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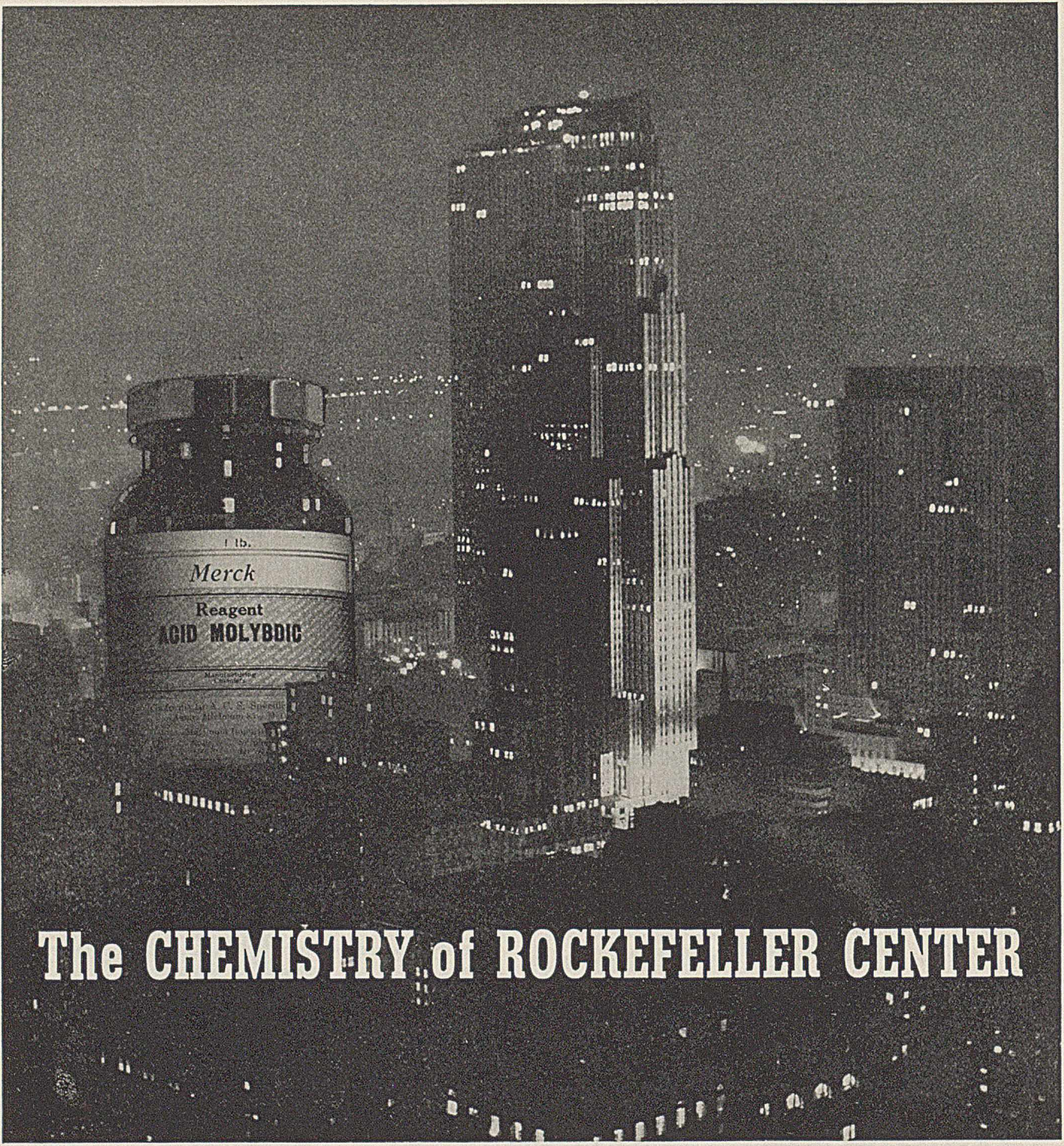
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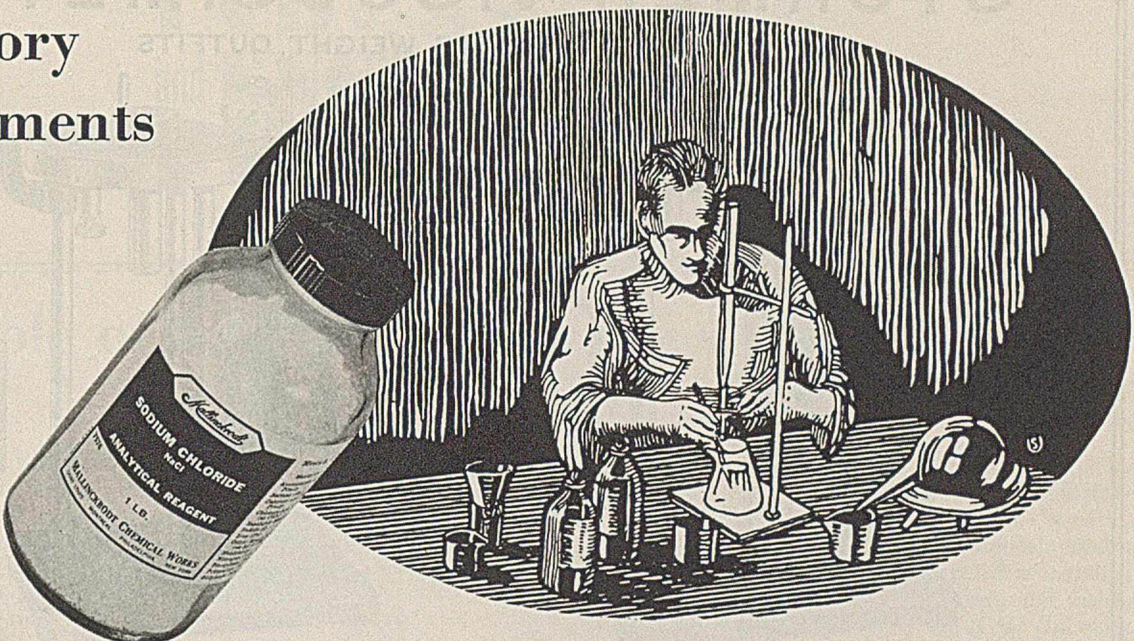
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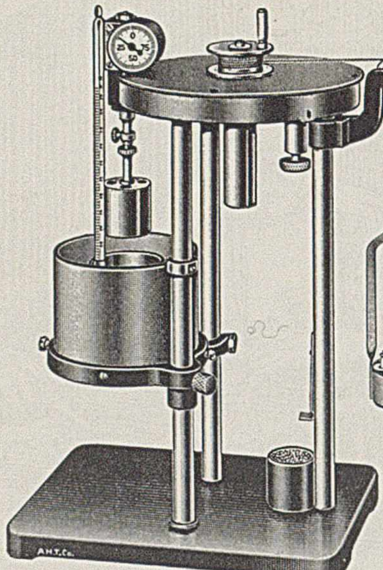

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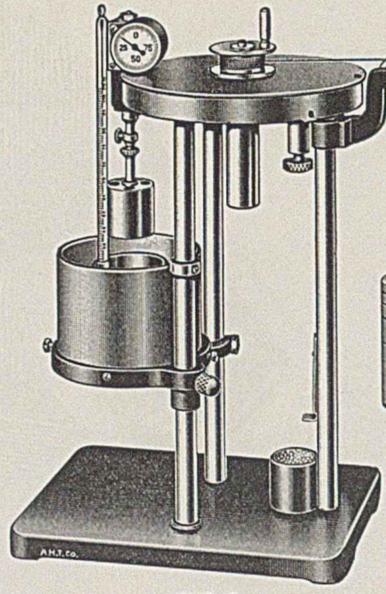

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The Role of Spectrophotometry in Colorimetry

M. G. MELLON, Purdue University, Lafayette, Ind.

OUTSIDE of the white polar regions, the black night, and the gray desert wastes, color plays a more important esthetic and practical part in our daily lives than is generally realized. The conference on color at the Massachusetts Institute of Technology in July, 1936, demonstrated the present physical and chemical interest in the subject. At this symposium more than 25 papers, mostly by industrial men, were presented on various subjects relating to the measurement of color and the use of colorimetric data in formulating useful specifications.

In the work of the analytical chemist colorimetric phenomena have at least the following important applications (*33*): (a) the marking of the course of various chemical reactions incident to the determination of constituents; (b) the qualitative detection of various constituents by means of specific colorimetric reactions; (c) the quantitative determination of constituents by appropriate means; and (d) the actual "color analysis" of an object. The present paper is concerned with both qualitative and quantitative aspects, in so far as the spectrophotometer may be utilized in evaluating the color analytically.

The word colorimetry implies measurement of color. In chemistry the practice of colorimetry involves almost entirely a comparison of an unknown system with a known system to determine whether they have the same intensity of color. The process of comparison is carried out in a number of different ways. One method is to use what the chemist calls a colorimeter. As Hardy and Perrin have pointed out (*22*), such instruments should really be called color comparators, since there is no measurement of color in the sense that physicists use the term colorimetry.

In physics colorimeters are instruments in which stimuli are combined in such a manner that the resultant color sensation is the same as that of the object being measured. This result may be achieved in several ways by a number of different instruments which serve to synthesize stimuli. In general, such apparatus is of the trichromatic or monochromatic type. In the former the color to be measured is matched by a mixture of the three primaries, red, green, and violet, produced in some suitable manner. In the latter the color under test is matched by a mixture of white light with monochromatic light produced by a dispersing system. Such colorimeters have not found extensive use in chemistry. The chief difficulties are to maintain the desired quality of the light source and to obtain observers having normal vision.

Although spectrophotometers have been known for many years, it is only in the last decade or two that their value has begun to be generally appreciated in chemical work (*50*), and there are still few laboratories equipped with such instruments. With increased production, decreased prices should result in a more widespread distribution of spectrophotometric equipment.

Principle of Spectrophotometry

Essentially, a spectrophotometer is a device for determining, wave length by wave length, the proportion of radiant energy incident upon a body that is reflected or transmitted by it. In order to measure the transmission of a colored solution, for example, the arrangement of a number of instruments is

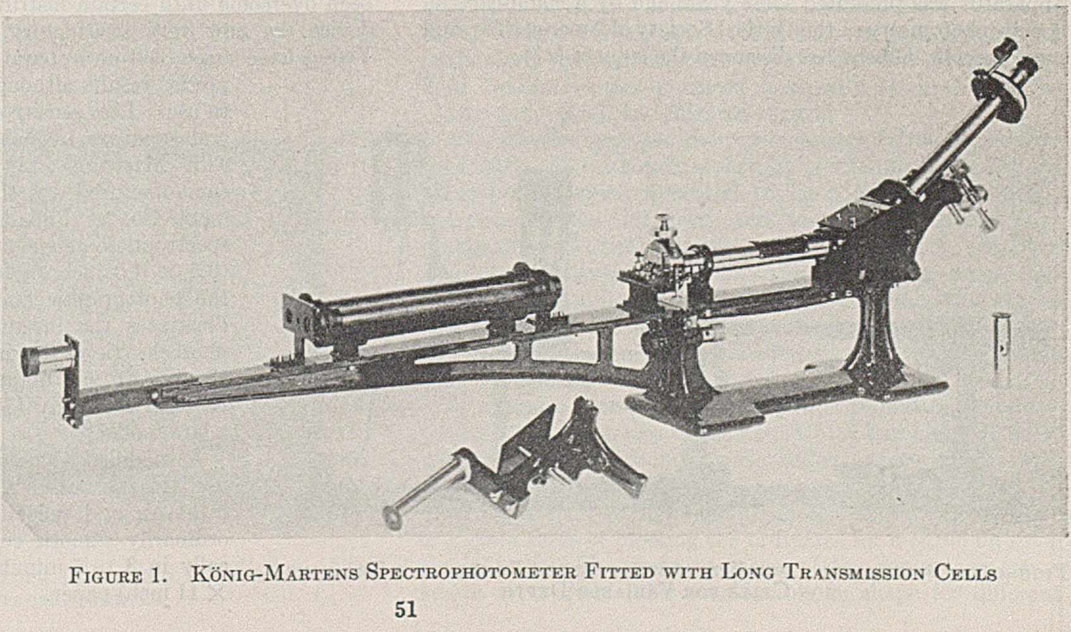

FIGURE 1. KÖNIG-MARTENS SPECTROPHOTOMETER FITTED WITH LONG TRANSMISSION CELLS

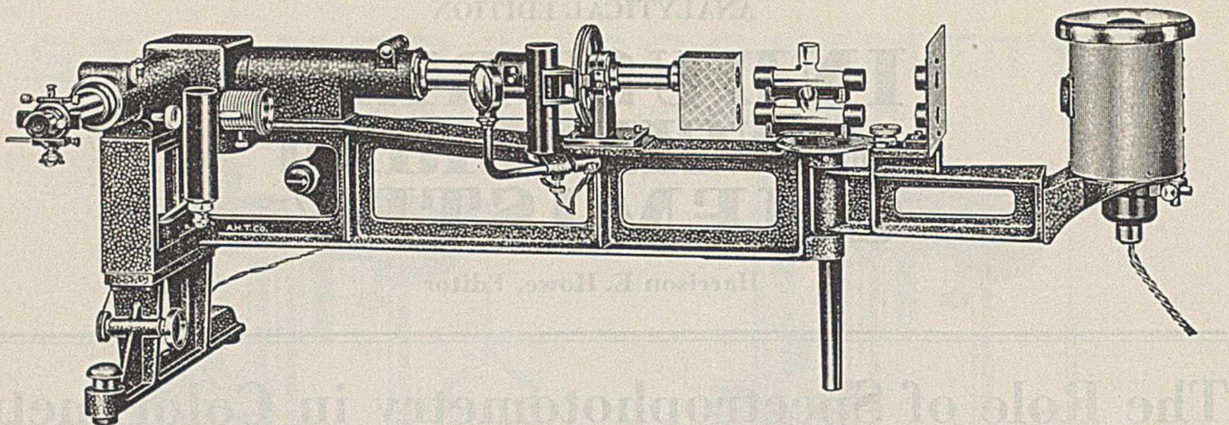

FIGURE 2. HILGER SPECTROPHOTOMETER

such that the light from a suitable source is divided into two beams of equal intensity. As these pass through a monochromator, a narrow spectral band of the width and wave length desired may be selected. The solution, in a suitable cell, is placed in one of the two beams; and the solvent only, in an identical cell, is placed in the other beam. Since the solution will absorb more light than the solvent, the emergent beams are of unequal intensity. By means of a photometer in the light path the more intense beam may be reduced to match the other, as determined by bringing the two halves of an optical field to equal intensity. The graduation of the instrument enables one to determine the proportion of the light incident on the solution that is transmitted by it. This value is known as the per cent transmittancy (*43*). By placing the sample in a different position, reflection values can be obtained for such materials as paper, textiles, and paint panels.

Spectrophotometric Apparatus

In contrast to the chemist's "colorimetric" determinations, spectrophotometric measurements are not limited to colored systems. For many years absorption spectra have been determined, chiefly by photographic means, for the ultraviolet and infrared regions of the spectrum. The present discussion is limited to instruments used for the visual region, which are the most useful for measuring colored systems, both opaque and transparent. A general review of such apparatus was presented some years ago by a committee on spectrophotometry of the Optical Society of America (*18*), and more recently Gibson has discussed the subject (*17*).

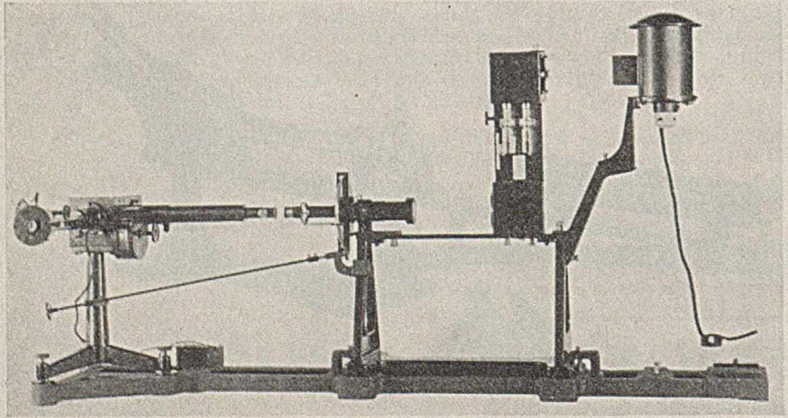

FIGURE 3. BAUSCH AND LOMB SPECTROPHOTOMETER FITTED WITH TRANSMISSION CELLS FOR VARIABLE DEPTH

For work in the visual region the type of instrument largely used consists of a light source, a monochromator, a photometer, an eyepiece for observing the photometric field, and a holder for the sample. The holder is a cell for transmission measurements of a liquid, or a device for supporting an opaque object on which reflection measurements are to be made. Such instruments are illustrated in Figures 1 to 3. Figure 1 shows the König-Martens type, manufactured by Schmidt and Haensch, which is the visual instrument used by the U. S. Bureau of Standards. Another foreign instrument is illustrated by the Hilger form shown in Figure 2, arranged for transmission measurements. It has a unique construction for making reflection measurements on opaque samples. Figure 3 illustrates one of the best known instruments made in this country, as manufactured by Bausch and Lomb for measuring in the same cell different thicknesses of a liquid. All the better instruments have variable, calibrated slits for controlling the width of the spectral band of light admitted. Various details of operation and a thorough discussion of sources of error for the König-Martens instrument are contained in a publication by McNicholas (*28*).

