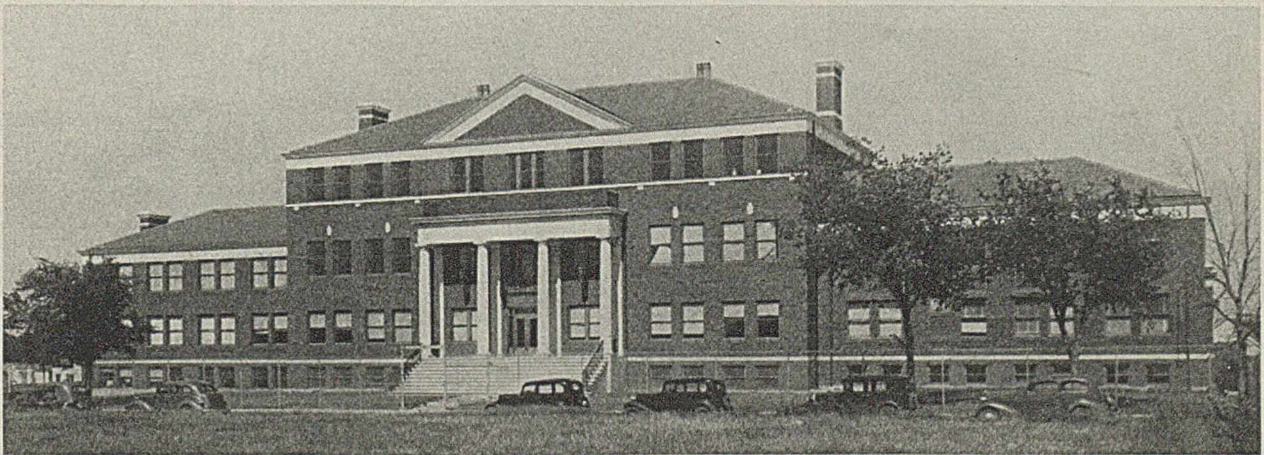
THE United States Department of the Interior research activities on petroleum and natural gas are centered at the Bureau of Mines Petroleum Experiment Station at Bartlesville, Okla., where there has been established one of the largest and best-equipped public institutions in the world devoted exclusively to the study of the problems and difficulties confronting the petroleum and natural gas industry. The station's work may be classified under the general heading of: (1) problems in the production of petroleum and natural gas, including related problems of pipe-line transportation; (2) engineering field studies of typical oil and gas fields; (3) chemistry and refining of petroleum; and (4) special technical studies, such as losses by evaporation, corrosion of oil and gas-field equipment, methods of "shutting in" oil and gas wells to prevent damage during periods of inactivity, disposal of oil-field brines, and the general subject of safety in oil fields and refineries.

The general and routine work includes crude oil distillation analyses, lamp and bomb sulfur determinations, water analyses, viscosity and specific gravity determinations, porosity and permeability determinations on oil-sand cores, gas analyses, and miscellaneous tests of a more or less standardized nature. Some of the present research activities include separation of petroleum into small fractions; determination of the physical and chemical properties of these fractions, including detailed studies on certain properties; removal of occluded salt in crude oil; corrosion studies; natural gas solubilities; pressure-volume-temperature relationships; and related problems pertaining to the chemistry and physics of petroleum. This abstract of the activities of the station shows at once the need for laboratory facilities that are widely different from those found in the usual university or industrial laboratory.

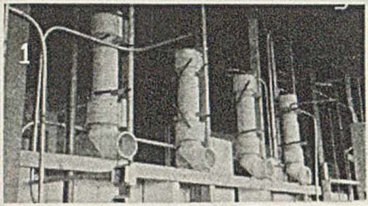
An opportunity to design and equip laboratories in keeping with the needs of the institution occurred in 1935 when the Public Works Administration allotted funds for a laboratory and office building. This article presents the more important features of construction and equipment. To a large extent these features represent the combined ideas and efforts of the laboratory staff. Architectural requirements were found to be a restricting force in some instances, but on the whole the plans and descriptions given below constitute the fulfillment of the laboratory worker's ideas to a degree not generally found.

Properly planned laboratories should have, among other things, a minimum number of places where dirt and dust can collect; noncorrosive hardware and fixtures; adequate services and outlets; easily cleaned, well lighted hoods; suitable general illumination; easily cleaned, durable walls and floors; and safe construction and equipment.

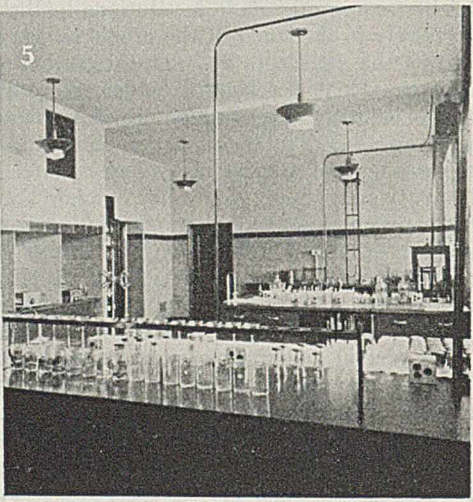


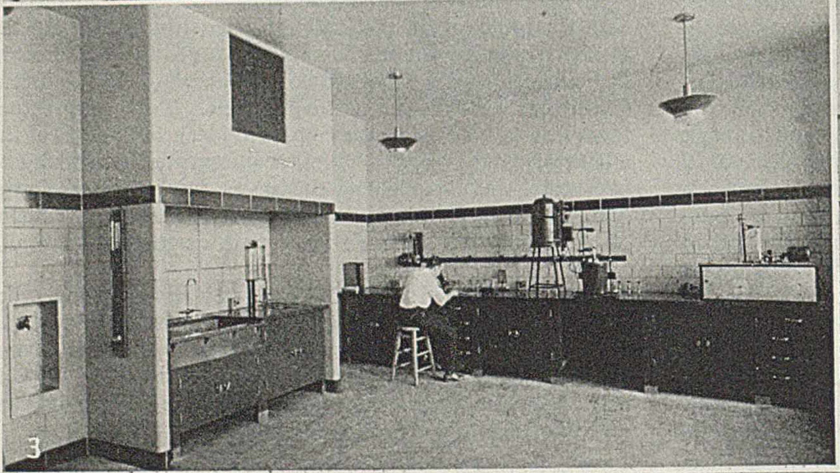
New Bureau of Mines Petroleum Experiment Station

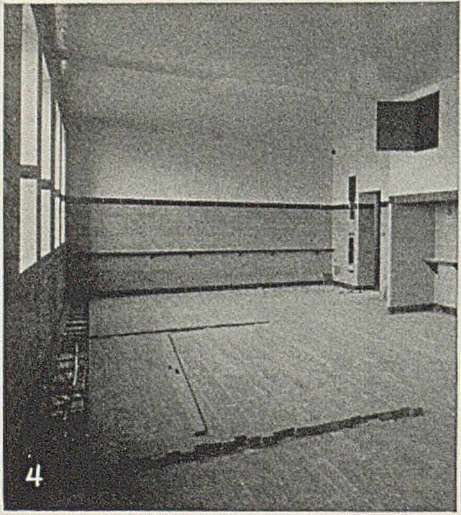
The possibility of fire and explosion can be lessened by proper attention to venting of all pipe-chases in both walls and floors; using a color code for easy and positive determination of service lines; suitably located easily worked shut-off valves; regular testing of high-pressure equipment, such as gas storage cylinders; using a color code to distinguish the several gases; adherence to code requirements in electrical installations; and taking precautionary measures for the storage of easily inflammable material. In case of fire there should be readily available fire extinguishers in working condition, quick-acting showers or fire blankets, and suitable alarm devices. Injury due to mechanical causes can be minimized by providing adequate lighting, especially in hoods, halls, and stairways and at machines; by suitable guards for belts and other moving machinery; by removing obstructions in passageways, and by suitable location and construction of doors. First-aid equipment in usable condition should be readily available, and each laboratory should have posted conspicuously information as to the location of master switches and valves.

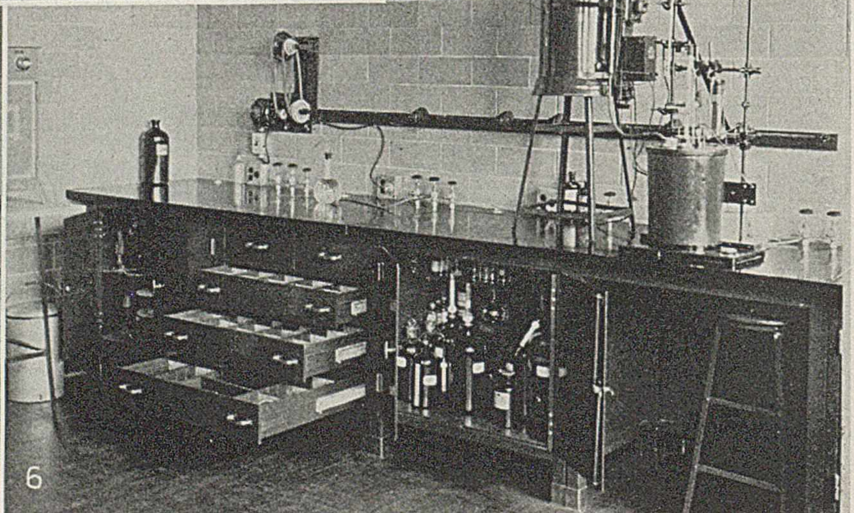


1. Transite Pipe Hood Ducts
2. Section of Workshop
3. Section of Research Laboratory
4. Wood-Block Flooring and Service Shelves
5. Section of General Laboratory
6. Details of Desk Construction









Laboratory Arrangement

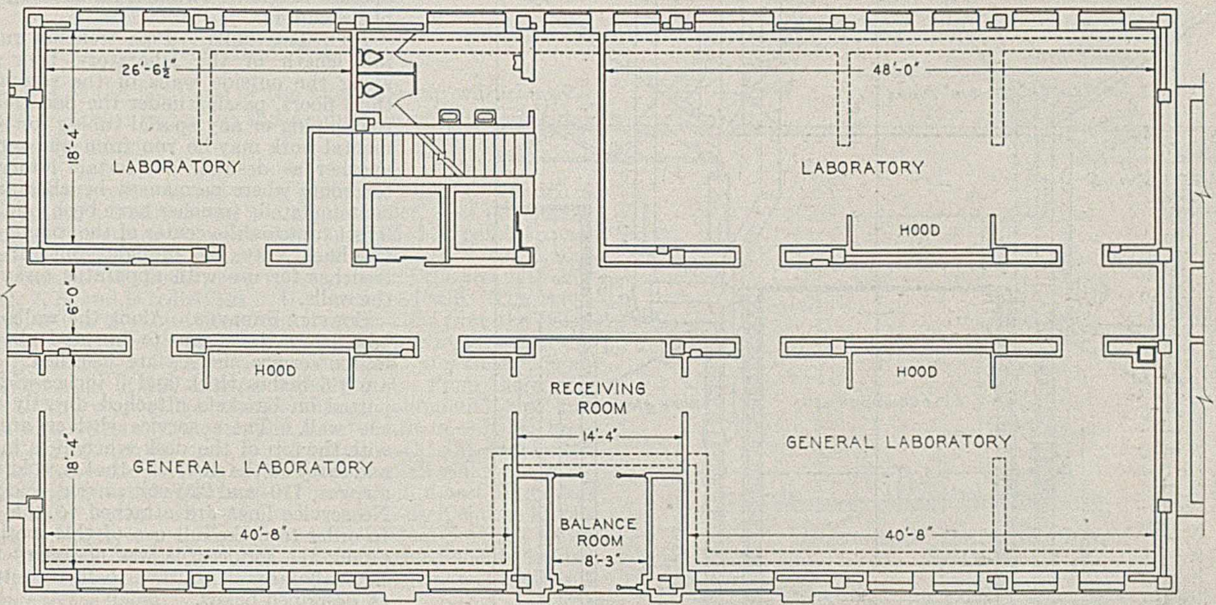
The laboratories occupy the second and third stories of the center section of the new building. The general construction of both stories is identical, but the second story is largely planned for general laboratory work, and the third story for research. The floor plans show the layout of the rooms and their approximate size. Several photographs of various parts of the laboratories are included in this article.