During the last 15 years many efforts have been made to substitute a photoelectric cell for the human eye as the "seeing" mechanism of such instruments. The eye has two definite disadvantages in being easily fatigued, and in having a very low sensitivity at 400 and 700 mμ, where the normal visibility curve is practically zero. Early difficulties with cells have been overcome until certain instruments equipped with this device are now very satisfactory. Zscheile, Hogness, and Young have assembled an apparatus (*52*) which gives very precise results although it is somewhat tedious to use. Less sensitive instruments of this general type are available commercially. Razek and Mulder (*38*) devised an instrument (manufactured by the Thwing-Albert Instrument Co. of Philadelphia) that provides a spectrophotometric curve, 8.75 × 11.25 cm. (3.5 × 4.5 inches), for the sample as soon as the photographic film is developed. Figure 4 illustrates the instrument. A third type of photoelectric instrument is that devised by Hardy (*20*) and manufactured by the General Electric Company (*33A*). Figure 5 illustrates a late model.

A modified General Electric instrument is used in the author's laboratory for all transmission and reflection measurements. Any ordinarily smooth curve is plotted automatically in 3 to 5 minutes on 20 × 27.5 cm. (8.5 × 11 inch) paper.

The Nature of Spectrophotometric Data

The fundamental data provided by a spectrophotometer show the proportion of the light incident upon a sample which is reflected or transmitted by it. There may be a single value for a given wave length, or values may be determined to cover the whole visible range. In the latter case the results are generally plotted in the form of a curve with transmission or reflection as ordinates and wave length as abscissas.

When a curve is to be made covering part or all of the visible range, the question arises as to the wave-length interval at which to determine the individual points, and the width of spectral band to use for the light source. If the curve is steep and contains small sharp absorption bands, the points may need to be taken at every millimicron with a spectral band as narrow as possible. Zscheile found such precautions necessary in determining chlorophyll (*51*). If the curve is smooth and not steep, points at each 10 mμ are adequate, and spectral bands of 3 to 10 mμ are sufficiently narrow. Recording instruments provide a continuous curve.

If instruments are graduated to read directly, the values will be in one of several possible terms, such as percentage, optical density, or extinction coefficient. The percentage system is probably the most commonly used at present, although the others have merit in special cases. Benford has discussed the plotting of spectrophotometric data (*5*), and Twyman and Allsopp include definitions of terms (*45*). In instruments such as Zscheile's, operating on a substitution basis, the ratio of two deflections of a galvanometer or electrometer must be calculated for each wave-length setting. For many purposes curves of the percentage–wave-length type are sufficient in themselves. Figures 6 and 7 show such curves for several different systems.

For certain purposes it is desirable or necessary to convert the data of the percentage–wave-length curve to the trichromatic or monochromatic basis, thus providing a real analytical measurement of the color. In this sense the spectrophotometer becomes a colorimeter, yielding values on the subtractive or additive system. The trichromatic, or tristimulus, values are in terms of the percentages of the three primaries, red, green, and violet, required to match the object. The monochromatic values are in terms of dominant wave length and of percentages of brightness and purity. Reference is made in the section on color analysis to the method of making such calculations.

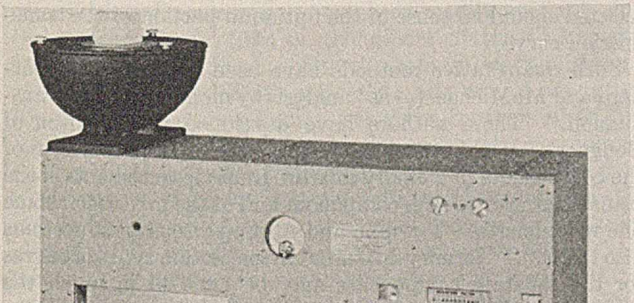

FIGURE 4. RAZEK-MULDER RECORDING PHOTOELECTRIC SPECTROPHOTOMETER

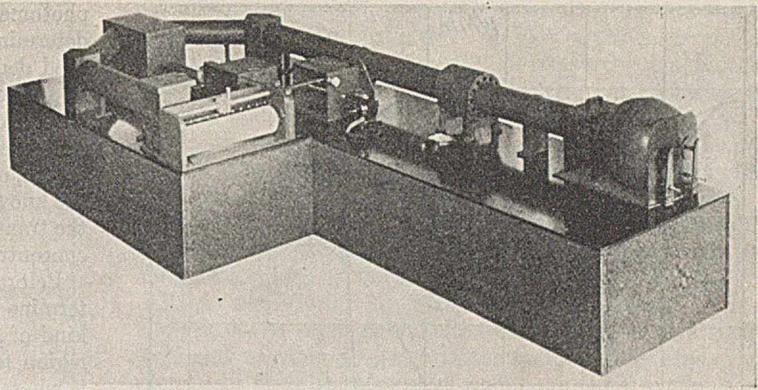

FIGURE 5. GENERAL ELECTRIC RECORDING PHOTOELECTRIC SPECTROPHOTOMETER

Applications

Although the analytical applications of spectrophotometry are mentioned only occasionally in books on general analytical methods, or even in works dealing with colorimetric methods of analysis, a survey of the literature reveals many papers. These cover a variety of specific applications, and they are to be found in a number of different fields. The outline below is intended to be representative of the kinds of applications that are being made.

QUALITATIVE USES. The transmissive or reflective characteristics of a system may be very specific. Thus, there are probably no other solutions having the same spectral transmission curve as those of neodymium salts which show a number of sharply defined large and small bands in the visual region. In such a case as this the spectrophotometric evidence is quite definite. One must always keep in mind, of course, that the shape of the curve will be changed by the presence of any other substance showing a different selective absorption or reflection.

Many solutions, glasses, and substances such as paper and paints yield curves which are relatively flat and regular. Usually the farther they go in this direction the greater is the possibility of finding several systems having about the same curve. The curves for many solutions have been determined, particularly for organic compounds in the ultraviolet region. This qualitative use of curves is equally applicable in the ultraviolet, visual, and infrared regions.

As a specific example, the recent paper of Ruehle may be cited (*39*). In the course of a study of vitamin B he obtained a compound which appeared to be a thiazole derivative. Solutions of the unknown and known compounds gave practically identical curves. As confirmatory evidence various derivatives of the known and unknown compounds were prepared and measured similarly. On obtaining curves which again agreed closely with each other for the two products the conclusion was reached that the two compounds were the same.

As a second example we may consider peanut oil and mustard oil. Two samples of such oils which had identical color values on the Lovibond scale yielded curves significantly different (*14*).

Such examples as those just given illustrate the desirability in certain cases of plotting the ordinates for a curve on some special basis. Transmission curves of the percentage–wave-length type often differ considerably in shape for different

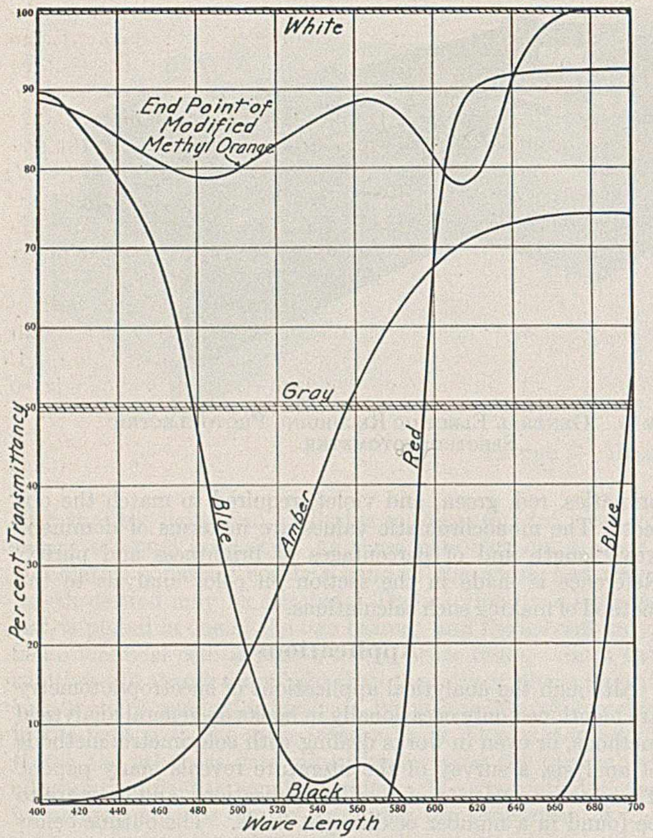

FIGURE 6. SPECTRAL TRANSMISSION CURVES

For standard red, amber, and blue glasses, and for a solution containing modified methyl orange at the end point. The location is shown for the curves for a perfect black, white, and gray (50 per cent).

thicknesses of the system measured. If one plots the logarithm of the optical density (density = 1/transmission), the curves will all have the same shape regardless of thickness. Of course one can readily convert transmissions for any given thickness to any other by means of a special slide rule, mentioned below, which has a scale based on Bouguer's law.

In a general way it may be said that this use of spectrophotometric curves applies to a variety of products for the establishment of standards and for the comparison of subsequent products with the standards. In this sense the data are comparable to measurements such as refractive indices. In a paint or dye laboratory, for example, curves would be obtained for the best obtainable or standard grades of the materials to be tested. These data are permanent and can be filed for reference at any future time. They have all the advantages inherent in any numerical specification. The effects of impurities, methods of manufacture, and other significant factors can be determined in so far as they influence the curves of the standards. Adjustment can then be made until the permissible color tolerance is attained, as measured by conformity to the standard curves. There is a wide application possible in this direction. Two examples of such uses are for dyes and textiles (*9, 35, 36, 40*), and for paint (*1, 16, 25*).

QUANTITATIVE USES. The possibility of applying spectrophotometry for making quantitative determinations by means of absorption has been recognized since the time of Vierordt (*48*). For some years such methods have been recognized by physicists (*15, 27, 41*). In more recent years chemists have begun to apply such methods to a variety of systems. Representative examples include dyes (*2, 3, 6, 13, 19, 23, 24, 49*), hydrogen-ion concentration (*7, 12*), nitrogen (*29*), hemoglobin (*10*), bilirubin (*11*), chlorophyll (*51*), vitamins and hormones (*34*), and general applications (*44, 46*).

The common method of measuring a constituent spectrophotometrically has been applied recently by Mehlig for the determination of manganese in steel (*30*). The procedure used depends upon the fact that the transmittancy of light at a given wave length is a function of the concentration for a solution such as permanganate. If a reference curve is constructed, plotting the transmittancy, at the given wave length, of a series of standard permanganate solutions against the known manganese concentrations, it is possible to convert the transmittancy of an unknown permanganate solution into concentration of manganese by use of the curve.

Before constructing such a reference curve, one should determine the transmission curve from 400 to 700 mμ for the kind of solution to be measured in order to select a suitable region for making the readings. The preferable wave length is where there is least change in transmittancy for a given change in wave length—that is, where there is a maximum or minimum in the transmission curve. On steep portions of a curve a small error in wave length results in too great an error in the transmittancy. For visual instruments the wave length selected should be as near as possible to the peak of the relative visibility curve to take advantage of the maximum sensitivity of the eye. Likewise, an inspection of the curve coördinating concentration and transmittancy shows that certain portions will yield results of greater accuracy than others. Readings in the optimum range can be obtained by suitable dilution of the sample.

In a later paper Mehlig modified the scheme for calculating the results in applying the method for the determination of copper in ores (*31*). For solutions conforming to the Bouguer-Beer equation

$$I = I_0 \times 10^{-elc}$$

in which I_0 represents the intensity of the incident light of given wave length entering the solution, I the intensity on leaving the solution, l the length of the cell in centimeters, c the moles of absorbing substance per liter of solution, and e the molecular extinction coefficient. Solving for c, we have

$$c = \frac{\log \frac{I_0}{I}}{el} \text{ moles per liter}$$

The values for I_0, I, and l are known for any given determination. It is necessary to prepare a solution containing a known concentration, c, in order to calculate the value of e for the desired wave lengths for use in subsequent work. As in the use of a concentration-transmittancy curve, the wave lengths selected should be those of the optimum portion of the transmission curve.

Such quantitative methods have been designated by Barnard and McMichael (*4*) as "analysis by monochromatic transmission." These authors have developed a derivation of Bouguer's law which enables one to calculate the proportions of the components in a binary mixture from measurements of the transmittancies of each component and of the mixture at some one wave length. Twyman and Allsopp discuss such systems also (*46, 47*). Ternary mixtures having certain types of curves for the separate components may be handled in much the same way. Except under the best of conditions, the accuracy of the results obtained in this way is not all one would wish.

In connection with his work on copper ores, Mehlig reached the conclusion that the spectrophotometric method gave results as good as the titrimetric iodide method and that the data were obtained more rapidly and more conveniently. At present such methods seem of value chiefly for colored systems, since photographic methods have hardly sufficient accuracy. As reliable apparatus is expensive for the ordinary laboratory, the present outlook is that this kind of method will be of value chiefly in situations where some other method is not available, as in the work of Zscheile on chlorophyll.

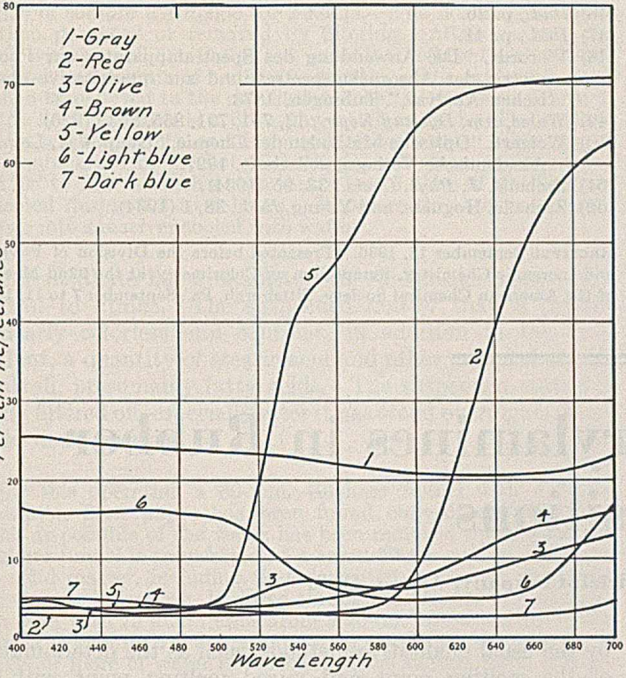

Figure 7. Spectral Reflection Curves

For porcelain enamel paint standards

Color Analysis. Current chemical publications are almost devoid of suggestions for using the results of "color analysis." As generally understood, the expression refers to the combination of stimuli found to be equivalent to the color being measured or analyzed. The results are expressed numerically and represent a unique specification of the color. The results for the trichromatic system are expressed in percentages of the three primary stimuli, red, green, and violet, while those for the monochromatic system are expressed in dominant wave length and in percentages of brightness and purity. The latter values may be taken, respectively, as measurements of the three attributes of color—hue, relative brilliance, and saturation.

The ordinary spectrophotometer yields directly only data upon the basis of which one may plot graphs such as transmittancy-wave-length curves. In such cases the values mentioned above must be calculated. The means for accomplishing the calculation have been readily available since the appearance in 1922 of the report of the Colorimetry Committee (*43*). For use with the data in this publication a special Keuffel and Esser color slide rule was of advantage. An example of its application was given by the author (*32*). In 1931 the International Commission on Illumination adopted more reliable data (*21*, *26*) which have now superseded those used earlier. Using the selected ordinate method, outlined by Hardy (*20*, *21*), calculations on an adding machine are accomplished fairly rapidly. A device developed in the author's laboratory (*42*) facilitates the operation still more. Hardy designed a calculating machine (*20*) for operation in conjunction with his recording photoelectric spectrophotometer, and Pineo has recommended its use for testing textile dyeing (*37*).

So little has been accomplished to bring these numerical evaluations of colorimetric characteristics into everyday use that one can hardly predict to what extent they will become a part of our thinking about colors in the near future. Undoubtedly the invention of rapid, reliable spectrophotometers and the simplification of the tristimulus calculations will do much to extend the application of such data.

The numerical values represent a kind of color language which is more definite than a system based upon samples of colored materials. They provide a specification for a color so that one can form from them an idea of the color without seeing it. A few examples will illustrate the possibilities. Pineo (*37*) has pointed out the value of trichromatic characteristics in measuring color fading, in color matching, and in dyeing control. Shelton and Emerson comment on the possibility of using such data for dyed fabrics (*40*). Hardy (*21*) gives the brightness, dominant wave length, and purity of some colors that are widely used. Since January, 1935, the colors of the United States flag have been specified in trichromatic values by the Bureau of Standards (*8*).

Research Work. In many research problems, both in analytical and other fields, one encounters color as a significant and variable property in the system under study. In such cases chemists who have such equipment available are coming more and more to rely upon spectrophotometers as an important means for obtaining valuable information. In some instances it represents the most important use of such instruments. Objective data are provided showing at once the effect on the color of variables such as pH value, concentration and purity of reagents, constituents in the system affecting the color, the order of adding reagents, the stability of the color, and other factors.

A photoelectric instrument, on account of the sensitivity of the cell in the violet and red regions, is particularly valuable for detecting small differences in the spectrophotometric curves. Nutting has reported (*35*, *36*) recent observations on this point. A recording instrument enables one to obtain a series of curves quickly on the same sheet of paper. By using pens containing different colored inks, especially interesting comparisons can be brought out.

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Determination of Diarylamines in Rubber Compositions

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THIS paper deals with semi-quantitative methods for the determination of certain typical diarylamine age resisters—namely, diphenylamine, phenyl-β-naphthylamine, and *N,N'*-diphenyl-*p*-phenylenediamine. It serves as an essential feature of a study of the general behavior of these materials in rubber to be discussed in a subsequent communication.