Laboratory Construction and Equipment

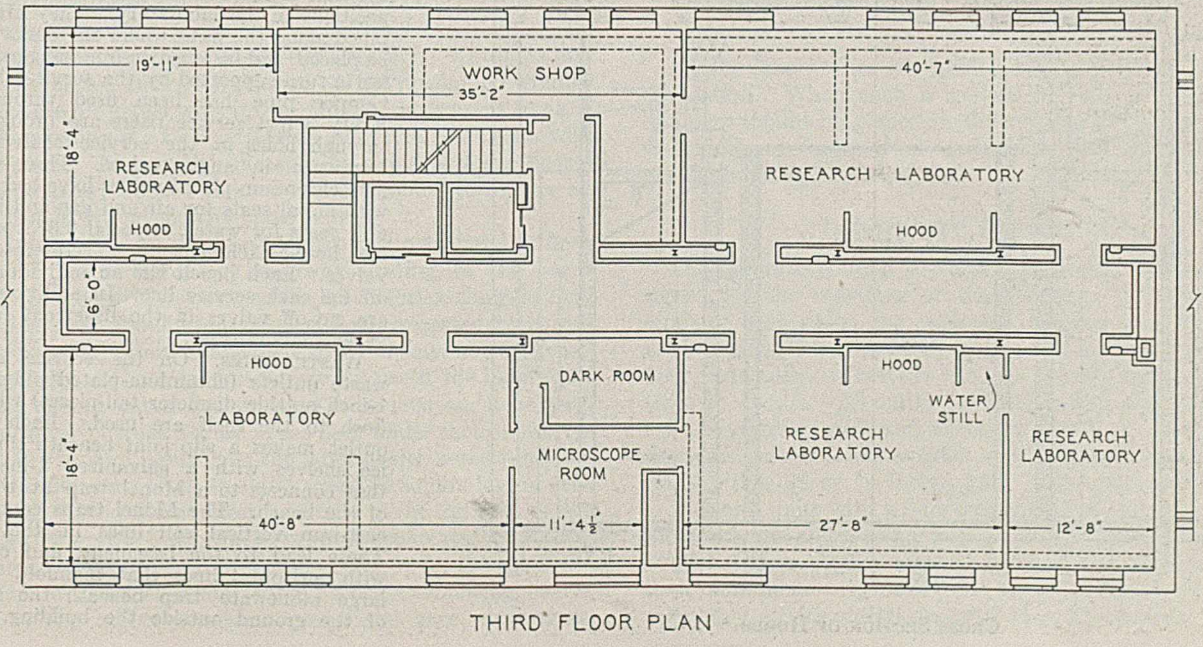
Floors. The floors are of Douglas fir blocks 2 × 4 inches in cross section and 3.75 inches thick, set with the end grain up on a reinforced concrete floor coated with asphalt. The blocks are locked together near the base with wooden splines. These wooden floors do not fatigue the feet of the laboratory worker and after several oilings are dark brown and blend well with the laboratory finish. They also are easily kept clean.

Walls. The walls up to a height of 6.5 feet are cream "enamel"-finish hollow tile, 5 × 12 inch face. The upper part of the walls is cement plaster on wire lath or on gypsum blocks and is finished with light-cream laboratory paint. The ceilings are cement plaster coated with white laboratory paint. A band of dark-brown tile is used at the base of the wall, and makes a square corner with the floor so that equipment may be pushed flush with the wall. Another dark band is used at the top of the tile. At certain intervals in the walls 0.25-inch steel plates 5 × 12 inches have been bolted and grouted into the walls so that equipment may be fastened to the wall without drilling the tile. Where it is necessary to drill the tile, Rawl plugs for holding the screws have been found satisfactory. In most cases it is possible to drill the mortar between the tile, but the tile itself may be drilled if necessary, as for the service shelves, and toggle bolts used. Small star drills are satisfactory for this purpose.

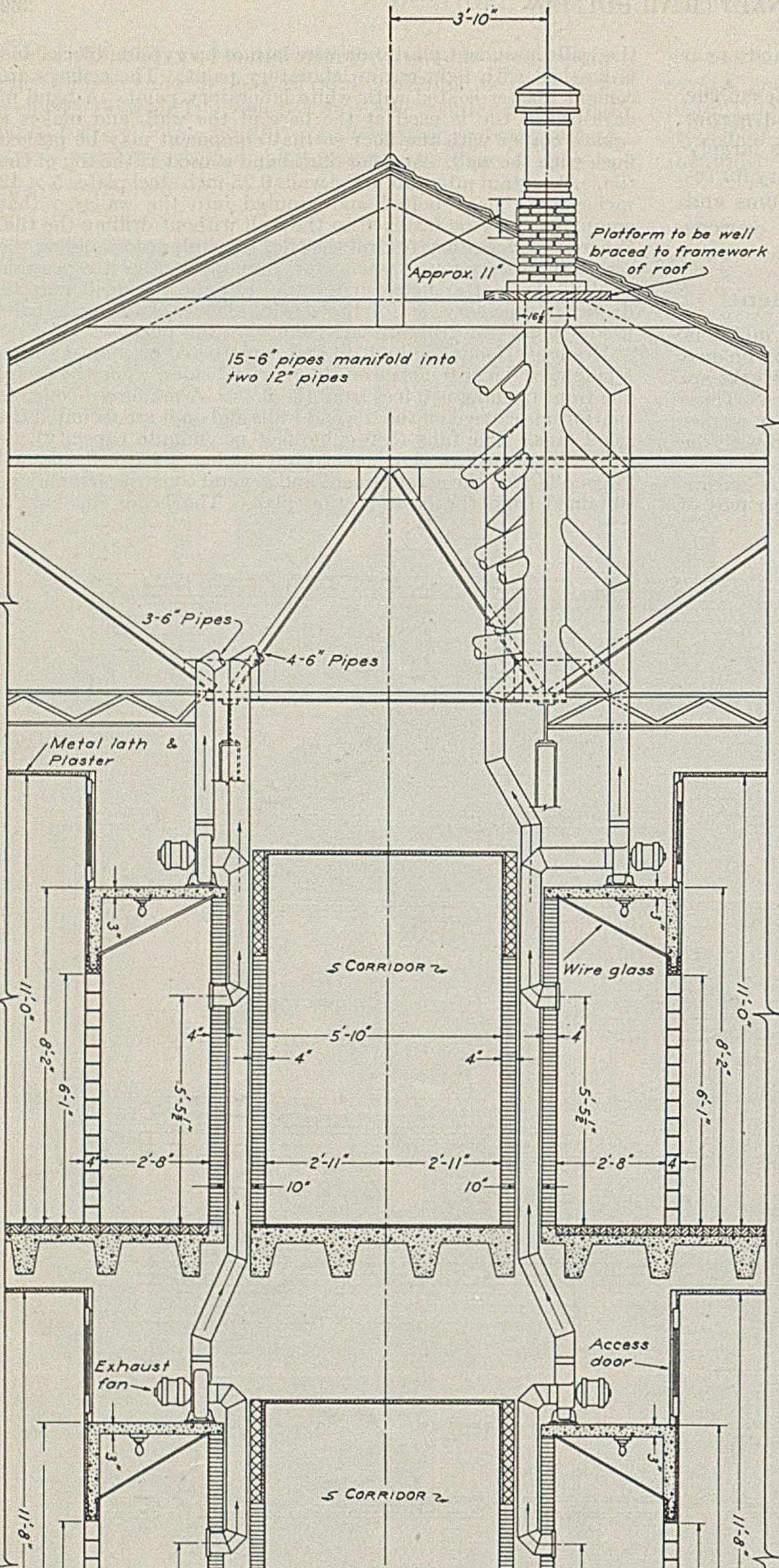
Hoods. Hoods are built in and constructed of enamel tile to a height of 8 feet 6 inches on the rear and sides, while the top of the front opening is 6 feet from the floor. A reinforced-concrete platform is carried on the tile end walls and on it are mounted the hood fans. The fans (300 cubic feet per minute capacity) are direct-connected to 0.5 horsepower, 3-phase, 220-volt motors. A good idea of the arrangement and general construction may be obtained from the cross section plan. The hoods are on the


26'-6½"
48'-0"
18'-4"
LABORATORY
LABORATORY
HOOD
6'-0"
HOOD
HOOD
RECEIVING ROOM
14'-4"
18'-4"
GENERAL LABORATORY
GENERAL LABORATORY
BALANCE ROOM
8'-3"
40'-8"
40'-8"

SECOND FLOOR PLAN


19'-11"
WORK SHOP
35'-2"
40'-7"
18'-4"
RESEARCH LABORATORY
RESEARCH LABORATORY
HOOD
HOOD
6'-0"
HOOD
DARK ROOM
HOOD
WATER STILL
LABORATORY
RESEARCH LABORATORY
RESEARCH LABORATORY
MICROSCOPE ROOM
18'-4"
40'-8"
11'-4½"
27'-8"
12'-8"

THIRD FLOOR PLAN



Cross Section of Hoods

corridor walls, which are rather thick to accommodate air-conditioning ducts, and where possible the hoods have been set back in the wall, thus saving some laboratory space. The hoods are vented through 6-inch Transite pipes concealed in the walls to 12-inch manifolds which pass through the roof. One fan is used for every 3 linear feet of desk space in the hood, and when the desks are in place there are approximately 9 square feet of opening for each fan. Each hood is baffled on the inside with 0.25-inch sheet Transite mounted on aluminum channel in such a way that the draft is distributed between the top and bottom of the fume space. Arrangements are also provided whereby Transite partitions may be inserted every 3 feet, thus dividing a long hood into sections if desired. Lights are provided on the under side of the concrete top and shielded with clear wire glass set at an angle of about 30°, sloping upward from the front. Switches for both lights and fans are situated in the end walls of the hoods. These fan switches operate magnetic switches for starting the 3-phase motors.

Pipe Trenches. Pipe trenches run the full length of the laboratory floor space along the outside walls of the second and third floors, passing under the partitions, so that piping or any special tubing for experimental work may be run from one room to another as desired. At certain intervals in the room where permanent benches are not contemplated, trenches have been run about 9 feet towards the center of the room. Service lines may be brought out in these trenches for use with apparatus away from the walls.

Service Shelves. Along the walls where laboratory desks are to be used ebony-asbestos service shelves are installed. These are 1.5 inches thick and 6 inches wide supported on brackets attached directly to the tile wall. These service shelves are flush with the top of the desk when it is in place and carry all the services—that is, cold water, air, gas, 110- and 220-volt current, and waste. No service lines are attached to the desks. In order to make full use of this method of piping the services, it was necessary to design laboratory furniture to fit the situation as described below.

Water, Air, and Gas Lines. Cold water, air, and gas are brought to each laboratory direct from the mains in the basement, or in the case of large laboratories to two different positions in the laboratory. They are then piped along the walls where the desks are to be placed, and fastened on iron hangers which are in turn supported by the service shelves. Copper pipe has been used throughout. Every 3 feet service risers are brought up through holes in the service shelves and terminate in angle valves. Three-eighth-inch chromium-plated valves have been used, with metal seats for air and gas and renewable seats for water. Special 0.375 × 0.25 inch hose-attachment nipples screw into these valves. Each bench has an individual cut-off for each service line. In addition there are cut-off valves in the basement for the various laboratories.

Waste Lines. On the service shelves waste outlets (chromium-plated plugs with 1-inch outside diameter tail-pieces) which fit flush to the shelf are used. Each waste outlet makes a slip joint beneath the service shelves with a galvanized 1-inch line that connects to a Monel trap at the end of the bench. The Monel traps connect to cast-iron vertical soil lines in the walls. These lead to the basement, and connect with horizontal lines that manifold into a large stoneware trap beneath the surface of the ground outside the building. Vent lines are carried into the attic, manifolded together, and finally vented through the roof.

Electric Conduits and Lines. Each laboratory is supplied with 110- and 220-volt single-phase alternating current service. Individual mains are brought direct from the main switchboard in the basement to a switchboard beside each laboratory doorway. In this switchboard is a main switch that cuts off power in the whole room or, in the case of a large room, a section of it. The switchboard also contains automatic cut-outs that open at 25-ampere load and are manually reset. No fuses are used. From the switchboard separate conduits run within the walls to each desk location, coming out just below the service shelves. This conduit is carried along the wall just above the waste line and at 3-foot intervals risers pass through the service shelf to cast-aluminum boxes, each of which contains two 110-volt receptacles and one 220-volt receptacle. In addition to the outlets on the benches, outlets are also provided at convenient locations in the laboratory walls, and special receptacle boxes may be used.

Sinks. The sinks are designed to fit in with the desk assembly and have special 10-inch service shelves back of them which carry service outlets for both hot and cold water. The sinks are of acid-proof stoneware with either a left-hand or right-hand drain board or both, depending upon the location. When this type of sink is used care should be exercised to see that well-processed even units are provided by the manufacturer.

Distilled Water

Because of the hardness of the available tap water, a system using cistern water for the production of distilled water has been installed.

The cistern water is fed from a supply tank, 1, through a pump, 2, into a 2-horsepower water-tube boiler, 3, at 60 pounds' pressure. The steam from this boiler is divided at point 4: part of it passes through the steam coil, 5, of a Barnstead still, 6, and then returns to the boiler; the other portion of the steam is condensed, 7, 8, and is redistilled in the Barnstead still. The boiler and still are on the third floor, and the vapor line from the Barnstead still, 9, passes through the ceiling into the attic, where the vapor is condensed, 10, and the final distilled water collects in an aluminum tank of 100 gallons' capacity, 11. From there it is piped to the various laboratories through aluminum pipe and Monel bibs. The entire operation is automatic once it has been started. Provision is made for draining both still and boiler. The distilled-water outlets in reality are small sinks about 12 inches wide, 8 inches deep, and 30 inches tall of cast aluminum set vertically in the wall. At the bottom of each sink is a connection to waste, and a 3-inch lip at the bottom prevents water from running out into the room. By this arrangement distilled water may be easily run to flasks, beakers, and cylinders without drippage to the floors.

Safety and Miscellaneous Features

The laboratories are of entirely fireproof construction, with the exception of the floors. However, since these are a solid mass on concrete they will not burn readily. All doors and door casings are steel with grained walnut finish, and window casings are also steel with brown finish. At present some of the door panels are steel or frosted glass and some clear wire plate glass. As a safety measure to avoid striking people when doors are opened suddenly, it is planned to replace all steel panels with clear wire plate glass.