Previous methods for the detection and estimation of rubber age resisters have been of limited though of useful application. Thus Endô (*3*) described the colors produced by the action of sulfuric acid on a large number of commercial age resisters unmixed with rubber. Later Endô (*4*) published papers dealing with the action of concentrated nitric acid and Erdman reagent (solution of 0.5 ml. of concentrated nitric acid in 100 ml. of concentrated sulfuric acid) as well as of Mandelin reagent (solution of 1 gram of ammonium vanadate in 200 grams of concentrated sulfuric acid) and of concentrated sulfuric acid containing 1 per cent of arsenic acid.

Tests similar to those of Endô have been used in this laboratory. For example, a good test for the presence of *N,N'*-di-β-naphthyl-*p*-phenylenediamine in a rubber mixture involves cutting a gram of the stock into fine pieces and covering them with concentrated sulfuric acid. After several minutes the acid layer, which is usually straw-colored, is decanted and treated with one drop of a 10 per cent mixture of concentrated nitric acid in concentrated sulfuric acid. If the diamine is present a blue color appears immediately. The presence of *N,N'*-diphenyl-*p*-phenylenediamine is attended by the formation of a red color under these conditions. This test is not vitiated by the presence of the usual quantities of diphenylamine or the phenylnaphthylamines which may be present in the rubber. If neither a red nor a purple color is produced it is probably safe to say that less than 0.1 per cent of either diamine is present. Interfering substances sometimes produce colors with sulfuric acid alone—for example, 2,4-diaminodiphenylamine produces a deep red which changes somewhat when nitric acid is added.

Usually age resisters cause staining of the surface of light-colored stocks during cure or during aging. The colors produced, especially those arising from exposure to light, are more or less characteristic of the age resister present. Kirchof (*6*) has suggested the use of metallic salts with or without exposure to light for the purpose of distinguishing certain antioxidants, but this suggestion seems not to have been adopted. Morris (*7*) has published preliminary data on the fluorescent colors of several antioxidants.

Sometimes an age resister will bloom in sufficient amounts so that it can be removed, purified, if necessary, and identified by the usual qualitative methods, such as the determination of the melting point and mixed melting point with an authentic specimen. Thus *N,N'*-diphenyl-*p*-phenylenediamine, phenyl-β-naphthylamine, *p*-phenylphenol, *p*-hydroxy-*N*-phenylmorpholine, *p*-triphenylmethyldiphenylamine, and others have been detected and identified. In a similar manner antioxidants have been recognized occasionally in the sediment from rubber cements. No one seems to have subjected rubber to very low temperatures for the specific purpose of causing age-resister bloom, although icebox temperatures have been tried occasionally. A microscope for the examination of rubber surfaces is of great help in identifying the presence of certain antioxidants.

The isolation of age resisters from rubber by extraction with solvents (*1*, *5*) has been infrequently reported in the literature, including those which are removable from crude rubber by extraction with acetone.

At the beginning of the present work it was found possible to remove phenyl-β-naphthylamine from rubber by extraction with acetone or with constant-boiling methanol-benzene mixture. The amine could then be steam-distilled from the dried extract or it could be precipitated from hexane or benzene solution as phenyl-β-naphthylammonium chloride. The extracts, however, were rather intractable, and the recovery of amine was low in all experiments.

A much better method involved the steam-distillation of diarylamines from rubber. The preliminary results were successful and seem to be of sufficient interest to warrant publication. Thus it is possible to isolate such amines as phenyl-β-naphthylamine, *N,N'*-diphenyl-*p*-phenylenediamine, and diphenylamine from rubber as the pure compounds or in the form of suitable derivatives.

Procedures

DETERMINATION OF PHENYL-β-NAPHTHYLAMINE. Aside from the removal of sulfur and other alkali-soluble materials by reaction with sodium hydroxide, the only reactions involved in this determination are the formation of the hydrochloride of the amine and the subsequent hydrolysis of the hydrochloride.

The stock is preferably either ground to pass a 14-mesh screen or is sheeted on a tight mill. For batches containing between 1 and 2 per cent of antioxidant a 30-gram sample is used, but for higher concentrations the weight can be reduced correspondingly. The 30-gram sample is refluxed with 600 ml. of water and 7.5

grams of sodium hydroxide for 2 hours. The hot mother liquor is then decanted or removed by filtering. After washing the stock with a small amount of hot water it is refluxed with 600 ml. of water and 1 gram of sodium hydroxide. The extracted stock is then transferred to the distillation tube, *A*, shown in Figure 1, in the neck of which is a filter plug of glass wool. The stock is finally washed with a small amount of hot water. The tube is then submerged in the hot oil bath, *D*, and steam is introduced at 170° to 180° at such a rate that 4 to 4.5 liters of distillate are collected during 2.5 to 3 hours. It passes through an air condenser into a receiver cooled with water.

The distillate has a characteristic rubber-like odor. It is neutral to litmus. The suspended matter that is present is nearly colorless and contains, in addition to the antioxidant, a quantity of stearic acid and other material soluble in alkali, presumably fatty acids. The suspended matter is easily filtered off, especially after it has stood overnight, which is the usual practice.

For this operation a 60-mm. Büchner funnel with a No. 2 Whatman filter paper has been found convenient. When as much as possible of the water has been removed by suction, the Büchner funnel is transferred to a tared 50-ml. suction flask and the solid matter, including that deposited in the air condenser and the receiving flask, is rinsed through the funnel into the suction flask with 75 ml. of ether from a 10-ml. pipet. Much of the ether is lost through evaporation during the rinsing operation. If 0.5 cc. or more of water is collected in the suction flask, it is removed by means of a pipet and washed with a little ether, using the pipet also for this washing operation. The wash ether is then added to the suction flask and all the ether is evaporated on the steam plate. Small amounts of water can be removed by adding 10 ml. of benzene and evaporating until the benzene is removed. The last traces of water are removed by heating for 20 minutes in an oven at 120° to 130°.

The solid remaining, to be referred to as the "residue from the ether evaporation," is weighed to 0.01 gram, and dissolved in 10 to 20 ml. of warm hexane. A stream of hydrogen chloride is allowed to play for a few minutes over the surface of the solution while it cools to room temperature. The hydrogen chloride causes phenyl-β-naphthylamine hydrochloride to precipitate as a clot that clings firmly to the bottom and walls of the flask. The precipitation is complete when the mother liquor becomes clear or has stood for 2 hours. The mother liquor is then poured into another tared flask and the hydrochloride washed with a few milliliters of hexane. The washings are united with the mother liquor and evaporated to dryness, finally, in the oven at 120° to 130° for 20 minutes. The residue, known as the "residue from the hexane evaporation," is then weighed to 0.01 gram. It contains nonbasic materials.

The flask containing the hydrochloride is quickly evacuated in a vacuum desiccator and weighed to 0.01 gram. The hydrochloride is not pure, but seems to contain traces of free hydrochloric acid and possibly traces of other difficultly volatile material. It is hygroscopic. In order to determine the phenyl-β-naphthylamine content, the hydrochloride is hydrolyzed. This is easily done by boiling with 10 ml. of benzene and 10 ml. of water until the solid has dissolved. The water layer is then separated and washed with ether by means of a pipet. The ether washings are added to the benzene layer, which is then evaporated on the steam plate until the solvent is removed. The last traces of water are removed by heating for 20 minutes in an oven at 120° to 130°. The residue is phenyl-β-naphthylamine, and is weighed to 0.01 gram.

A description in more detail of the apparatus shown in Figure 1 follows.

The distillation tube, *A*, is made by bending a piece of Pyrex tubing 30 cm. (12 inches) long and 4.4 cm. (1.75 inches) in outside diameter, so that it can be submerged in the oil bath, *D*. A neck made from a piece of 1.25 cm. (0.5 inch) outside diameter tubing is attached and bent so that it can be connected to the short air condenser, *E*. The thermometer well in *A* is inserted by means of a ring seal. The brass superheater, *B*, of the type sold by the Fisher Scientific Company, is fitted with a thermometer well and 0.6-cm. (0.25 inch) copper tubing connections. The steam generator, *C*, is a 20-liter (5-gallon) steel drum. Service line steam is unsatisfactory because of admixed oxygen. The still head on *C* has a bulb of 300-ml. volume. The steam generator, *C*, the superheater, *B*, and the oil bath, *D*, are heated with gas burners. The receiver, *F*, is a 5-liter balloon flask cooled with tap water. The various parts of the apparatus are connected by means of rubber tubing or rubber stoppers.

It is probable that the precision and speed of conducting the determinations would be improved by the use of small all-glass apparatus, thus making it possible to use small samples.

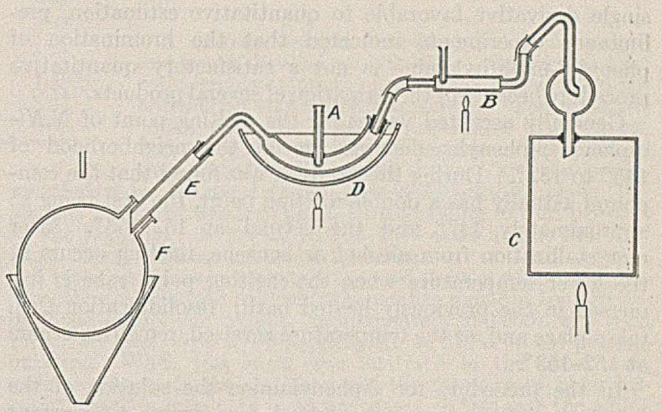

FIGURE 1. DIAGRAM OF APPARATUS

DETERMINATION OF *N*,*N*′-DIPHENYL-*p*-PHENYLENEDIAMINE. The procedure is the same as that for phenyl-β-naphthylamine up to the point of the hydrochloride precipitation. Here benzene must be substituted for hexane, and benzene must be used instead of ether to wash the product into the precipitation flask.

Since the hydrochloride does not adhere well to the precipitation flask, filtration is necessary in order to separate the mother liquor. The hydrochloride is collected in the precipitation flask and hydrolyzed by boiling for several minutes with a mixture of 5 ml. of water, 3 ml. of concentrated ammonium hydroxide, and 5 ml. of benzene. The water layer is separated by means of a pipet and washed with a few milliliters of benzene. The benzene layers are united and evaporated to dryness. Finally the residue is heated for 20 minutes at 120° to 130° C. and weighed. It should melt at approximately 145°.

DETERMINATION OF DIPHENYLAMINE. The procedure given for phenyl-β-naphthylamine can also be used for diphenylamine if due allowance is made for volatility and for solubility in the extracting solutions. It is more convenient, however, since diphenylamine is volatile in steam at 100°, to use a modification of Cook's method (*2*) for diphenylamine in smokeless powder.

A 30-gram sample of the stock, 5 grams of sodium hydroxide, and 3 liters of water are distilled in a 5-liter distilling flask until 4 liters of distillate have been collected. Water is added to the distillation flask from time to time as necessary. The diphenylamine is extracted from the distillate with three 75-ml. portions of petroleum ether. The extracts are collected in a tared 150-ml. flask and evaporated to a volume of about 5 ml. Five milliliters of ether and 8 ml. of a 10 per cent solution of bromine in carbon tetrachloride are added. The solvents are boiled off and the residue is heated in a current of air at about 80° during 20 minutes. It is then dissolved in 5 to 10 ml. of hot benzene. The benzene is removed in a current of air at about 80° and heated to constant weight at this temperature. The melting point of the residue, which is 2,2′,4,4′-tetrabromodiphenylamine, should be between 178° and 185°. A low melting point usually indicates incomplete bromination, although aged rubber usually gives a product of somewhat lower melting point.

Notes on Procedures

Several solvents were used for extracting small amounts of the diarylamines from water. Ether was objectionable because of its high solubility in water. Hexane and petroleum ether (b. p. 40° to 50°) were satisfactory for phenyl-β-naphthylamine and diphenylamine. *N*,*N*′-diphenyl-*p*-

phenylenediamine was usually extracted with benzene in which it is rather soluble. This amine is almost insoluble in hexane.

Diphenylamine can be isolated as the hydrochloride by a method similar to that for phenyl-β-naphthylamine, provided ample precautions are taken to prevent loss by volatilization. Although bromination of diphenylamine gives a single derivative favorable to quantitative estimation, preliminary experiments indicated that the bromination of phenyl-β-naphthylamine is not a satisfactory quantitative procedure because of the formation of several products.

Generally accepted values for the melting point of *N,N'*-diphenyl-*p*-phenylenediamine are in the neighborhood of 145° to 152°. During this study it was found that the compound actually has a double melting point, the first being at approximately 147° and the second at 152–153°. After recrystallization from alcohol or benzene, melting occurs at the lower temperature when the melting point tube is immersed in the previously heated bath; resolidification then takes place and, as the temperature is raised, remelting occurs at 152–153°.

In the procedure for diphenylamine the solution of the tetrabromo derivative in benzene before drying to constant weight is not necessary although it aids somewhat in removing hydrobromic acid.

Results and Discussion

PHENYL-β-NAPHTHYLAMINE WITHOUT RUBBER. In a few leading experiments this amine was steam-distilled in the absence of rubber. At 100° the rate was too slow to be practicable, but at a higher temperature a convenient rate was obtained.

A quantity (0.50 gram) of phenyl-β-naphthylamine was placed in the distilling tube, *A* (Figure 1), and 4100 ml. of distillate were collected with the temperature in *A* at 165° to 175°. The distillate was worked up in the usual manner except that the hydrochloride precipitation was omitted. The yield of recovered phenyl-β-naphthylamine was 0.49 gram. It melted at 108–109°. The filtrate (4000 ml.) was extracted with 100 ml. of hexane and then with 50 ml. of hexane. A large rubber stopper was used to close the flask during extraction. The hexane extracts were united and evaporated to dryness, leaving an oily residue of 0.0306 gram. Solution of this in 5 ml. of hexane and treatment with hydrochloric acid gave 0.0049 gram of precipitate from which no phenyl-β-naphthylamine could be isolated by treatment with benzene and water in the usual way.

PHENYL-β-NAPHTHYLAMINE FROM HIGH-GUM STOCK A. A sheet of stock A, cured 70 minutes at 126.67° C. (260° F.), was used. The recipe for stock A is:

High-Gum Stock A	
Rubber	100
Phenyl-β-naphthylamine	1
Zinc oxide	2
Stearic acid	2
Accelerator	0.3
Sulfur	1.25
	106.55

On milling, a crumbly sheet resulted and a 20-gram sample was analyzed in the usual way except that the steam-distillation was conducted at 165–170°.

	Gram
Residue from ether evaporation	0.27
Weight of hydrochloride	0.22
Residue from hexane evaporation	0.08
Yield of phenyl-β-naphthylamine (m. p. 107–108°)	0.17

The yield of 0.17 gram of phenyl-β-naphthylamine represents a recovery of 90.5 per cent of that added to the stock.

When 3 liters of the filtrate from this experiment were extracted with 100-ml. and 50-ml. portions of petroleum ether, and the extracts united and evaporated, a residue of 0.015 gram remained. This residue was oily and gave a few crystals when seeded with phenyl-β-naphthylamine. However, when dissolved in 10 cc. of hexane and treated with hydrochloric acid, a precipitate weighing less than 0.005 gram resulted. On boiling with water and benzene no phenyl-β-naphthylamine could be isolated. From this it is certain that the amount of phenyl-β-naphthylamine remaining dissolved in the filtrate from the distillate is less than 0.0017 gram per liter.

PHENYL-β-NAPHTHYLAMINE FROM TREAD STOCK APPLIED BY DIPPING. The stock used had the following composition:

Tread Stock B	
Rubber	100
Sulfur	3
Mercaptobenzothiazole	1
Stearic acid	4
Zinc oxide	5
Gas black	50
	163

A sheet of this stock cured 80 minutes at 128.89° C. (264° F.) was divided into two equal parts. Each part was cut into strips approximately 2.5 × 10 cm. (1 × 4 inches), and weighed 37 grams. The following procedure was used for both parts in order to test the reproducibility of the experiments. The 37 grams of strips were immersed for 10 minutes in a solution prepared from 7 grams of phenyl-β-naphthylamine and 70 ml. of benzene-methanol constant-boiling mixtures. After draining the solution from the strips, the solvent was evaporated and the weight of residue determined. This residue represents the unabsorbed phenyl-β-naphthylamine. The strips which were covered with a layer of powdery phenyl-β-naphthylamine were cut up into small pieces about 2.5 × 0.15 × 0.023 cm. (1 × 0.063 × 0.093 inch) in size. They were then introduced into the steam-distillation tube and steam-distilled in the usual way but with the omission of alkali extraction.

Table I summarizes the data for both parts of stock used.

TABLE I. TESTS ON TREAD STOCK B

	First Part		Second Part	
		Melting Point		Melting Point
	Grams	° *C.*	*Grams*	° *C.*
Total phenyl-β-naphthylamine in solution	7.00	108–109	7.00	108–109
Phenyl-β-naphthylamine unabsorbed	6.79	106–108	6.80	106–108
Residue from ether evaporation	0.83	...	0.87	...
Phenyl-β-naphthylamine after hydrochloride precipitation and hydrolysis	0.25	104–107	0.24	104–107
Phenyl-β-naphthylamine unabsorbed plus that absorbed	7.04	...	7.04	...

It can be seen from Table I that the results for the two parts check nicely but that the amounts of phenyl-β-naphthylamine accounted for are somewhat high. This can be explained as being due to impurities in the recovered phenyl-β-naphthylamine indicated by the low melting points. The low melting point of the phenyl-β-naphthylamine recovered by the steam-distillation indicates the possible presence of thiophenyl-β-naphthylamine formed by reaction with free sulfur.