A 1-quart carbon dioxide–type fire extinguisher has been placed in each laboratory doorway leading to the corridors. In the corridors between the laboratories, showers have been installed about every 20 feet, each operated by a pull chain hanging within convenient reach of anyone traversing the hallway. These are for emergency use if the laboratory worker should catch fire or have a serious accident with chemicals. There is a drain in the floor under each shower.

All the general lighting in the laboratories is semi-indirect with one 300-watt lamp to about every 80 square feet of ceiling area. Good illumination not only saves the eyes of the laboratory worker but helps to prevent accidents.

One room has been set aside as a workshop for the use of the research workers only and contains a glass-blowing bench, glass tubing cabinet, vacuum pump and gage, drill press, grinder, small (3.5 feet by 9 inch) lathe, tool chest, and soldering bench. In addition, supplies such as bolts, screws, pipe fittings, paint, and wire are stored here. This room makes it possible for the research worker to make and repair his apparatus outside of the actual laboratory and under better conditions. This in turn keeps the laboratory cleaner and helps to eliminate accidents due to the close proximity of pipe wrenches to glass apparatus.

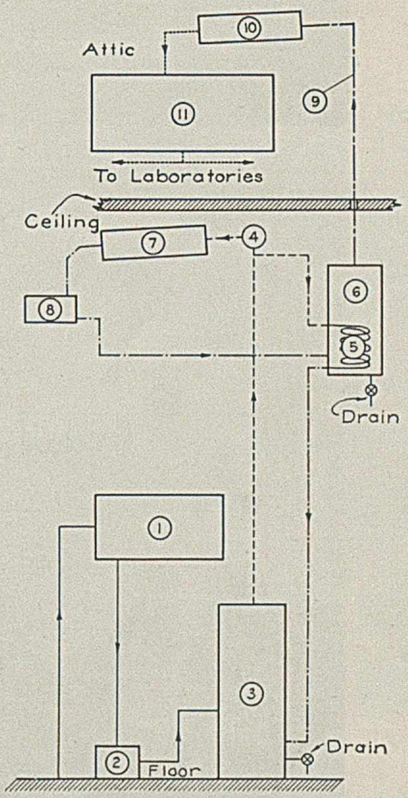


Diagram of Distilled Water System

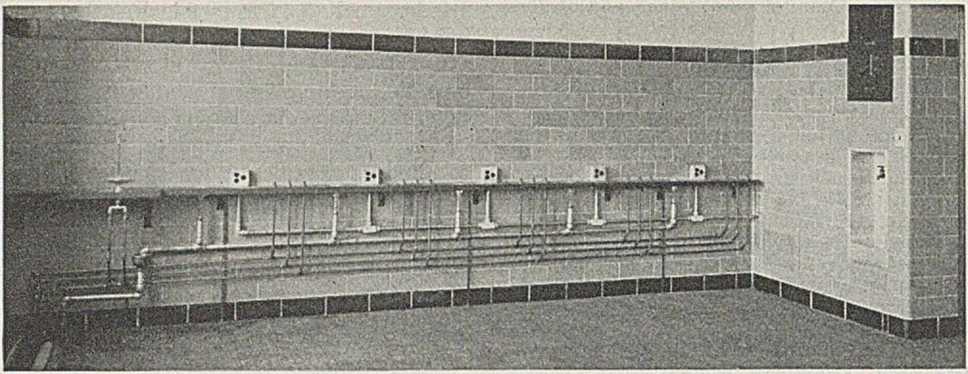
1. Boiler supply tank
2. Pump
3. Boiler
4. Valve
5. Steam coil
6. Barnstead still
7. Condenser
8. Barnstead still supply tank
9. Vapor line
10. Distilled water condenser
11. Distilled water tank

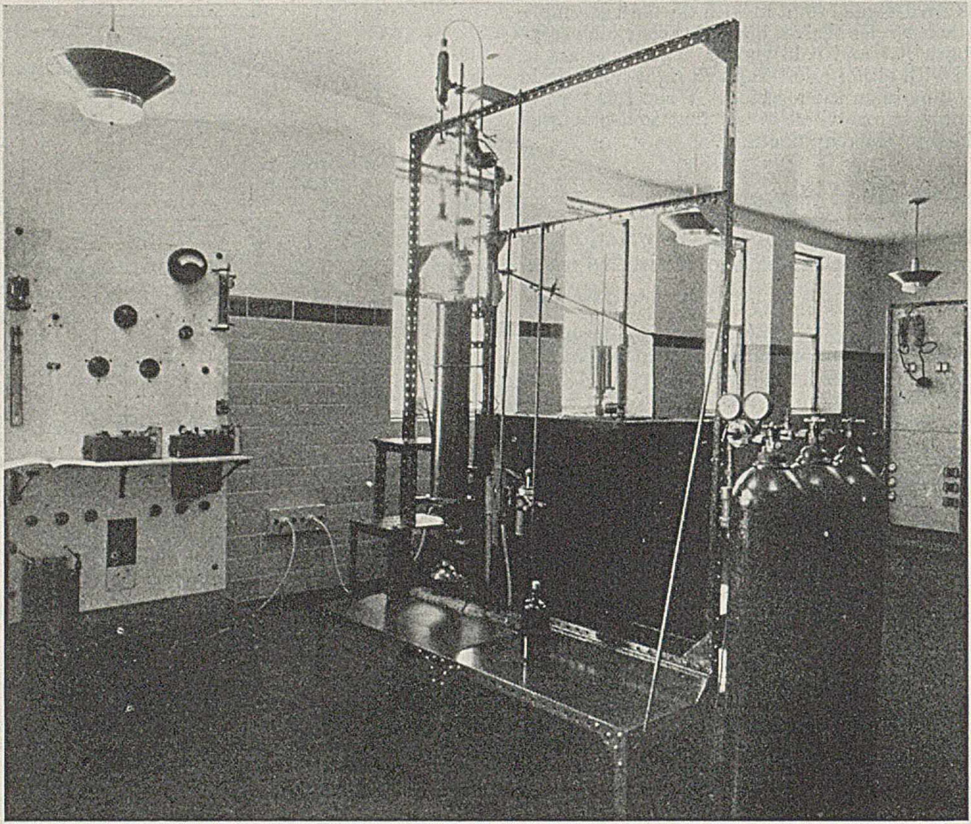
— Cistern water
—— Steam from boiler
— · — Condensed boiler steam
——-—— Barnstead still vapor line
------· Distilled water

All the laboratories are heated and cooled by forced air circulation. When such a system is used in laboratories dampers should be placed in the returns so that obnoxious and dangerous fumes, if released in one room, will not permeate the building.