PHENYL-β-NAPHTHYLAMINE FROM TREAD STOCK B INCORPORATED BEFORE VULCANIZATION BY MILLING. Table II summarizes the results for phenyl-β-naphthylamine for an undercure and an overcure, and indicates that the per cent recovery of antioxidant is not dependent to any great extent on the time of cure. If the amount of amine recovered is measured by the weight of hydrochloride and the equivalent weight of amine calculated on the basis of one molecule of hydrochloric and for each amine molecule, the results will be too high, owing to difficultly volatile impurities. If the weight of residue from the hexane evaporation is added to the weight of phenyl-β-naphthylamine in each case, the value approaches the weight of residue from the ether evaporation. The material in the residue from the hexane evaporation is partly soluble in dilute sodium hydroxide and con-

TABLE II. STEAM-DISTILLATION RECOVERY OF PHENYL-β-NAPHTHYLAMINE FROM TREAD STOCK B

(Cured at 264° F.)

Time of Cure	Weight of Sample	Amine Added on the Rubber	Amine Present in Sample	Residue from Ether Evaporation	Hydrochloride Yield		Recovery of Amine		Residue from Hexane Evaporation
						Amine Equivalent			
Min.	*Grams*	%	*Gram*	*Gram*	*Gram*		*Gram*	%	*Gram*
20	30	1	0.183	0.25	0.18	0.16	0.15	82	0.11
	30	2	0.364	0.39	0.36	0.31	0.29	79	0.10
	20	3	0.362	0.38	0.35	0.30	0.28	76	0.09
160	30	1	0.183	0.28	0.17	0.15	0.14	76	0.12
	30	2	0.364	0.43	0.36	0.31	0.28	76	0.14
	20	3	0.362	0.39	0.36	0.31	0.26	71	0.11

sists in part of stearic acid. Fatty acids could arise from the hydrolysis of soaps or glycerides during the steam-distillation. The reproducibility of the recovery of antioxidant is believed to be within 5 per cent.

It was of interest to test the steam-distillation of the ground stock before alkali-extracting it. The determination for the 20-minute cure of tread stock B containing 3 per cent of age resister on the rubber was therefore repeated omitting the extraction. The residue from the ether evaporation weighed 0.99 gram and on treatment with hexane in the usual manner not quite all of this dissolved. Dry hydrochloric acid was passed into the flask. The yield of hydrochloride amounted to 0.41 gram. On hydrolysis in the usual way 0.32 gram of crude phenyl-β-naphthylamine resulted (m. p. 103–106°). From the rather turbid hexane mother liquor when allowed to stand overnight there was precipitated 0.05 gram of solid which was thoroughly washed with benzene. The crystals remaining were identified as sulfur by melting point (115–118°) and mixed melting point (117–119°) with an authentic specimen. Not only does free sulfur steam-distill from rubber but undoubtedly it begins to react with the antioxidant at 170–180°, thus justifying the alkali-extraction previous to the steam-distillation.

N,N'-DIPHENYL-*p*-PHENYLENEDIAMINE INCORPORATED BEFORE VULCANIZATION BY MILLING. High-gum stock C which was used in some of the experiments had the following composition: Optimum cure was 60 minutes at 125.56° C. (258° F.).

High-Gum Stock C	
Rubber	100
Stearic acid	1
Sulfur	3
Zinc oxide	2
Tetramethyl thiuram disulfide	0.1
	106.1

Table III shows the recovery of antioxidant from tread stock B (cured 160 minutes at 128.89° C., 264° F.) and high-gum stock C (cured 60 minutes at 125.56° C., 258° F.) in per cent of that added.

DIPHENYLAMINE INCORPORATED BY MILLING. The results for tread stock B (cured 160 minutes at 128.89° C., 264° F.) and high-gum stock C (cured at 125.56° C., 258° F.) are shown in Table IV.

The volatility of diphenylamine probably explains the relatively low recovery from the stocks containing 3 per cent of diphenylamine. When tread stock B, originally containing 3 per cent of diphenylamine on the rubber, was allowed to stand in the ground condition for 10 weeks and then analyzed, a recovery of only 72 per cent was obtained. The recovery of 80 per cent, shown in Table IV, was obtained shortly after mixing and curing.

APPLICATION OF METHOD TO OTHER HIGH MOLECULAR WEIGHT MATERIALS. It has been recorded in the literature that phenyl-β-naphthylamine is active for controlling the polymerization of chloroprene. In order to see if the commercial polymer contained this antioxidant, a sample of Duprene was sheeted out on the mill.

A 40-gram sample was wrapped in cheesecloth and steam-distilled at 170–180°. During this time considerable amounts of acid were evolved and the cheesecloth was badly decomposed. The distillate, which was oily, was extracted first with 100 ml. and then with 50 ml. of hexane. The extracts were united, evaporated to dryness, and the residue was analyzed in the usual way for phenyl-β-naphthylamine. The amount recovered was 0.10 gram, corresponding to 0.25 per cent on the Duprene. It melted at 105–107° alone and at 106–109° when mixed with an authentic specimen.

A stock similar in composition to tread stock B with mercaptobenzothiazole omitted and with the rubber replaced by polyisobutylene (molecular weight, approximately 100,000) was used with 1 per cent of phenyl-β-naphthylamine based on the polyisobutylene. When this stock was analyzed in the usual way, sulfur appeared in the distillate and the recovery of phenyl-β-naphthylamine amounted to 55 per cent. In this case the amine was separated from the sulfur by hexane extraction before precipitation with hydrogen chloride. The amine recovered melted at 100–104° and probably contained some thiophenyl-β-naphthylamine formed by reaction with sulfur not completely removed by alkali extraction.

TABLE III. RECOVERY OF ANTIOXIDANT

Concentration of Antioxidant on Rubber	Recovery of Antioxidant	
	Tread stock B	High-gum stock *C*
	%	%
0.5	16	65
1.0	44	83
3.0	64	85

TABLE IV. RECOVERY OF ANTIOXIDANT

Concentration of Antioxidant on Rubber	Recovery of Antioxidant			
		High-gum stock C		
	Tread stock B	30 min.	60 min.	120 min.
	%	%	%	%
0.5	85	87	89	93
1.0	90	..	91	..
3.0	80	..	78	..

The procedures outlined have been used in analyzing factory stocks for age resisters. They have many times been found useful in clearing up questions as to the identity of certain stocks. Other applications, such as those relating to the behavior of age resisters during aging, will be treated in a subsequent communication.

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Determination of Quartz in the Presence of Silicates

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A new method in which silicates are decomposed by fluoboric acid is proposed for the determination of free silica in the presence of silicates. This acid has less action on quartz than fluosilicic acid and is more stable at elevated temperatures. The decomposition of a number of common, insoluble silicates has been determined, and the analyses of several synthetic silicate-quartz mixtures are reported. These results show that the amount of quartz in the synthetic mixtures can be determined with a precision of approximately 1 per cent.

THE existing methods for the determination of free silica in the presence of silicates are unsatisfactory from the point of view of general applicability, accuracy, and time required. The most reliable method, that of "ultimate analysis," is time-consuming. The Lunge-Millberg (*8*) method of "rational analysis," which has been modified by Selvig, is applicable only to special kinds of silicates—the coal measure rocks and shales. The modified petrographic immersion method of Ross and Sehl (*7*) is capable of only a "reasonable accuracy." The simple, rapid method of Knopf (*2*), in which the silicate is dissolved in fluosilicic acid after preliminary treatment and petrographic examination of the sample, is unsatisfactory because of the large correction factor resulting from the action of this acid on quartz. In some cases the petrographic examination of a thin section of the rock or material may permit an estimate of the quartz by the Rosiwal method (*5*, *7*).

A new method in which silicates are decomposed by fluoboric acid, which attacks free silica much less than does fluosilicic acid, is here proposed for the determination of free silica in the presence of silicates (*1*).

Fluoboric acid was prepared by the method of Berzelius by adding boric acid to a concentrated (48 per cent) solution of hydrofluoric acid. The reaction is supposed to be

$$H_3BO_3 + 2H_2F_2 = HBF_4 + 3H_2O$$

but doubt was cast upon the correctness of this reaction by the work of Travers and Malaprade (*9*) who state that hydrofluoric and boric acids instantly react to form a fluoboric acid different from HBF_4. Mellor (*6*) states that a compound such as $HBF_4 \cdot 2HF$ or $BF_3 \cdot 3HF$ has been reported, but that the work has not been confirmed. That such a compound may readily be formed is borne out by the fact that when hydrofluoric acid is added to fluoboric acid and the mixture shaken, no test for fluoride can be obtained with either lead nitrate or calcium chloride solutions.

The acid obtained by the above reaction is a slightly yellow, fuming, sirupy liquid with a specific gravity of about 1.45. It is a moderately strong acid which decomposes slowly at its boiling point. Its salts, most of which are soluble, slowly hydrolyze in warm water. Dilute solutions of the acid attack glass only very slowly, and even concentrated solutions can be filtered in glass apparatus without appreciable etching. The volumetric methods of analysis applicable to fluosilicic acid were found to be unsatisfactory for fluoboric acid. However, the gravimetric method suggested by Lange (*3*) in which HBF_4 is precipitated as nitron·HBF_4 has been successfully used for the analysis of the various fluoboric acid solutions prepared.

Action of Fluoboric Acid on Quartz and Silicates

The essential prerequisites for a reagent that is to be used for the determination of free silica in the presence of silicates are that its action on free silica be slight and its action on silicates be rapid. To determine the behavior of fluoboric acid toward silica and silicates, samples of these materials ground to pass a 150-mesh sieve and caught on a 200-mesh sieve were treated with this acid according to the following procedures. The results of these experiments are given in Table I.

A 0.5-gram sample was weighed in a platinum crucible and treated with 5 cc. of fluoboric acid. The crucible was held at 50–55° C. in an open air bath for definite periods. At the end of each period, the residue was transferred to an ashless filter, washed acid free with hot water, ignited, and weighed. This procedure was repeated on the ignited residue until nearly constant weight was obtained.

The procedure of Knopf with fluosilicic acid was followed in determining the solvent action of fluoboric acid on quartz and silicates at room temperature.

At room temperature, quartz lost only 0.03 per cent per day in fluoboric acid as compared to a loss of 0.7 per cent per day for fluosilicic acid; while the silicates considered dissolved more readily in fluoboric than in fluosilicic acid. Fluoboric acid, unlike fluosilicic acid, may be used at higher temperatures without appreciable decomposition, thus hastening the solution of silicates.

The action of fluoboric acid on quartz is negligible at room temperature, but becomes appreciable at higher temperatures. This is probably due to the formation of hydrofluoric acid in the solution. If this is true, then some reagent that will remove hydrofluoric acid or fluoride ion from the solution should decrease the action of fluoboric acid on silica, and possibly on silicates.

Use of Trivalent Cations and Phosphoric Acid to Decrease Fluoride-Ion Concentration

A number of ions such as trivalent iron, aluminum, and chromium are known to form complexes of the type $(MF_6)^{---}$. All three of these ions were tried, and the aluminum was eliminated because of the formation of a gelatinous precipitate when a mixture of fluoboric and aluminum chloride was allowed to stand. The effectiveness of ferric and chromic ions was determined by experiments conducted with quartz and silicates in the following manner:

A 0.15- to 0.5-gram sample ground to pass a 150-mesh sieve and caught on a 200-mesh sieve was weighed in a platinum crucible. To this were added 5 cc. of fluoboric acid and 1 to 2 cc. of 2 *M* ferric chloride (or chromic sulfate). The crucible was heated at 50° C. for 12- and 24-hour periods. After each period, the residue was transferred to an ashless filter and washed with *N* hydrochloric acid, 0.5 *N* sodium carbonate, and hot water. The paper was burned and the residue ignited and weighed. The procedure was then repeated. The data for these determinations are given in Table II.

The use of ferric chloride reduced the decomposition of quartz from 1.06 to 0.20 per cent per day in one case, and to 0.12 per cent in another, while the rate of decomposition of the silicates was not affected. This confirms the idea that free hydrofluoric acid is the active constituent in the decomposition of quartz by fluoboric acid, while the fluoboric acid itself must be responsible for the decomposition of the silicate.

TABLE I. ACTION OF FLUOBORIC ACID ON QUARTZ AND SILICATES

Sample *Gram*	Temperature *° C.*	Time *Hours*	Total Loss *Gram*	Total Loss *%*
On 150-Mesh Quartz				
0.5034	50–55	12	0.0029	0.57
		24	0.0049	0.98
			Av.	1.06 per day
		Days		
0.5020	ca. 20	3	0.0008	0.16
		20	0.0017	0.34
		25	0.0025	0.50
			Av.	0.03 per day
On Silicates				
Talc[a] 0.1038	ca. 20	5	0.0654	..
		10	0.0844	81.3
		Hours		
0.5089	50–55	12	0.2628	..
		24	0.4096	..
		36	0.4642	91.2
		Days		
Soda-lime feldspar 0.5007	ca. 20	13	0.2464	..
		18	0.3837	..
		23	0.4746	..
		29	0.4801	95.9

[a] 200-mesh samples of talc were used.

Ferric chloride was slowly decolorized when the crucibles were heated. This may have been due to the formation of the colorless $(FeF_6)^{---}$ complex ion or to the formation of ferric fluoborate, about which very little is known. While chromic ion was as effective as ferric ion, it was more difficult to wash from the residue; consequently, use of it was abandoned.

Lange and Stein (*4*) state that phosphoric and hydrofluoric acids react to form monofluorophosphoric acid according to the following reversible reaction:

$$H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$$

This suggested that phosphoric acid might be used in keeping the fluoride ion at a low concentration, which would decrease the action of fluoboric acid on quartz. The following experiments showed this to be the case.

A 0.15- to 0.2-gram sample of quartz ground to pass a 150-mesh and caught on a 200-mesh sieve was weighed in a platinum crucible. To this were added 5 cc. of fluoboric acid and 2 cc. of phosphoric acid having a specific gravity of 1.39. The crucible was heated at 50° C. for 48 hours, after which the residue was transferred to an ashless filter and washed with *N* hydrochloric acid, 0.5 *N* sodium carbonate, and hot water. The filter paper was burned off at a temperature as low as possible and the procedure repeated for 48 hours longer, after which the residue was washed, ignited, and weighed. This procedure was repeated for another 96-hour period. The data are given under sample A, Table III.

TABLE II. ACTION OF FLUOBORIC ACID IN THE PRESENCE OF TRIVALENT CATIONS

Sample *Gram*	Reagent	Time *Hours*	Total Loss *Gram*	Loss per Day *%*
On 150-Mesh Quartz				
0.4995	$FeCl_3$	12	0.0002	0.08
		24	0.0005	0.10
		36	0.0013	0.17
		76	0.0070	0.44
			Av.	0.20
0.1522	$FeCl_3$	24	−0.0001	−0.06
		48	0.0005	0.16
		72	0.0012	0.26
			Av.	0.12
0.1602	$Cr_2(SO_4)_3$	24	−0.0004	−0.25
		48	0.0007	0.22
		72	0.0018	0.38
			Av.	0.12
On Silicates				Total Loss *%*
Talc.[a] 0.4975	$FeCl_3$	12	0.1652	..
		24	0.2495	..
		64	0.3664	76.6
0.1649	$FeCl_3$	24	0.0860	..
		48	0.1156	..
		72	0.1447	..
		168	0.1594	96.6

[a] 200-mesh samples of talc were used.

Phosphoric acid was found to exert a retarding effect upon the decomposition of quartz in fluoboric acid, but this was not as effective as ferric chloride. If the retarding effects of these two reagents are additive, there should be an advantage in using them together. Most of the phosphates are soluble in strongly acid solutions, so there should be no objection to doing this. Since ferric phosphate is colorless and slightly dissociated, the color of the solution would indicate when the concentration of ferric ion was becoming small. The above procedure using 2 cc. of phosphoric acid and 2 to 4 cc. of 2 *M* ferric chloride was followed in studying this point. The data are given under samples B and C, Table III.

TABLE III. ACTION OF FLUOBORIC ACID ON 150-MESH QUARTZ IN THE PRESENCE OF H_3PO_4 AND $FeCl_3$

Sample *Gram*	Reagents	Time *Hours*	Total Loss *Gram*	Loss per Day *%*
A 0.1593	H_3PO_4	96	0.0021	0.33
		192	0.0039	0.31
			Av.	0.32
B 0.1530	H_3PO_4 and $FeCl_3$	96	0.0006	0.10
		192	0.0014	0.10
		288	0.0016	0.09
C 0.1748	H_3PO_4 and $FeCl_3$	96	0.0004	0.03
		192	0.0009	0.06
		288	0.0015	0.07
			Av. of B and C	0.07

Later experiments have shown that 1 cc. of phosphoric acid having a specific gravity of 1.39 gives the best results in the above procedure. An excess of phosphoric acid should be avoided.

Procedure for Determination of Free Silica

The optimum conditions found in these preliminary experiments for the maximum decomposition of silicates and the minimum decomposition of quartz have been correlated in developing a new procedure for the determination of quartz in the presence of silicates. The complete directions for this method involve preparation of fluoboric acid, decomposition of the silicate, and determination of free silica.

PREPARATION OF FLUOBORIC ACID. Dissolve 32 grams of purified boric acid in 75 cc. of pure 48 per cent hydrofluoric acid. Pour the hydrofluoric acid into a 125-cc. platinum dish and cool this in an ice bath. Keeping the dish in the ice bath, add the boric acid in small amounts, allowing each portion to dissolve before more is added. In this way the solution does not become overheated. When all the boric acid has been added (the last portion will not dissolve while the solution is cold), concentrate the solution to about 50 cc. on a steam bath. Cool to 0° to 5° and filter. The resulting acid is a slightly yellow, fuming, sirupy liquid that should have a specific gravity of about 1.45 and should analyze about 40 to 45 per cent HBF_4 by the Lange method. It should give no test for fluoride with calcium chloride or lead nitrate solutions. It must be stored in wax or rubber bottles, but the filtration may be done with glass apparatus.

DECOMPOSITION OF SILICATE. In a platinum crucible, weigh a 0.15- to 0.2-gram sample of material that has been ground to pass a 100-mesh sieve. To this add 5 cc. of fluoboric acid, 1 cc. of phosphoric acid, specific gravity 1.39, and 2 cc. of 2 *M* ferric chloride. Heat the crucible at 50° C. for 48 hours, adding more ferric chloride if the yellow color of the solution fades. Transfer the residue to an ashless filter and wash four times with *N* hydrochloric acid and five times with hot water. Unless the residue is negligible at this point, place paper and residue in the crucible and destroy the paper by heating the crucible only to dull redness. Repeat this treatment for 48 hours longer. Filter, wash, and determine the weight of the residue. Unless solution

Table IV: Determination of Correction Factor on 100-Mesh Quartz

Sample *Gram*	Time *Days*	Total Loss *Gram*	Loss per Day *%*
0.0260	4	0.0003	0.29
	8	0.0008	0.38
	12	0.0012	0.55[a]
0.0543	4	0.0008	0.37
	8	0.0016	0.37
	12	0.0024	0.37
0.1051	4	0.0021	0.50[a]
	8	0.0031	0.37
	12	0.0047	0.37
0.1543	4	0.0021	0.34
	8	0.0040	0.32
	12	0.0060	0.32
0.1501	4	0.0018	0.30
	8	0.0037	0.31
	12	0.0058	0.32
0.2544	4	0.0045	0.44[a]
	8	0.0065	0.32
	12	0.0100	0.33
		Av.	0.34

[a] These values were omitted from the average.

has been complete, repeat this treatment for 48-hour periods until a loss of only 1 to 2 mg. is found. This indicates complete solution of the silicate.

Some siliceous materials may be decomposed in less than 48 hours, in which case the treatment with fluoboric acid should be stopped as soon as complete decomposition is apparent. In other cases, even 8 to 12 days may not effect complete decomposition.

Determination of Free Silica. Treat the residue insoluble in fluoboric acid with 2 to 3 cc. of 48 per cent hydrofluoric acid, and repeat until constant weight is obtained after ignition. The loss in weight corresponds to the free silica content of the residue. This value must be corrected for the amount of free silica dissolved during the time required to decompose the silicate. The correction factor is 0.34 per cent per day.

When the residue is practically pure silica the treatment with hydrofluoric acid will give the correct value for quartz; if undecomposed silicates remain the loss with hydrofluoric acid will be too high, owing to attack of the silicates, but the authors obtained the correct result at least in the case of forsterite, as shown below. Data on other undecomposable silicates such as garnet and sillimanite are too meager to be included in this report.

Apparatus. For maintaining the crucibles at a constant temperature for long periods, a large vacuum desiccator was placed in an electric oven, the heating unit of which was controlled by a thermostat. An outlet tube was connected to a suction pump and a constant current of warm air to remove the fumes was drawn through the desiccator. The inlet tube was so arranged that a thermometer could be inserted into the desiccator to check the temperature without disturbing the apparatus.

The decomposition of quartz under these conditions is much less than in Knopf's method; but it is still large enough so that a correction factor must be applied. In the determination of this correction factor, the percentage loss due to the decomposition of quartz was found to be independent of the weight of the sample. This was ascertained by determining, by the above procedure, the decomposition of 0.025-, 0.05-, 0.01-, 0.15-, and 0.25-gram samples of pure quartz prepared as above. The data for these determinations are given in Table IV.

The scope of this method was studied by determining the rate of decomposition of a number of insoluble silicates. In order to subject the method to the most severe conditions, only those silicates which are not decomposed by mineral acids, other than hydrofluoric acid, were used. Pure crystals of talc, andalusite, zoisite, forsterite, cordierite, beryl, dumortierite, zircon, and sillimanite were obtained from Ward's Natural Science Establishment. The other silicate samples were furnished by John T. Sanford of the University of Rochester. The results of these determinations are given in Table V.

Table V. Analysis of Silicates

Silicate	Time *Days*	Silicate *%*	Silica *%*	Total *%*
Wollastonite[a]	2	99.8	0.2	100.0
Biotite[b]	4	99.6	0.1	99.7
Orthoclase[a]	5	99.5	0.4	99.9
Albite[a]	6	97.2	1.1	98.3
Muscovite[b]	6	99.9	0.1	100.0
Pyroxene[a]	6	99.8	0.2	100.0
Andalusite[b]	6	99.3	0.1	99.4
Cordierite[b]	6	99.3	0.5	99.8
Talc[b]	6	99.3	0.5	99.8
Amphibole[a]	6	97.3	1.3	98.6
Zoisite[b]	8	94.1	5.6	99.7
			Decomposition *%*	
Forsterite[b]	8		77.3	
Garnet[b]	12		69.4	
Dumortierite[b]	12		22.4	
Sillimanite[b]	8		21.9	
Beryl[b]	12		13.7	
Zircon[b]	8		8.8	

[a] Fluoboric acid, $HClO_4$, and $FeCl_3$ used.
[b] Fluoboric acid, H_3PO_4, and $FeCl_3$ used.

It may be seen from these data that the rate of decomposition of these silicates varies over a wide range. Garnet, sillimanite, zircon, beryl, forsterite, and dumortierite could not be completely decomposed; hence, this method is unsatisfactory for the precise determination of quartz in the presence of these silicates. On the other hand, eleven of the seventeen silicates were quantitatively decomposed as the fifth column of Table V shows. This means that quartz contained in mixtures of these silicates can be accurately estimated by this method.

In order to check the validity of this method, synthetic silicate-quartz mixtures have been analyzed. These mixtures were obtained by weighing in a platinum crucible a 0.15- to 0.2-gram sample of the silicate and then adding approximately 10 per cent of quartz. The results have been recorded in Table VI.

Table VI. Analysis of Silicate-Quartz Mixtures

Silicate	Weight of Silicate *Gram*	Weight of Silica Added *Gram*	Weight of Silica Found *Gram*	Difference *Gram*
Wollastonite	0.1644	0.0150	0.0148	0.0002
Biotite	0.1582	0.0103	0.0102	0.0001
	0.1546	0.0158	0.0158	0.0000
Orthoclase	0.1695	0.0164	0.0162	0.0002
Albite	0.1663	0.0221	0.0214	0.0007
Muscovite	0.1562	0.0178	0.0181	0.0003
Pyroxene	0.1507	0.0100	0.0109	0.0009
Andalusite	0.1536	0.0127	0.0126	0.0001
Cordierite	0.1605	0.0106	0.0103	0.0003
Talc	0.1535	0.0171	0.0162	0.0009
Amphibole	0.1577	0.0094	0.0102	0.0008
Forsterite	0.1523	0.0093	0.0094	0.0001

In eight of the twelve synthetic mixtures tested, the amount of free silica found varied only 0.1 to 0.3 mg. from the amount added. In the other mixtures wider deviations were observed, the largest deviation being only 0.9 mg. These values were obtained by correcting for the weight of silica dissolved during the treatment with fluoboric acid, and for the amount of free silica previously found in the silicate. Since the indeterminate errors would be about 1 per cent for samples containing about 10 per cent of free silica, this is the maximum precision that can be claimed for the method. The values obtained with the synthetic silicate-quartz mixtures substantiate this claim.

This method is an improvement on Knopf's procedure in the following ways: The correction factor is 0.34 per cent per day at 50° C. instead of 0.7 per cent per day at room temperature, fluoboric acid dissolves a variety of silicates more rapidly than does fluosilicic acid, and a greater number of more insoluble silicates can also be dissolved in fluoboric acid.

Quartz is the only form of silica which has been used in the synthetic mixtures. Such other forms as tridymite, cristabolite, and amorphous silica have not been considered.

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Examination of Rubber Latex and Latex Compounds

Part II. Chemical Testing Methods

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Methods of determining total solids, dry rubber content, ammonia, fixed alkali, hexamethylenetetramine, water-solubles, acetone extract, free sulfur, total and combined sulfur, copper, manganese, starch, sediment, and coagulum in rubber latex or latex compounds are described.

LATEX compounds are purchased either on the basis of total solids content or the so-called dry rubber content. The total solids probably furnish a more reliable basis of evaluation, as the determination can be made with a high degree of accuracy. The dry rubber content is not a precise determination, as the proteins, fatty acids, and other nonrubber constituents are included, and in the case of compounded latices some of the compounding materials are included in the value and some are not. Hauser (*8*) and Noble (*9*) include in their books useful chapters on testing latex.

Total Solids

The total solids are determined by weighing about 2 grams of the sample in a low covered weighing dish about 6.25 cm. (2.5 inches) in diameter on an analytical balance. A metal weighing dish is preferred for more rapid drying. Tinned 60-ml. (2-ounce) ointment cans are satisfactory and so inexpensive that they may be thrown away if they are at all difficult to clean. The sample is dried, preferably in a vacuum oven. The temperature may be increased to 120° C. in a vacuum without any apparent oxidation or deterioration of the rubber. A sample of normal latex may be completely dried in about 10 minutes if the drying arrangement is right. Results are accurate to better than 0.1 per cent.

Methods involving the use of specific gravity are worse than useless when applied to preserved latex as a concentration control. Even in the case of unpreserved, unwatered normal latex on the plantations, the hydrometers must be calibrated especially for the latex from the estate on which they are to be used.

Dry Rubber Content

A number of official methods for determining the dry rubber content have been described. Usually the diluted latex is coagulated with acetic acid and the coagulum dried. The various official methods usually differ only in minor details. The method as prescribed by the Customs of the Commonwealth of Australia (*4*) for evaluating latex for tariff purposes is as follows:

> Place a weighed quantity of latex (approximately 10 grams) in a porcelain or glass basin of about 200-ml. capacity. Add gradually, with constant stirring, a 1 per cent solution of acetic acid until the latex appears to be completely coagulated and the addition of more acid produces no apparent effect. Manipulate coagulum with stirrer until all particles are collected in one mass.
>
> Place basin on a steam bath for 30 minutes; pour off and wash coagulum with water.
>
> Remove coagulum from basin and pass it several times through rollers to squeeze out serum. Wash the thin rubber with water and finally dry it at 100° C. until the rubber no longer loses weight. The percentage of dry rubber so found shall be the crude rubber content of the latex tested.

The relationship between the acetic acid rubber (dry rubber content) and solids for unwatered normal latex is roughly

$$\text{Acetic acid rubber} + 2.3 = \text{total solids}$$

Determination of Ammonia

If ammonia alone has been added to latex, it is usually satisfactory to titrate directly with standard acid, using methyl red as indicator.

> Weigh about 10 grams to the nearest centigram in a 400-cc. rubber-extraction flask. Add about 200 cc. of water, a few drops of methyl red indicator, and titrate with 0.588 *N* acid, being careful to keep the solution well agitated throughout the determination. The volume of acid used divided by the weight of sample will give the percentage of ammonia. If only occasional tests are required, 0.5 *N* or 0.1 *N* acid may be used. The presence of hexamethylenetetramine does not interfere to any appreciable extent.
>
> If other alkaline materials, such as sodium or potassium hydroxide, borax, or sodium silicate, are present in addition to the ammonia, the ammonia may be distilled over into standard acid and titrated.
>
> Weigh about 5 grams of the sample from a weighing pipet into an 800-cc. Kjeldahl flask containing about 250 cc. of distilled water. Distill over about 200 cc. into an excess of 0.1 *N* sulfuric acid. Back-titrate the excess of standard acid with 0.1 *N* sodium hydroxide using methyl red as indicator.

$$\frac{(\text{cc. of acid} \times \text{normality factor} - \text{cc. of base} \times \text{normality factor}) \times 1.7}{\text{weight of sample}} = \%\ NH_3$$

In compounds which contain no fixed alkali, the distillation method will give only the free ammonia. Ammonium soaps are also included if a little sodium hydroxide is added before the distillation. One cubic centimeter of normal caustic will take care of all the ammonium soaps which are normally present in latex.

In the presence of the alkaline materials mentioned above, total ammonia may be determined by coagulating the latex and nesslerizing the clear serum. The method in detail is as follows:

NESSLER REAGENT. Dissolve 25 grams of potassium iodide in 20 cc. of distilled water. Add saturated mercuric chloride solution until a slight precipitate appears. Add 200 cc. of clear 36 per cent sodium hydroxide solution. Dilute to 500 cc., let stand one day or longer, filter through asbestos in a Gooch crucible, and place in a dark bottle. After about 24 hours the small amount of precipitate will have settled and the solution will be clear.

STANDARD AMMONIA SOLUTION. Dissolve 0.4176 gram of ammonium oxalate, $(NH_4)_2C_2O_4{\cdot}H_2O$, in distilled water and make up to 1000 cc. Pipet out 20-cc. aliquot and make up to 1000 cc. This solution contains 2 mg. of NH_3 per liter.

METHOD. Weigh about 10 grams of the latex from a weighing pipet into a 1000-cc. volumetric flask containing about 950 cc. of water. Shake and add a dilute solution of acetic acid, a few drops at a time, shaking thoroughly between additions until the latex is coagulated. Make the volume up to the mark, mix thoroughly, and filter a portion of the serum, rejecting the first 10 to 20 cc. which do not always come through clear.

In some cases, especially with latex compounds containing pigments, antioxidants, etc., it is necessary to refilter the solution with the aid of a little Celite in order to remove opalescence. The final solution should be perfectly clear and colorless.

Measure an aliquot of this clear filtrate into a 500-cc. volumetric flask and make up to the mark with distilled water. The size of the aliquot depends on the ammonia content of the sample. A 100-cc. aliquot is used when the ammonia content is expected to be about 0.1 per cent and proportionally smaller amounts for higher percentages.

After the aliquot has been made up to 500 cc., measure 25 cc. of this diluted solution in a graduated cylinder, and treat with 1 cc. of Nessler reagent added from a pipet. Compare the color in a colorimeter with that obtained from 25 cc. of the dilute standard ammonium oxalate solution obtained in the same way. Either the distillation or nesslerization method may be applied to black or colored compounds. The color is all carried down with the rubber on coagulation.

FIXED ALKALI. The amount of fixed alkali present may be estimated from the difference between the total alkalinity by direct titration and the ammonia as determined either by distillation or nesslerization.

Hexamethylenetetramine

Hexamethylenetetramine is frequently present in latex compounds. Its presence is of very little importance in most cases, as it is water-soluble and is usually removed from the finished product in the serum or by washing. It may be detected, however, by diluting the latex considerably, adding acid to coagulate and about 25 cc. of normal acid in excess, distilling off some of the water, and testing the distillate with fuchsin sulfite solution. A red or purple coloration indicates hexamethylenetetramine.

The fuchsin sulfite reagent is prepared by dissolving 0.5 gram of fuchsin and 9 grams of sodium bisulfite in 500 cc. of distilled water. Ten cubic centimeters of concentrated hydrochloric acid are added and the solution is kept well stoppered and away from light.

Hexamethylenetetramine may be determined quantitatively as follows:

Dilute the residue from the ammonia determination by distillation to about 250 cc. with water and add 25 cc. of normal acid from a buret. Boil the flask for about 5 minutes, cool, and add 26 cc. of normal caustic. Distill the ammonia into standard acid and titrate exactly as described in the ammonia by distillation method above. One cubic centimeter of normal acid is equivalent to 0.035 gram of hexamethylenetetramine.

Determination of Water-Solubles

The amount of water-solubles in latex cannot be easily and completely leached from a latex film by merely boiling with water or extracting with water as is done in the case of the acetone extract. Using such methods, the extraction is very likely to be incomplete and the results will depend on the amount of surface of the sample extracted.

The water-solubles may be removed from the uncoagulated sample by dialyzing through a parchment membrane with distilled water, but the determination is slow, a week or more being required to remove all the extractable materials. A coagulation method which has proved very satisfactory consists of boiling off the ammonia, diluting considerably, then coagulating by adjusting to the isoelectric point of the protective proteins with a known amount of acid, evaporating an aliquot of the serum, weighing, and correcting for the acid added. The method in detail is as follows:

Weigh about 5 grams of the sample accurately to a centigram in a 400-cc. beaker, add about 200 cc. of water at once, cover with a watch glass, and boil on a hot plate until the volume has been decreased considerably.

Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned), and make up to within about 10 cc. of the mark, add 1 cc. of a 0.1 per cent methyl orange indicator solution, and add *N* sulfuric acid from a buret until the red-orange color, indicating a pH of about 4.3, is obtained, and the rubber is well coagulated. Care must be taken not to add too much acid, as the sample will not coagulate so well at a lower pH. Shake well to complete coagulation and make up to the mark.

Filter and pipet 100 cc. of the clear serum into a weighed evaporating dish. Evaporate to dryness on a steam bath, dry in an air oven at 70° C., cool, and weigh.

Normal latex has water-solubles of about 8.5 per cent and centrifuged or creamed latices have water-solubles of about 2.6 per cent of the total solids.

$$E = \left\{ \frac{W\left(200 - \frac{S\,T\,R}{10{,}000\,D}\right)}{100} (-\,0.0049\,A + I) \right\} \frac{10{,}000}{S\,T}$$

E = per cent of water extract
W = weight of dry material in 100-cc. aliquot
T = per cent of total solids
R = percentage of rubber expected in the solids of the sample, for normal latex 92 per cent, for creamed latex 97 per cent, etc.
D = density of rubber (about 0.92)
A = volume of 0.1 *N* sulfuric acid used
I = weight of indicator used, in grams
S = weight of sample

Acetone Extract

The acetone extract is not of very much value as a control test for consignments of raw latex, but may be of great assistance in examining samples of unknown composition, particularly compounded samples, and is a necessary part of the usual method of determining free or combined sulfur.