Laboratory Furniture

The laboratory desks are interchangeable steel units designed by the members of the station. There are three kinds of desk units, the cupboard, drawer, and open type. Each unit is 36 inches wide, 34.5 inches high, and 26 inches deep. Adjustment bolts in the legs provide for small variations in height. All units are lead-coated and finished in dark olive-green acid- and alkali-proof enamel. Tops are of ebony asbestos 1.5 inches thick and 28 inches deep, and generally either 38 or 74 inches long. This provides tops for 1, 2, 3, or 4 units with a 2-inch overhang at the ends. When the desk units and tops are in place there is a working surface 36 inches from the floor and 34 inches deep. This is deeper than most laboratory desks, but the increased space is very useful and service outlets may still be easily reached.





Upper. Service Lines
Lower. Angle-Iron Support Unit

One of the greatest aids to an orderly laboratory is a place to keep small items. To assist in this the drawers were made with slots on all sides, and partitions can be made at the laboratory or tin shop that will provide many bins for clamps, thermometers, corks, etc. In the cupboard units shelves of two different widths, adjustable on 0.5-inch centers, are provided. The open unit makes an available storage space for stools when they are not in use.

Balance cases and tables are also of steel construction with enamel finish. The tables have linoleum tops, and the cases are of the sliding-door type. Although no special feet have been provided, there is no vibration so long as the tables do not touch the walls.

Sinks are mounted on steel cabinets that harmonize with the other units and have doors in front that permit access to the trap and also to storage spaces.

For equipment that does not fit well on desks, such as gas-analysis and distillation apparatus, special units of punched angle iron have been designed. To these may be bolted angle-iron frames of desired size and shape. One-quarter-inch iron pipe and lock nuts provide rods where needed, and also are used for braces. Several layers of plywood with a 0.25-inch ebony-asbestos top make a satisfactory table top for these units.

Acknowledgments

The design and construction of these laboratories necessarily contain the ideas of many men, and to all who contributed the author acknowledges his indebtedness. To one man, N. A. C. Smith, supervising engineer of the station, we owe a great deal, not only for his suggestions but also for his encouragement and coöperation in the development of new ideas of various members of the staff. Many of the unusual and different features are due to Harry T. Rall, and his help is gratefully acknowledged. The book entitled "The Construction and Equipment of Chemical Laboratories" by the National Research Council was also of considerable value.

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BECKMAN pH METERS

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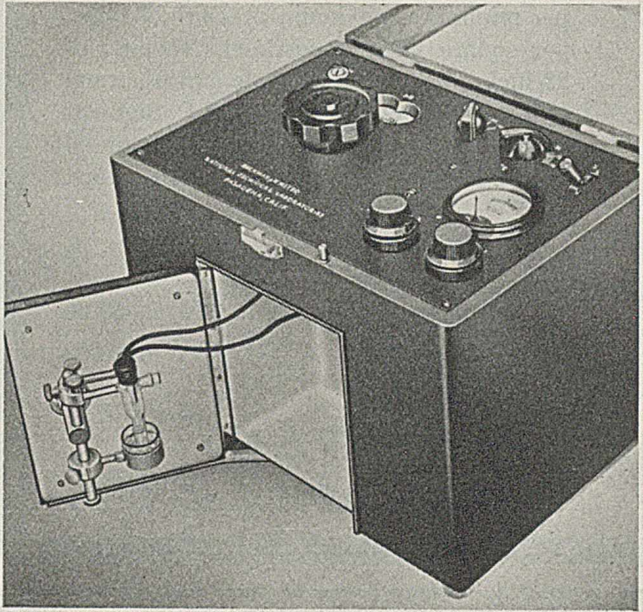

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THE LABORATORY MODEL has been recently improved to further increase its utility for both pH determinations and oxidation-reduction measurements. Rapid and accurate pH measurements in the range 0 to 13 can be made in an almost unlimited variety of solutions or substances. Immediate conversion of the circuit for measuring oxidation-reduction potentials directly in millivolts is made by merely changing a switch position. Either a scale range of 0 to 1300 millivolts or minus 1300 to plus 1300 may be selected.

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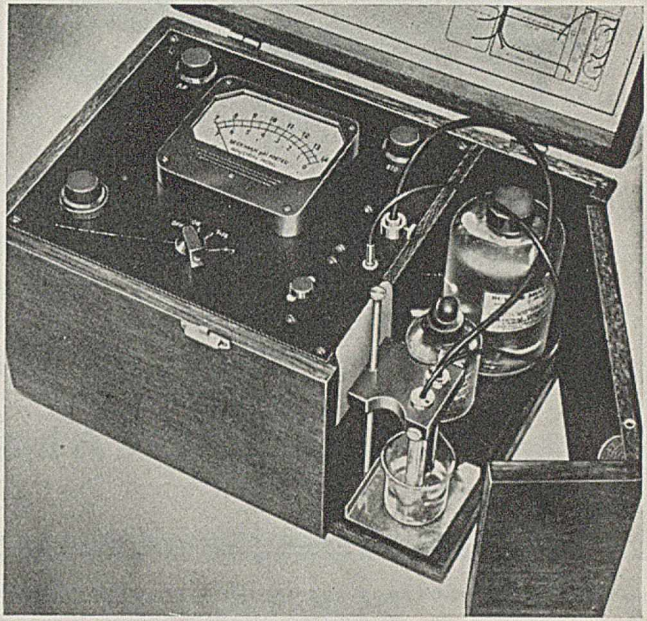

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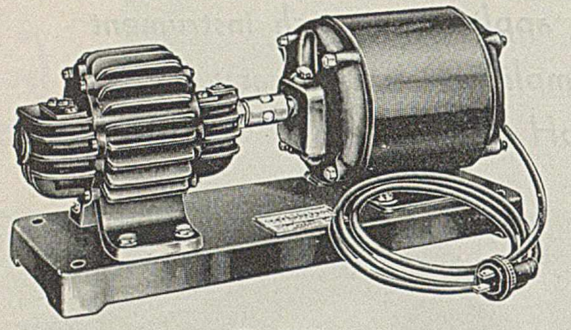

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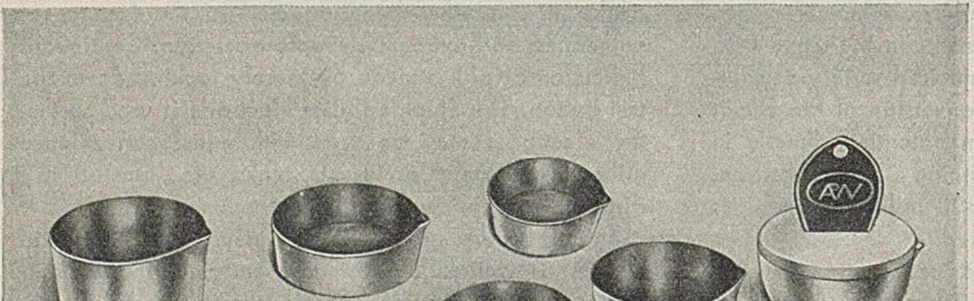