The film should be laid down by pouring some of the latex into a shallow glass tray, which is easily prepared from a pane of window glass and some glass rods or tubing. The glass rod is cut to fit around the edge of the plate and is stuck on with paraffin wax. The edges of the plate are then dipped in molten paraffin wax, thus making a ridge of wax supported by the rods all around the glass plate. The film should be thin and dried at room temperature until it is clear. An electric fan blown over the film hastens drying considerably. The film is then sheeted out as thin as possible on a cold roll but not broken down.

The prepared film is cut in narrow strips and 1 gram is weighed in an extraction thimble and extracted for 16 hours, according to the method and using the apparatus recommended by the committee on Methods of Analysis of the Rubber Division of the AMERICAN CHEMICAL SOCIETY for rubber goods (*2*). Part of the acetone may be removed by boiling on a hot plate or steam bath, but great care must be observed and the flask must not go dry. It is possible to scorch the extract on a hot plate with as much as 10 cc. of acetone remaining in the flask, and if the sample goes dry on a steam bath appreciable amounts of free sulfur may be lost. It is best to stand the flasks in a bath of warm water, 40° to 70° C., remove the acetone by gently blowing air into the flask until it is dry, and finally dry in an air oven at 70° C.

The time of extraction of 16 hours is empirical. The greater part of the extract is removed in this time, but some less easily soluble materials will not be entirely removed if the extraction is continued for several days. The thickness of the film also has some bearing on the quantity of extract removed, as has the rate of boiling.

Free Sulfur

Free sulfur is usually determined on the acetone extract of the film. The bromine method (*2*) is most commonly used and is satisfactory, except that the results generally contain some if not all of the sulfur of the accelerator and may be rather confusing. The method of Bolotnokov and Gurova (*5*), in which the rubber film is heated with a solution of sodium sulfite, the excess of sulfite destroyed with formaldehyde, and the thiosulfate which was formed titrated with iodine, is very convenient, but some accelerators interfere. This method was modified by Oldham, Baker, and Craytor (*10*) to prevent interference by mercaptobenzothiazole and is satisfactory in most cases, but tetramethylthiuram disulfide will give high results.

The method has been further modified in the author's laboratory to make it possible to run sulfur on the uncoagulated latex.

Weigh about 10 grams of the latex compound into a 400-cc. rubber-extraction flask and add 100 cc. of a 5 per cent sodium sulfite solution. Bring to the boiling point and boil gently for 5 minutes on a hot plate. Care must be taken to avoid vigorous boiling or the mixture will froth over the neck of the flask. Remove the flask from the hot plate and add 100 cc. of a 0.5 per cent strontium chloride solution and 4 cc. of glacial acetic acid. Stir until the rubber is coagulated. Remove the lump of rubber, washing it with a jet of water and squeezing it with the fingers to express as much of the liquid as possible.

To the solution add 6 cc. of 37 per cent formaldehyde, then a few drops of phenolphthalein and sufficient sodium hydroxide to turn the indicator pink. Add normal acid until the pink color completely disappears but avoid any considerable excess. Let the mixture stand about 10 minutes, then filter it, receiving the filtrate in a 1000-cc. flask. Wash the filter paper twice with a jet of hot water. Acidify the filtrate with 10 cc. of glacial acetic acid, add cracked ice to bring the temperature below 15° C. and the volume to about 600 cc., and titrate with 0.1 *N* iodine, using about 5 cc. of a 3 per cent starch solution as indicator.

1 cc. of 0.1 *N* iodine = 0.003206 gram of sulfur

Sulfur-bearing accelerators, such as mercaptobenzothiazole, xanthates, carbamates, and thiuram monosulfides, do not interfere with the determination but tetramethylthiuram disulfide is dissolved and one-fourth of its sulfur is titrated.

The above method gives the true free sulfur of the sample. The sulfur is in a fine state of division and is reacted on by the sodium sulfite almost immediately, and all chance of loss of free sulfur because of vulcanization during the determination is eliminated. When the other methods are used there is always a chance that the rubber has cured up somewhat and part of the sulfur has combined while the film was being dried or extracted.

Total Sulfur

The Parr sulfur bomb method (*11*) and the nitric acid–bromine method (*2*) are both satisfactory. The author has, however, found the perchloric acid (*12*) method more convenient, rapid, and highly dependable. The perchloric acid method may be carried out as follows:

To a 1-gram sample of the latex film in a 250-cc. rubber-extraction flask add 20 cc. of a nitric acid solution 1 to 1 and warm on an electric hot plate for 1 or 2 minutes until brown fumes appear and the reaction has subsided. Then add 10 cc. of concentrated nitric acid and continue heating for about 15 minutes or until the rubber is nearly entirely dissolved. Add 10 cc. of a 60 per cent solution of perchloric acid and heat until dense white fumes appear and the solution (in the absence of insoluble inorganic compounds) is clear and colorless. Allow to cool somewhat and slowly add 5 cc. of concentrated hydrochloric acid, once more heat until white fumes appear, cool, and wash into a 250-cc. beaker. If the solution is not perfectly clear and free from sediment it should be filtered. Dilute with distilled water to about 200 cc., precipitate the sulfur as barium sulfate in the usual manner, and weigh. If the sample contains free carbon, the free carbon need not be completely oxidized and may be filtered off after diluting. If an insoluble inorganic material is found and the presence of barium sulfate is suspected, this should be filtered off, dried, fused with sodium carbonate, and examined for sulfates.

Combined Sulfur

The sulfur which is left in the rubber sample after extraction with acetone is usually considered as the combined sulfur. It may be determined directly on the extracted sample by the perchloric acid method described for total sulfur or may be computed as the difference between the total and free sulfur.

Combined sulfur is valued as a measure of the degree of vulcanization of a rubber stock and is frequently considered as a measure of the sulfur which has actually combined with the rubber. In most stocks, however, this is only partly true, for the combined sulfur figure would include sulfur which had been changed into or added as sulfides or other inorganic sulfur compounds. A very careful consideration of the compound and method must be made in interpreting combined sulfur values.

The T-50 test, described in a previous paper (*6*) is a reliable measure of state of cure and may be correlated with the true combined sulfur value of any latex compound that can be stretched considerably.

Copper

The determination of copper and manganese in latex and compounding materials should be made occasionally. Traces of both of these elements are troublesome and cause poor aging, but quantities of either element up to 0.0015 per cent will do no harm.

Sodium dimethyldithiocarbamate is a very satisfactory reagent for determining copper. It is very sensitive and if the details listed below are followed, iron and other usually occurring elements do not interfere.

Weigh about 10 grams of the dry film into a 150-cc. beaker, and ignite in a muffle at about 400° C. to a white ash. Cool and take up the ash with about 1 cc. of hydrochloric acid and a drop of concentrated nitric acid. Evaporate to dryness on a water bath and take up with distilled water.

Treat the aqueous solution with 2 grams of citric acid and a drop of phenolphthalein, and add ammonia until a red color is produced. To this solution add 10 cc. of a 0.1 per cent aqueous solution of sodium dimethyldithiocarbamate, and extract the brown solution with successive small portions of carbon tetrachloride until the extract is only faintly yellow.

After the copper has been extracted add 1 cc. of the standard copper solution (1 cc. = 0.0001 gram of copper) to the extracted liquid, and extract the color thus produced with carbon tetrachloride, the extract being used as the comparison standard.

A blank determination on all materials must be run in exactly the same way as the sample.

The color of the extract from the sample is compared with the standard in Nessler tubes or a colorimeter, and the amount of copper estimated. The blank is also compared with the standard, the copper in the blank subtracted from the copper found in the sample, and the difference reported as per cent of copper on the original latex solids.

After the color has been developed and extracted, it is important that the solution not be left for a long time before comparison is made, as the color fades slowly.

Sodium diethyldithiocarbamate (*7*) may be used equally well.

Manganese

The periodate method for manganese has given more reliable results in the author's laboratory than either the persulfate or bismuthate methods.

Weigh about 10 grams of the latex film into a large porcelain crucible and ash in a muffle furnace at as low a temperature as possible.

Add 5 to 15 grams of potassium bisulfate to the ash (depending on how much ash is present) and fuse cautiously until effervescence ceases, then put into the muffle at moderately low red heat, and fuse until the carbon particles are burned off.

Cool, dissolve in 80 cc. of 5 per cent sulfuric acid, filter if necessary, add 5 cc. of 85 per cent H_3PO_4, and 0.5 gram of periodic acid, and heat until the color appears, boiling 15 minutes thereafter. Cool, dilute to 100 cc. in a volumetric flask, and compare with a standard in a colorimeter or Nessler tubes.

The standard solution is prepared by diluting carefully standardized 0.05 *N* potassium permanganate to such a volume as to contain 0.02 mg. of manganese per cc. with distilled water which has been slightly acidified with sulfuric acid, boiled with a little periodic acid, and then cooled.

Starch

Starch may be detected in latex compounds by acidifying with hydrochloric acid and then adding a solution of iodine in potassium iodide. A blue or black coloration indicates starch.

Starch may be quantitatively determined by the following procedure:

Weigh 15 grams of the sample into a 500-cc. Erlenmeyer flask fitted with a glass condenser tube. Add 100 cc. of distilled water and 4 cc. of *N* sodium hydroxide and heat the mixture on a water bath, with air being blown over the surface until the ammonia is removed. Then cool the mixture and add water to replace any that may have evaporated. Add 20 cc. of concentrated hydrochloric acid rapidly while swirling the flask. This prevents the latex from coagulating to a solid mass. Add 40 cc. of 95 per cent alcohol and 60 cc. of benzene, attach the flask to the condenser, and allow to reflux at gentle heat for 2 hours. Refluxing for longer periods was found to give lower results.

Remove the condenser and evaporate the benzene and alcohol by blowing air over the surface of the mixture on a steam bath. Decant the clear water layer, wash the rubber residue several times with hot water, and combine the washings with the extract. Add 10 per cent potassium hydroxide solution to bring to neutrality and then bring just on the acid side with hydrochloric acid. Evaporate to a smaller volume if necessary, and make up to volume in a volumetric flask of such a capacity that a 25-cc. aliquot will yield between 15 and 500 mg. of cuprous oxide on oxidation. A precipitate of about 100 mg. of cuprous oxide is most conveniently handled. Direct boiling of the solution containing the sugar over an open flame is to be avoided, as this decomposes some of the sugar and causes low results.

The dextrose in the extract is determined by Allihn's gravimetric method as follows:

REAGENT. Allihn's modification of Fehling's solution, prepared by mixing, immediately before use, equal volumes of (a) and (b).

(a) Copper sulfate solution: Dissolve 34,639 grams of copper sulfate ($CuSO_4 \cdot 5H_2O$) in water and dilute to 500 cc.

(b) Alkaline tartrate solution: Dissolve 173 grams of Rochelle salt and 125 grams of potassium hydroxide in water and dilute to 500 cc.

DETERMINATION. Place 30 cc. of the copper sulfate solution, 30 cc. of the alkaline tartrate solution, and 60 cc. of water in a 250-cc. beaker, cover with a watch glass, and heat to boiling. From a pipet add 25 cc. of the material to be examined, and boil for exactly two minutes, keeping the beaker covered. Filter immediately through an asbestos Gooch, wash thoroughly with water at 60° C., once with acetone, and dry at 100° C. for 30 minutes.

The weight of dextrose corresponding to the weight of cuprous oxide may be obtained by referring to Allihn's sugar table (*1, 3*). The factor for converting dextrose to starch is 0.90. The weight of cuprous oxide may be converted to weight of dextrose or starch by multiplying by a factor, which varies with the weight of cuprous oxide and may be found by interpolating in Table I.

TABLE I. FACTOR FOR CONVERTING CUPROUS OXIDE TO DEXTROSE OR STARCH BY ALLIHN METHOD

Cu_2O Weighed	Dextrose per Mg. of Cu_2O	Starch per Mg. of Cu_2O	Cu_2O Weighed	Dextrose per Mg. of Cu_2O	Starch per Mg. of Cu_2O
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
15	0.520	0.468	150	0.452	0.407
20	0.493	0.443	200	0.454	0.409
40	0.467	0.420	300	0.457	0.411
60	0.459	0.413	400	0.468	0.421
80	0.455	0.410	500	0.478	0.430
100	0.453	0.408			

Sediment and Sludge

Fill a 15-cc. centrifuge tube to the mark with the sample, stopper, and centrifuge. Decant the latex off, fill the tube with a 2 per cent solution of sodium oleate, shake up the sediment, and centrifuge again. Repeat until the sediment has been washed free from latex. Transfer the sediment to a weighed Gooch crucible, wash with water, dry, and weigh.

Results by methods which depend on measuring the volume of the sediment are not reliable, as they are too dependent on the time and speed of centrifuging as well as the physical nature of the sediment.

Determination of Coagulum

Measure or weigh about 100 cc. of the sample and dilute with a 2 per cent sodium oleate solution until it has the consistency of normal latex. Cut a circular piece of 80-mesh wire screen cloth of such a size that it will fit inside a 5-cm. (2-inch) ordinary pipe union. Weigh and place tightly in the union and press down in the middle so that the upper surface will be concave. Clamp the pipe union in a vertical position. Pour the latex through the screen and wash with a 2 per cent sodium oleate solution and finally with water. Remove the screen, dry, and weigh. If a large amount of coagulum is expected a smaller sample should be used.

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Determination of Iron

Colorimetric *o*-Phenanthroline Method

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IN THE determination of the iron content of various fruit products and materials utilized in their production, two methods have been used previously by the authors. With dried fruits (*5*) a dry-ashing was followed by a determination of the iron using the colorimetric thiocyanate method of Stugart (*6*). In early studies on fruit juices and wines (*4*) essentially the colorimetric mercaptoacetic acid method of Lyons (*3*) and Leavell and Ellis (*2*), with sulfuric and perchloric acid wet-ashing, was used. The latter methods were also used in a study of certain filter aids and asbestos filtering products.

The dry-ashing and Stugart procedure require considerable time, so that where several hundred determinations are to be made, a more rapid and simple, yet accurate, method is desirable. For over 2 years an adaptation of the wet-ashing method of Leavell and Ellis has been successfully employed with the usual ashing times of 3 to 7 hours for wines and many fruit juices reduced to periods of 2 to 10 minutes for each sample.

Because of the difficulty in color comparison with concentrations lower than 2 or 3 parts per million (p. p. m.) and the occasional fading of the mercaptoacetic acid colored complex, it appeared desirable to have a method of equal or greater sensitivity and accuracy, with a higher degree of precision.

Experimental

It has been pointed out by Walden, Hammett, and Chapman (*7*) that the ferrous *o*-phenanthroline complex ion discovered by Blau (*1*) may be used as a reversible oxidation indicator of high potential. The ferrous complex gives an intense red color.

The authors have observed that the color, when once formed in slightly acid to neutral solutions, is very stable and standards have been kept for over 4 months without exhibiting differences from freshly prepared standards. Solutions containing a final iron concentration of 1 to 10,000,000 give color of sufficient intensity for colorimetric comparison. For iron concentrations of the same magnitude, the intensity of the color is proportional to the iron content. Concentrations of greater than 20 or 25 p. p. m. may be conveniently diluted by one-half, or smaller samples may be taken for analysis.

As the iron in the strongly acid solution remaining from the wet-ashing is in the ferric condition, reduction to the ferrous condition before the addition of the *o*-phenanthroline is necessary. Several reducing agents were studied, the best being sodium hypophosphite or hypophosphorous acid, and sodium formate, which were discontinued because of the considerable iron content of these products and the necessary correction therefor. The use of a concentrated solution of iron-free hydroxylamine hydrochloride has been adopted.

Numerous experiments were made to ascertain the most satisfactory procedure and conditions for the addition of the reagents. As a result it was observed that a treatment of the warm acid solution (remaining from the wet-ashing) with hydroxylamine, followed by the addition of *o*-phenanthroline and neutralization with concentrated ammonium hydroxide, using Congo red indicator paper, gave a quantitative development of the color due to the formation of ferrous *o*-phenanthroline complex. An excess of one or two drops of ammonium hydroxide is permissible.

Pyrex test tubes, 25 × 150 mm., are calibrated to contain 10 and 15 ml. Using such tubes the entire procedure of wet-ashing, development of color, and dilution may be carried out in the same tube without possible error of transfer and at a considerable saving of time. Iron-free concentrated sulfuric acid, 60 or 70 per cent perchloric acid, 10 per cent aqueous hydroxylamine hydrochloride solution, 1.5 per cent solution of *o*-phenanthroline in ethyl alcohol, and concentrated ammonium hydroxide are required. Congo red paper also is used.

A primary standard iron solution is prepared (*2*) by dissolving 1 gram of pure iron wire in dilute sulfuric acid and concentrated nitric acid. Oxides of nitrogen should be expelled by boiling to fumes of sulfur trioxide. The solution is then diluted to 1 liter. Other standard solutions may be prepared by diluting 20, 10, and 5 ml. of the primary standard to 1 liter each, these standards containing 20, 10, and 5 p. p. m. of iron, respectively. Further standards may be prepared as desired. All standards should be made acid with sulfuric acid.

Procedure

Samples of 2 ml. of a fruit juice or wine are digested with 1 ml. of concentrated sulfuric acid and 0.7 to 1 ml. of 60 to 70 per cent perchloric acid in the Pyrex test tubes over a free flame. It is convenient to hold the tube in a wire clamp and agitate contents vigorously during the heating, thereby greatly increasing the rate of heating and digesting. Digestion to a clear water-white liquid will occur ordinarily in 2 to 10 minutes. If combustion is not complete in this time an additional 0.5 to 1 ml. of perchloric acid should be used and digestion continued. When digestion is completed, 1 ml. of distilled water is added. This is followed by the addition of 1 ml. of the 10 per cent hydroxylamine hydrochloride solution, shaking, and the addition of 0.5 ml. of the 1.5 per cent *o*-phenanthroline solution. Concentrated ammonium hydroxide (about 2 ml.) is added until a light red or pink color develops, a small piece of Congo red indicator is dropped into the solution, and the addition of the ammonium hydroxide is continued until the Congo red paper is distinctly pink. In the meantime the full color of the ferrous *o*-phenanthroline complex will have developed. The solution is then diluted with distilled water to the graduation mark on the test tube indicating a volume of 10 ml. and thoroughly mixed. If the color intensity of this solution is greater than that of the highest standard available, the unknown solution may be diluted to the 15-ml. graduation mark and appropriate calculation made. Determinations may conveniently be made on a series of samples, and the reagents added consecutively from measuring pipets or burets.

Standards should be prepared by the same procedure. A blank determination on the distilled water and reagents used should also be made. For purposes of comparison with a colorimeter, standards containing 2.5, 5.0, 7.5, 10, and 15 p. p. m., respectively, have been convenient. For routine plant purposes where many determinations are being made, much time may be saved by having permanent standards of 1, 2, 4, 6, 8, 10, 12, and 15 p. p. m., respectively, in a rack so that it is only necessary to compare the solutions in two similar tubes. The iron content can be easily estimated to within 1 p. p. m. or better in this manner. For materials

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such as dried fruits, in which the iron content may be up to 40 to 60 p. p. m., it is desirable to weigh out a small sample of approximately 0.5 gram on a small piece of wax paper and ash the entire sample. One also may weigh out a larger sample, prepare a water solution or suspension of it, and use a suitable aliquot for ashing. In general, the authors have used original concentrations of up to 20 p. p. m. with a total of 0.04 mg. of iron present in each determination. Volumetric flasks and long tubes of small diameter for color comparison may also be used.

Examination of the possible interfering effect of copper, aluminum, and magnesium upon the test was made. To standards containing 10 p. p. m. of iron the corresponding metal salts were added to give concentrations of copper, aluminum, and magnesium up to 20, 100, and 100 p. p. m., respectively. These relative concentrations are greater than those usually found in the products analyzed. No interference was observed, though it was necessary to make the determinations with aluminum again acid to Congo red paper and reheat the solution to obtain a clear solution, for color comparison.

Standards were prepared containing 5, 10, 15, and 20 p. p. m. of iron, respectively, and the 10 p. p. m. standard was used for comparing the iron content of the others. Similar series and observations were made by each of three analysts. The results are tabulated in Table I. The numbers with three figures are calculated from the arithmetical average of colorimetric readings.

Similar series of standards of 2.5, 5.0, 7.5, 10.0, and 15.0 p. p. m. were prepared by the same three analysts, the series by the second and third analysts being compared by them with that of the first. These data are given in Table II. The numbers with three figures are calculated from the arithmetical average of colorimetric readings.

To two wines containing 3.8 and 2.9 p. p. m. of iron, respectively, were added 2.5 and 5.0 p. p. m. of iron. The results of the duplicate determinations are given in Table III.

A group of four wines of varying sugar and alcohol contents was taken for duplicate analysis by each of four analysts. The data are presented in Table IV.

Another group of six wines was analyzed in duplicate for iron by the mercaptoacetic acid, Stugart (*6*), and *o*-phenanthroline methods. The data are given in Table V.

The *o*-phenanthroline method has been found to have a considerable range of applicability and has been applied to fruit juices, wines, and vinegars. Comparative tests on apple and grape juices and vinegar, using the mercaptoacetic acid and *o*-phenanthroline methods, parallel those on wines reported in Table V. In general, the variations between duplicate determinations with the mercaptoacetic acid method tend to be greater than with the *o*-phenanthroline method. Three samples of prunes on which the iron had previously been determined by the Stugart method (*6*) and having 39, 28, and 42 p. p. m. of iron, respectively, were also analyzed by the *o*-phenanthroline method; these analyses indicated iron contents of 35, 30, and 40 p. p. m., respectively.

Table I. Comparison of Iron Standards of Different Concentrations

Analyst	Standard 5 p. p. m.	10 p. p. m.	15 p. p. m.	20 p. p. m.
A	5.02	10	15.1	19.5
B	5.06	10	14.8	19.7
C	4.95	10	14.7	19.0

Table II. Comparison of Iron Standards of Equal Concentration

Analyst	Standard 2.5 p. p. m.	5.0 p. p. m.	7.5 p. p. m.	10 p. p. m.	15 p. p.m.
A	2.5	5.0	7.5	10.0	15.0
B	2.52	4.93	7.63	9.95	14.8
C	2.58	5.10	7.57	9.97	15.1

Table III. Recovery of Added Iron

	Iron Recovered			
	Sauterne		Claret	
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
Original wine	3.8	3.8	2.9	2.9
Original + 2.5 p. p. m.	6.3	6.3	5.4	5.4
Original + 5.0 p. p. m.	8.7	8.8	7.8	7.9

Table IV. Iron Content of Wines

Analyst	Iron Content Muscat	Haute Sauterne	Dry Sauterne	Claret
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
A	2.4	7.6	7.4	5.9
	2.4	7.7	7.4	6.0
B	2.3	7.7	7.3	5.8
	2.4	7.7	7.4	6.0
C	2.4	8.0	7.5	6.0
	2.3	7.9	7.3	6.0
D	2.4	7.7	7.5	6.0
	2.5	7.6	7.5	5.9

Table V. Iron Content of Wines

Method	Iron Content Muscat	Sherry	Port	Sauterne	Riesling	Claret
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m*
Stugart	3.3	3.1	3.5	4.8	7.4	3.9
	3.1	3.5	3.2	4.9	7.8	3.8
Mercaptoacetic acid	3.2	2.8	3.1	5.4	7.1	3.7
	3.4	2.9	3.3	5.0	7.8	4.0
o-Phenanthroline	3.4	3.3	3.2	5.2	7.4	3.9
	3.5	3.3	3.2	5.3	7.3	4.0

Two samples of cellulose-asbestos filtering pads which had been analyzed for total iron by the mercaptoacetic acid method, using a concentrated hydrochloric acid extract, were also analyzed for iron, using a direct wet-ashing of a 0.020-gram sample of each, followed by the *o*-phenanthroline procedure. The iron contents by the mercaptoacetic acid procedure were 0.09 and 0.30 per cent, respectively, and by the *o*-phenanthroline method 0.11 and 0.31 per cent, respectively. Comparisons of the tartaric acid–soluble iron of diatomaceous silica filter aids (*4*) were also made by the two methods, with results comparable to those obtained for the cellulose-asbestos filtering pads.

The iron contents of several well waters used in wineries has been determined by the *o*-phenanthroline method, a 5- or 10-ml. sample of the water being wet-ashed. For three representative waters the iron contents were 0.3, 0.4, and 0.3 p. p. m., respectively.

Summary

The use of the *o*-phenanthroline method by the authors for several months has indicated its value for the rapid and accurate determination of small amounts of iron in biological substances, such as plant tissues and their extracts, and for similar analysis of inorganic substances, such as industrial products and dilute salt solutions.

The use of the same tube for wet-ashing, color production, and volumetric dilution further facilitates attaining accuracy and rapidity of procedure. Possible losses due to dry-ashing and to transferring for dilution are avoided.

Under the conditions of this study, the use of *o*-phenanthroline as a colorimetric reagent for the determination of iron offers the advantages over the mercaptoacetic reagent of having a relatively more intense color for a given iron concentration, a greater working sensitivity, a color apparently more desirable for colorimetric comparison purposes, and a color which is stable over considerable periods of time, no

fading of standards or routine determinations having been observed.

The data presented in this paper indicated that the method gives results with a high degree of both accuracy and precision. When comparisons are made of solutions with iron contents varying not more than 25 per cent, the iron recovery is within the accuracy of colorimetric methods. For these studies, with iron concentrations less than 5 p. p. m. the results were accurate to within less than 10 per cent. For higher concentrations variations are probably not more than 5 per cent. For wide differences (100 to 200 per cent) in iron concentration of compared samples the iron content appears to be somewhat less than theoretical for the sample of high concentration.

Copper, aluminum, and magnesium in the relative concentrations ordinarily occurring in plant tissues do not interfere with the accuracy of the test. Copper in concentrations up to twice that of the iron, and aluminum and magnesium up to ten times that of the iron did not cause interference.

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Determination of Sulfur in Rubber

Use of Tetrahydroxyquinone as a Titration Indicator

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A back-titration method for the determination of sulfur in rubber with the use of tetrahydroxyquinone as an internal indicator is described. The sulfur in the soluble sulfate form is precipitated by excess standard barium chloride; the zinc, iron, and other heavy metals are precipitated by potassium hydroxide at pH 8.3, and these joint precipitates are filtered off; the barium in the filtrate is determined by titration of an aliquot with standard sodium sulfate using tetrahydroxyquinone as an indicator, the colorimetric change being from red to yellow. The time of a single determination is 20 minutes, showing considerable saving of time over gravimetric analysis. The method is accurate and sulfur control is maintained very well within acceptable limits.

THE use of tetrahydroxyquinone was first suggested as an indicator for the direct titration of sulfate by Schroeder (*1*) and the application of the method was extended by Sheen and Kahler (*2*). This method allows the direct titration of sulfate in a sample with standard barium chloride solution, the end point being indicated by a change from the yellow sodium salt to the red barium salt of the tetrahydroxyquinone.

It has been necessary to determine the sulfur in rubber by gravimetric precipitation as barium sulfate, inasmuch as most rapid methods proposed up to the present time have not been found sufficiently accurate to warrant acceptance by the field. The method proposed allows for the oxidation of sulfur by standard procedures to sulfate, precipitation of the sulfate with excess barium chloride, as well as precipitation of the zinc, iron, and other heavy metals by potassium hydroxide, filtration of the precipitate, neutralization of the filtrate to the acid side of phenolphthalein, and the back-titration of excess barium ion with the standard sodium or potassium sulfate to a colorimetric end point from the red barium salt of tetrahydroxyquinone to the yellow sodium salt of tetrahydroxyquinone. This method requires only a small fraction of the time consumed in a gravimetric analysis and the accuracy is well within acceptable limits for sulfur control.

Experimental

The indicator used throughout this study was manufactured in the Betz laboratories and considerable quantities have been furnished for the determination of sulfur in coal, oil, water, and cement, and in other fields where the determination of sulfate has previously been performed mainly by gravimetric precipitation. The indicator is a dispersion in potassium chloride of the disodium salt of tetrahydroxyquinone, ground to pass a 100-mesh screen, and is supplied under the name of THQ.

Materials and Reagents. Standard barium chloride solution, 1 cc. = 3 mg. of sulfur. Standard sodium sulfate solution, 1 cc. = 0.8 mg. of sulfur. Hydrochloric acid, 0.02 *N*. Tetrahydroxyquinone indicator. Ethyl alcohol or ethyl denatured by formula 30, 3-A, or 2-B, or isopropyl alcohol. Freshly prepared 10 per cent solution of potassium hydroxide (carbonate-free). Phenolphthalein indicator. Measuring dipper capacity 0.2 gram of tetrahydroxyquinone.

Procedure. Oxidize the sulfur from the rubber by one of the standard methods. Select a volume of the solution equivalent to a 1-gram sample of rubber and precipitate the sulfate by pipetting into the solution 50 cc. of standard barium chloride in the cold (1 cc. = 3 mg. of sulfur). (This amount of barium chloride solution will allow a sufficient excess to precipitate up to 13 per cent of sulfur in rubber. Higher percentages can be determined by using a higher excess.) Introduce phenolphthalein indicator and add 10 per cent freshly prepared potassium hydroxide just to the alkaline side of the phenolphthalein. Zinc, iron, and other heavy metals will be precipitated.

TABLE I. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD

(In determination of total sulfur in rubber[a])

Sample No.	Volume of Na_2SO_4[b]	Sulfur		Difference	Other Materials Present
		THQ	Gravimetric		
	Cc.	%	%	%	%
1	35.20	2.02	2.02	0.00	ZnO 4.50
	35.10	2.07	2.05	0.02	
2	35.18	2.03	2.02	0.01	ZnO 10.3
	35.20	2.02	2.02	0.00	
3	35.14	2.05	2.06	0.01	ZnO 14.8
	35.18	2.03	2.03	0.00	
4	36.68	1.37	1.33	0.04	ZnO 5.5
	36.58	1.42	1.37	0.05	CaO 7.5
					Fe 2.6
5	22.04	7.81	7.87	0.04	ZnO 5.4
	22.10	7.78	7.85	0.07	

[a] Analyses were performed in the laboratories of W. H. & L. D. Betz.
[b] Na_2SO_4, 1 cc. = 0.549 mg. of sulfur. $BaCl_2$, 1 cc. = 3.496 mg. of sulfur.

Filter through coarse rapid paper. It will be found that a gelatinous precipitate of zinc hydroxide, etc., will occlude the precipitated barium sulfate in such a manner that a fine paper is not required. Wash the precipitate carefully with small portions of cold distilled water, keeping the volume of filtrate at a minimum. Make the filtrate up to a volume of 200 cc. in a volumetric flask and pipet 25 cc. of the total volume into a 125-cc. Erlenmeyer flask. Discharge the red color of the phenolphthalein with $0.02\,N$ hydrochloric acid, add 25 cc. of alcohol (ethyl, denatured by formula 30, 3-A, or 2-B, or isopropyl) and one dipper of tetrahydroxyquinone, and titrate with standard sodium sulfate until the red color of the solution changes to a yellow. Shake the flask thoroughly during the titration to establish equilibrium conditions.

CALCULATION OF RESULTS. With the above conditions Equation 1 can be used to calculate the percentage of sulfur present in 1 gram of the original sample.

$$0.1\,[150 - (\text{cc. of } Na_2SO_4 \times 0.80 \times 8)] = \text{per cent of total sulfur in rubber} \quad (1)$$

where

0.1 is a factor involving the change of mg. of sulfur to grams of sulfur and 100
150 is the number of mg. of sulfur equivalent to 50 cc. of barium chloride
cc. of Na_2SO_4 is the volume of Na_2SO_4 required in the back-titration of a 25-cc. sample
0.80 is the strength of Na_2SO_4 in mg. of sulfur per cc. used in the back-titration
8 is a factor for the aliquot of the sample taken in the titration

Some of the routine work done in the application of the method to date has shown that a 0.25-gram sample gives excellent results. With this size of sample, precipitate the sulfate with 10 cc. of barium chloride (1 cc. = 7.5 mg. of sulfur), proceed as above, and back-titrate with sodium sulfate (1 cc. = 0.40 mg. of sulfur). The formula then for the total sulfur is:

$$0.4\,[75 - (\text{cc. of } Na_2SO_4 \times 0.40 \times 8)] = \text{per cent of total sulfur in rubber} \quad (2)$$

In the determination of free sulfur, use the procedure advanced for total sulfur with the following modifications:

Convert the sulfur in a 2-gram sample by the customary procedure and precipitate the sulfate in the cold by introducing 20 cc. of barium chloride (1 cc. = 3 mg. of sulfur). Proceed as above with the addition of potassium hydroxide and filtration (use a fine paper, which will retain barium sulfate), making the filtrate up to 100 cc. It is possible to confine the filtrate to this volume, even after thorough washing, because of the absence of zinc, iron, etc.

The sulfur content is computed by Formula 3.

$$0.05\,[60 - (\text{cc. of } Na_2SO_4 \times 0.80 \times 4)] = \text{per cent of free sulfur in rubber} \quad (3)$$

The validity of the method was established under both research and routine conditions. Under research conditions, a number of solutions were prepared in the laboratories of the Firestone Tire & Rubber Company and the method for the determination of sulfur was applied in the Betz laboratories. The results are given in Tables I and II, showing a comparison of gravimetric precipitation as barium sulfate with the results obtained with tetrahydroxyquinone. Table I gives results with total sulfur and Table II with free sulfur.

In Table I the maximum difference in the gravimetric analysis was 0.04 per cent with an average of 0.025 per cent and the greatest difference of the tetrahydroxyquinone method was 0.05 per cent with an average of 0.033 per cent. The average difference between percentage of sulfur determined by gravimetric analysis and tetrahydroxyquinone is 0.03 per cent. These percentage differences are well within the limits of 0.1 per cent as set up by the A. S. T. M.

Table II shows that the maximum difference obtained in sulfur percentage when the tetrahydroxyquinone method is compared to the gravimetric method is 0.03 per cent, while the average percentage difference is 0.01 per cent. Here again the tetrahydroxyquinone method gives results very safely within the limits of tolerance set up by the A. S. T. M.

Under routine conditions in the Firestone Tire & Rubber Company, the total sulfur in four different types of stocks was determined by gravimetric analysis and tetrahydroxyquinone method. Five cubic centimeters of barium chloride (1 cc. = 4.110 mg. of sulfur) were used to precipitate the sulfate except in the case of sample 3, mechanical goods stock, where 6 cc. were employed. Results obtained by these two methods are presented in Table III.