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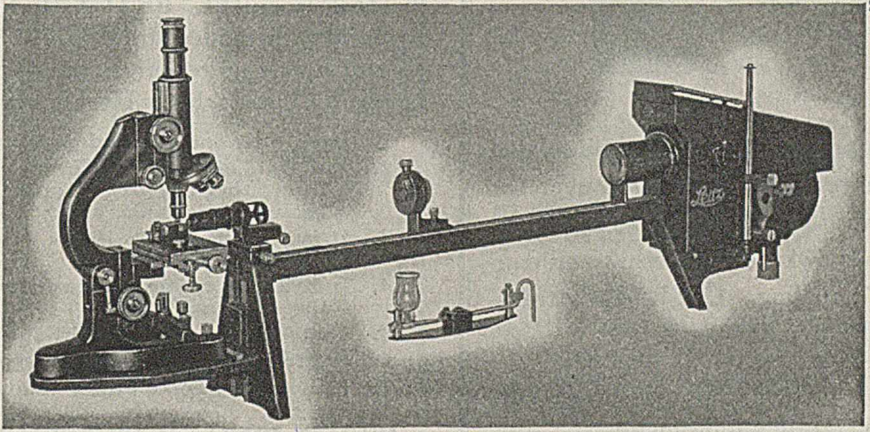

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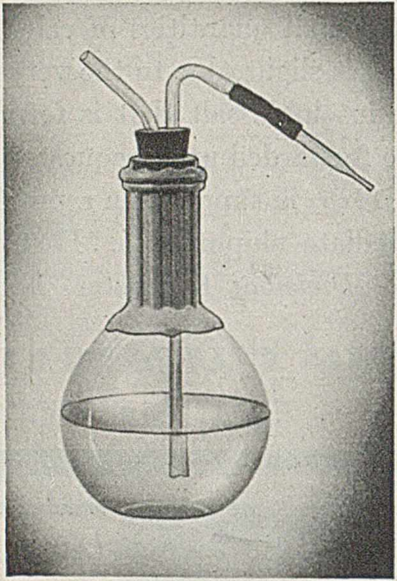

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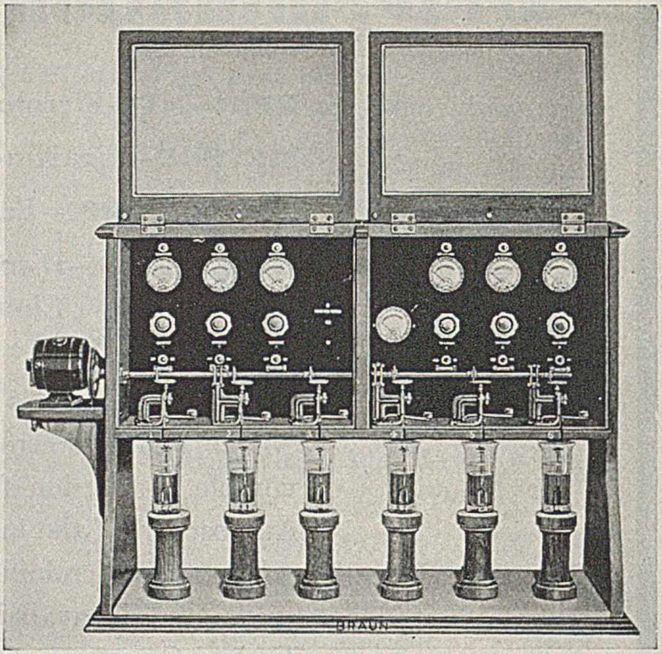

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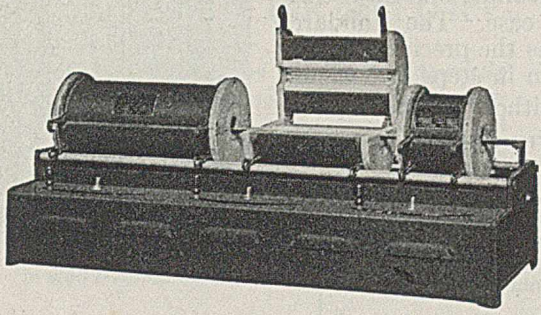

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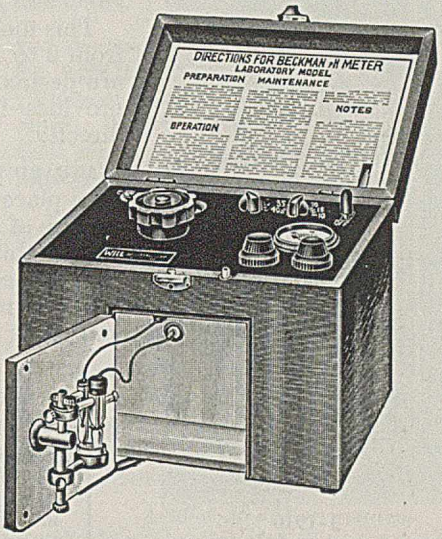

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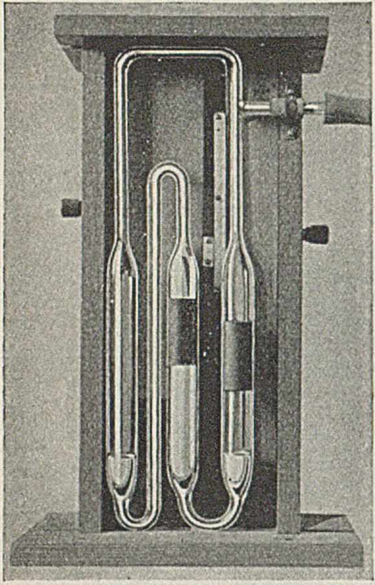

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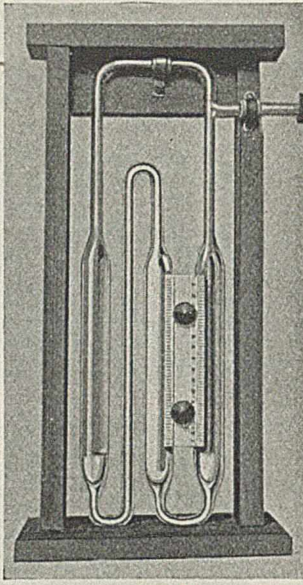

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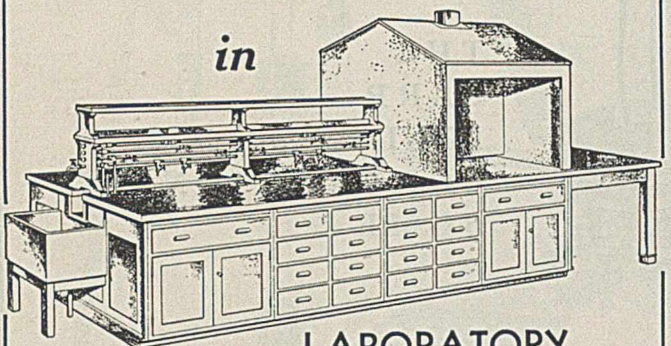

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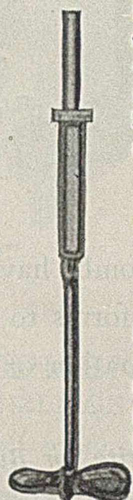

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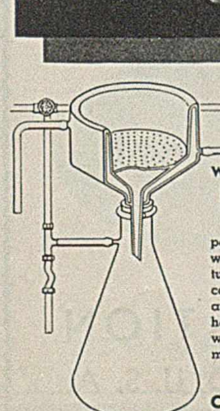

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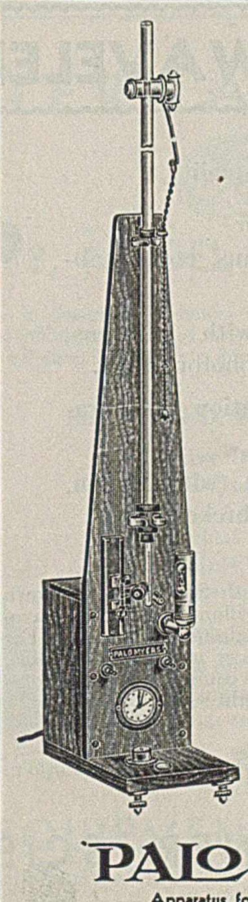

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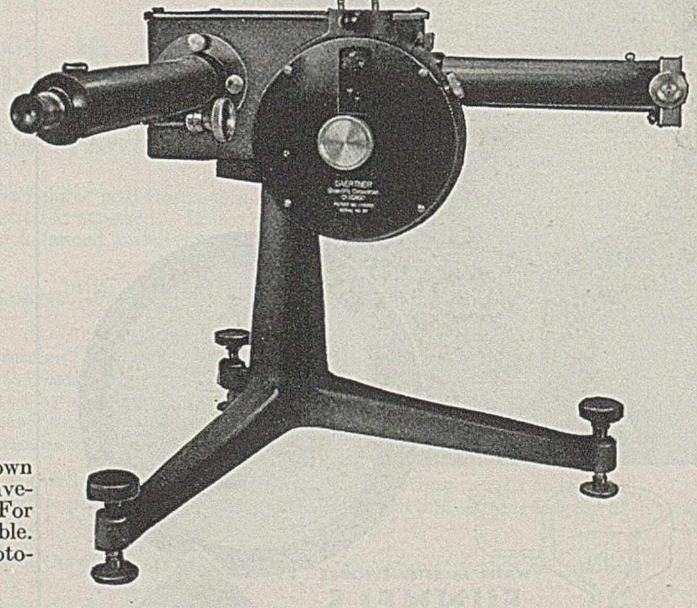

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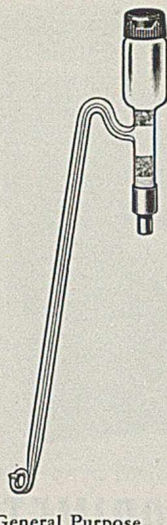

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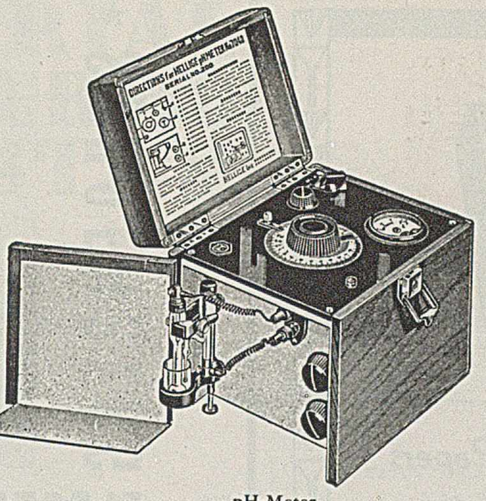

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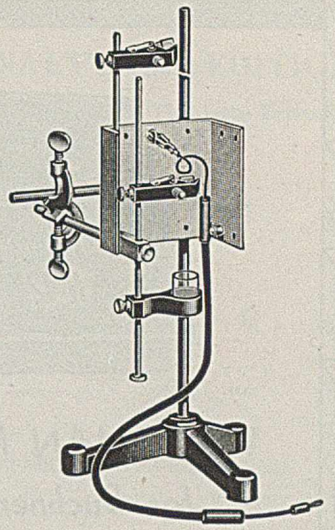

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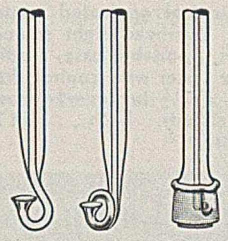

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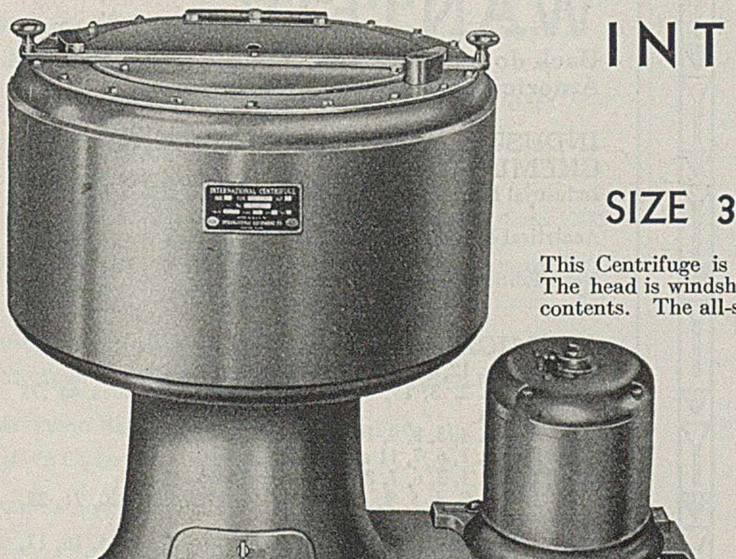

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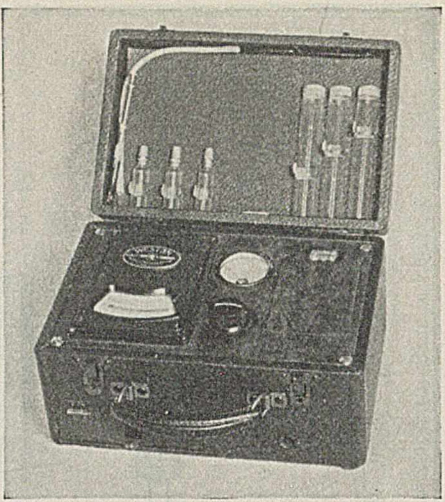

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