Table III shows that with various types of rubber stocks the tetrahydroxyquinone method gave results within an

TABLE II. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD

(In determination of free sulfur in rubber)

Sample No.	Volume of Na_2SO_4[a]	Sulfur		Difference
		THQ[b]	Gravimetric[c]	
	Cc.	%	%	%
1	30.88	0.100	0.106	0.006
	30.96		0.097	0.003
2	27.40	0.500	0.490	0.010
	27.52		0.480	0.020
3	22.95	0.973	0.977	0.004
	23.00		0.973	0.000

[a] Na_2SO_4, 1 cc. = 0.549 mg. of sulfur. $BaCl_2$, 1 cc. = 3.496 mg. of sulfur.
[b] Analysis completed in laboratories of W. H. & L. D. Betz.
[c] Analysis completed in laboratories of Firestone Tire & Rubber Co.

TABLE III. COMPARISON OF GRAVIMETRIC ANALYSIS AND TETRAHYDROXYQUINONE METHOD[a]

(In determination of total sulfur in rubber)

Sample	Volume of Na_2SO_4[b]	Sulfur		Difference
		THQ	Gravimetric	
	Cc.	%	%	%
		Tread stock		
1	12.70	2.63	2.61	0.02
2	13.20	2.41	2.43	0.02
3	14.80	1.71	1.67	0.04
		Ply stock		
1	12.90	2.54	2.52	0.02
2	14.00	2.06	2.04	0.02
3	13.90	2.10	2.07	0.03
4	12.35	2.78	2.80	0.02
		Extra tread ply		
1	12.60	2.68	2.63	0.05
2	14.40	1.88	1.87	0.01
3	13.60	2.24	2.22	0.02
4	14.20	1.97	1.98	0.01
		Mechanical goods stock		
1	12.35	2.78	2.74	0.04
2	8.90	4.30	4.25	0.05
3	5.38	5.85	5.80	0.05
4	14.65	1.77	1.73	0.04

[a] Analyses were performed in laboratories of Firestone Tire & Rubber Co.
[b] Na_2SO_4, 1 cc. = 1.100 mg. of sulfur. $BaCl_2$, 1 cc. = 4.110 mg. of sulfur.

average of 0.03 per cent of gravimetric analysis in fifteen determinations, the greatest difference between the two methods being 0.05 per cent.

Prior to the establishment of the method as presented, a direct titration of sulfate was attempted by employing tetrahydroxyquinone after the removal of the zinc, iron, etc., which offered interference in the quantities present in these samples. Exhaustive work proved that the removal of the zinc, iron, etc., by precipitation through the addition of potassium hydroxide, potassium carbonate, trisodium phosphate, and potassium ferrocyanide over various pH ranges from 4 to 8 removed a high percentage of sulfate, probably by occlusion and the formation of the insoluble sulfate complexes. All results were low, in some cases to the extent of 50 per cent, and therefore the direct titration of sulfate was discarded and the back-titration was investigated and found to be successful.

Conclusion

The determination of sulfur in rubber by the precipitation of oxidized sulfur as sulfate by means of barium chloride and the back-titration of the excess barium has been shown to be as accurate as the gravimetric procedure in solutions of these characteristics for the determination of sulfur, with the use of tetrahydroxyquinone as the indicator. The method is very rapid compared to the gravimetric procedure and after oxidation to the sulfate form in solution, a determination can be made on a single sample in 20 to 30 minutes; with groups of analyses this time can be greatly reduced when compared to the time required for a single analysis.

Acknowledgment

This problem was studied as a joint project by the Firestone Tire & Rubber Company, Akron, Ohio, and the W. H. & L. D. Betz laboratories, Philadelphia, Pa., and the aid of both companies is gratefully acknowledged.

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Determination of Carotene in Forage

A Modification of the Guilbert Method

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GUILBERT (*1*) has reported a method for the determination of carotene in forage which, it is claimed, gives consistently reproducible results, comparable to those obtained by the acetone-ether extraction method of Schertz (*3*). The main features of the Guilbert method are as follows:

> The sample is digested for 0.5 hour with a saturated solution of potassium hydroxide in ethyl alcohol. Ethyl ether is added to the digestion mixture and the chlorophyllins and flavones are separated by washing with water. The ether solution containing carotene and xanthophyll is evaporated on a steam or water bath to remove the ether. The residue is extracted with petroleum ether, and xanthophyll is removed by the usual method with 90 per cent methyl alcohol. The petroleum ether solution, containing the carotene, is brought to volume and compared in a colorimeter against Sprague's (*4*) dye standard.

In a number of preliminary determinations in this laboratory on commercially dehydrated alfalfa meal using the Guilbert method, consistently reproducible results were obtained only when special precautions were taken. It was found necessary to purify the ether shortly before using in order to remove ether oxides. To avoid losses of carotene during evaporation of the ether from the carotene-xanthophyll solution, it was found advisable to remove the ether by vacuum distillation, or distillation with a stream of nitrogen at a temperature of less than 40° C.

During the past year a modification of the Guilbert method has been used in the authors' laboratories which is considerably shorter, eliminates several possibilities of carotene loss in manipulation, and gives results which are readily reproducible. The original ether extraction of the Guilbert method has been eliminated entirely. Instead, petroleum ether (b. p. 40–60°) is used. This obviates the necessity of carrying on a single solvent evaporation during the course of the determination, and excludes the possibility of carotene decomposition which might occur during the ether evaporation required in the original method. The method is considerably shortened, inasmuch as the chlorophyllins, flavones, alkali, and xanthophyll can be removed directly from the petroleum ether exactly as Guilbert describes their removal from ether and petroleum ether, respectively.

The method has been further improved by the use of spectrophotometric methods in the determination of carotene concentration. For each determination optical density measurements are made at wave lengths 4550, 4700, and 4800 Å. Using the absorption coefficients calculated for β-carotene in petroleum ether at these wave lengths, the carotene concentration is determined at each wave length from the equation $c = D/kb$, where b is the thickness in centimeters of the layer of solution, c is the concentration in grams per liter of the carotene, D is the optical density (read directly from the spectrophotometer), and k is the extinction coefficient (frequently designated as the specific transmissive index or absorption index). The extinction coefficients for β-carotene in various solvents are recorded in Table I.

The carotene concentration obtained should be identical for each of the three wave lengths. Thus, for each analysis, the purity of the carotene in solution is definitely established and the complete removal of other pigments ensured. When variations in the concentration calculated for the various wave lengths are within the normal limits of error for spectro-

Table I. Extinction Coefficients for β-Carotene

Wave Length	80% Ethyl Alcohol, 20% Ethyl Ether, Miller (*2*)	Petroleum Ether (b. p. 40–60°), Seibert[a]	Skellysolve B (b. p. 60–70°), Authors[b]
4500	247	243	238
4550	243	231	227
4700	210	207	200
4800	221	212	212

[a] These coefficients were obtained from H. F. Seibert of the S. M. A. Corporation, Cleveland, Ohio, and checked by the authors.

[b] Skellysolve B, a special commercial grade of petroleum ether, can be successfully substituted for petroleum ether (b. p. 40–60°) in the modified method described.

photometric measurements, the average of the three values is taken as the final figure for the carotene concentration.

A series of determinations on commercially dehydrated alfalfa meal by the original Guilbert method, but using specially purified ether and carrying out all solvent distillations with a stream of nitrogen at less than 40°, gave an average of 98 p. p. m. of carotene. The modified method gave 94 p. p. m. Similarly a sample of feed gave 13.7 p. p. m. by the Guilbert, and 14.0 p. p. m. by the modified method.

Summary

The Guilbert method for the determination of carotene in forage has been modified. Petroleum ether (b. p. 40–60°) has been substituted for diethyl ether in the extraction of the digested sample.

Spectrophotometric methods have been used in the determination of carotene concentration.

Specific absorption coefficients for β-carotene in a number of solvents are reported.

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Determination of Sodium

Removal of Phosphorus before Determining Sodium by the Uranyl Zinc Acetate Method

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BARBER and Kolthoff (*1*), in 1928, published their method for the rapid and direct determination of sodium in which the sodium is precipitated by means of uranyl zinc acetate. Later they (*2*) indicated that phosphates and arsenates interfere in the determination and recommended removal with magnesia mixture. Butler and Tuthill (*4*) removed phosphates from urine samples by the addition of powdered calcium hydroxide. Bougault and Cattelain (*3*) used lead acetate and removed the excess lead with magnesium sulfate. Peters and Van Slyke (*5*) precipitated with barium chloride and removed the excess barium with ammonium carbonate. All these methods introduce into the sodium solution a considerable concentration of salts. Before adding the uranyl zinc acetate it is necessary to reduce the volume of sodium solution to 1 or 2 ml. It was the experience of the authors that, when the above methods for the removal of phosphorus were used, crystallization of the excess salts began at a volume considerably above 2 ml., so that the sodium solution could not be reduced to the proper volume.

In a search for a reagent for the removal of the phosphate ion preliminary results indicated that powdered zinc carbonate could be used successfully. In order to test the efficiency of this reagent, it was tried on combined solutions of pure salts having the following composition:

2.5 mg. of potassium per ml. as KCl and KH_2PO_4
2.0 mg. of calcium per ml. as $CaCO_3$
1.5 mg. of phosphorus per ml. as KH_2PO_4
0.2 mg. of magnesium per ml. as $MgSO_4 \cdot 7H_2O$
0.05 to 1.0 mg. of sodium per ml. as NaCl

With the exception of sodium, this is the approximate ratio of the occurrence of these elements in the ash of milk. Ten milliliters of each solution were used for a determination. The results, shown in Table I, indicate that the method is satisfactory so long as the amount of sodium in the sample is not too great. Past workers have given 8 mg. as the upper limit for the amount of sodium to be used in a determination.

Salt solutions similar to the ones above but containing sodium in 0.05-mg. increments beginning at 5.00 mg. per determination were made. Results on these solutions were compared with results on solutions containing only sodium. The comparisons, shown in Table II, indicate that the method is as accurate for determining sodium after the removal of the phosphate ion with zinc carbonate as it is when used on solutions containing only sodium.

The method was applied to the determination of sodium in the ash of cow milk. To some of the samples of milk ash there were added known quantities of sodium before removing the phosphorus. The accuracy of the entire procedure in recovering this sodium is shown by the results in Table III.

In order to observe the influence of various elements and certain other ions on the method, solutions were made containing these ions along with sodium and phosphorus. They were then subjected to the procedure for the removal of phosphorus and the determination of sodium. The results are reported in Table IV.

The $C_2O_4^{--}$ ion was the only anion studied which caused an appreciable error in the determination. In this case a slight precipitate was formed after filtration of the zinc carbonate and zinc phosphate. Although this precipitate was dissolved on the addition of a drop of acetic acid, it

Table I. Determination of Sodium

Sodium in Sample	Sodium Determined: Duplicates		Average	Difference
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
10.0	9.82	9.89	9.86	−0.14
5.0	5.00	5.06	5.03	+0.03
2.0	2.06	1.99	2.03	+0.03
1.0	1.02	1.01	1.02	+0.02
0.5	0.53	0.52	0.53	+0.03

Table II. Comparison of Results on Solutions of Identical Sodium Concentration

Sodium in Sample	Sodium Determined: Solutions Containing only Sodium	Difference	Solutions Containing Na, Ca, Mg, K, P	Difference
Mg.	*Mg.*		*Mg.*	
5.00	5.01	+0.01	5.03	+0.03
5.05	5.08	+0.03	5.06	+0.01
5.10	5.11	+0.01	5.10	...
5.15	5.13	−0.02	5.17	+0.02
5.20	5.19	−0.01	5.20	...

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Table III. Recovery of Sodium Added to Samples of Milk Ash

Sample No.	Sodium Determined Milk ash	 Milk ash + Na	Sodium Added	Sodium Recovered	
	Mg.	*Mg.*	*Mg.*	*Mg.*	%
A 7	3.97	5.17	1.20	1.20	100.0
A 18	4.98	7.42	2.40	2.44	101.7
A 22	1.79	2.99	1.20	1.20	100.0
B 1	6.69	9.04	2.40	2.35	97.1
B 12	7.82	10.22	2.40	2.40	100.0
B 14	7.60	10.09	2.40	2.49	103.7
B 25	6.14	8.63	2.40	2.49	103.7
				Av.	100.9

Table IV. Influence of Various Ions on the Method

Element Present[a]	Sodium in Sample	Sodium Determined	Difference
	Mg.	*Mg.*	*Mg.*
As as KH_2AsO_4	5.00	5.02	+0.02
C_2O_4 as $K_2C_2O_4$	5.00	5.08	+0.08
Mo as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	5.00	5.02	+0.02
Cr as $K_2Cr_2O_7$	5.00	5.01	+0.01
Al as $AlCl_3 \cdot 6H_2O$	5.00	4.74	−0.26
Ba as $BaCl_2 \cdot 2H_2O$	5.00	Does not filter clear	
Cd as $CdCl_2 \cdot 2H_2O$	5.00	Does not filter clear	
Cr as $CrCl_3$	5.00	Does not filter clear	
Co as $Co(NO_3)_2 \cdot 6H_2O$	5.00	Does not filter clear	
Cu as $Cu(NO_3)_2 \cdot 3H_2O$	5.00	Does not filter clear	
Fe as $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$	5.00	4.81	−0.19
Pb as $Pb(C_2H_3O_2)_2 \cdot 3H_2O$	5.00	4.97	−0.03
Mn as $MnSO_4 \cdot 4H_2O$	5.00	5.04	+0.04
Ni as $NiSO_4 \cdot 6H_2O$	5.00	5.02	+0.02

[a] In addition to Na and P, 5 mg. of each element in sample.

apparently reformed when the sodium precipitating reagent was added.

The filtrates from the solutions containing Ba^{++}, Cd^{++}, Cr^{++}, Co^{++}, and Cu^{++} came through the paper definitely cloudy. The cloudiness disappeared when a drop of acetic acid was added, but a very copious extraneous precipitate formed with the addition of uranyl zinc acetate which was almost impossible to filter through the sintered-glass crucibles. The low results when Al^{+++} and Fe^{++} were present may be accounted for on the basis of the gelatinous precipitates which form with these elements and which undoubtedly adsorbed some of the sodium. The filtrate in these two cases came through very clear. Pb^{++}, Mn^{++}, and Ni^{++} caused no interference with the determinations. Zinc carbonate is apparently as satisfactory for the removal of the orthoarsenate ion from solution as it is for the orthophosphate ion.

Experimental data indicated that complete precipitation of the phosphate ion occurred when the solution was allowed to stand at least 6 hours at room temperature. When 20 ml. of water were added, the beaker was covered with a watch glass, and the mixture slowly boiled until the volume was reduced to about 10 ml., the results on sodium were slightly less than 1 per cent low. When the mixture was shaken frequently with warming for 1 hour, the results were slightly less than 1 per cent high. Shaking in the same way at room temperature gave results slightly over 2 per cent high. Either boiling the solution as above or shaking and warming for at least 1 hour may be substituted for standing at room temperature for 6 hours without seriously affecting the results of the determination.

The method was applied to a solution of pure $NaNH_4HPO_4 \cdot 4H_2O$ containing 0.5 mg. of sodium per ml. An aliquot containing 5.0 mg. of sodium was taken for a determination which showed 5.22 mg. of sodium. When another aliquot of this solution was first digested with nitric acid, the nitric acid evaporated, and the phosphate ion precipitated in the usual way, 5.01 mg. of sodium were found in the solution. The filtrate from the zinc carbonate precipitation came through perfectly clear.

As a result of their experience, the authors propose the following procedure for the removal of the phosphate ion from a solution to be used for the determination of sodium by the Barber and Kolthoff method:

Take an aliquot of the solution containing 2 to 8 mg. of sodium in a small beaker (50 or 100 ml.). The volume of solution taken should be 10 to 15 ml. Add an excess of powdered zinc carbonate of reagent grade, cover the beaker, and let stand at room temperature at least 6 hours or overnight. If the solution contains too much hydrochloric acid there is likely to be rather violent effervescence which may result in the loss of material; also, too much zinc chloride will go into solution, which will cause difficulty later when the volume of solution is being reduced to the proper amount. If too much hydrochloric acid is present, evaporate to dryness, and add 10 ml. of water and just enough hydrochloric acid to take all the salts into solution. Then add the zinc carbonate. Filter through quantitative paper (9 cm.) and wash thoroughly 5 or 6 times with cold water. Catch the filtrate in a 50-ml. beaker, as this is a satisfactory size in which to make the precipitation of sodium. Carry a blank through the entire procedure. If a slight precipitate forms when the solution is being evaporated, a drop of acetic acid usually will redissolve it and does not interfere with the final determination of sodium.

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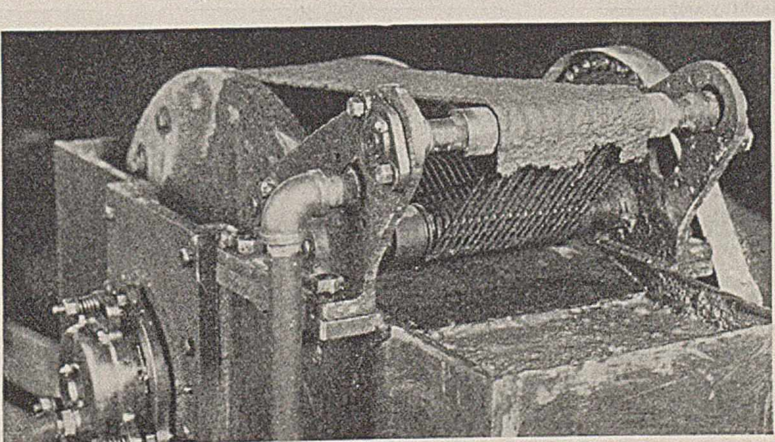

Courtesy, Goslin-Birmingham Manufacturing Company

Determination of Small Quantities of 2-Naphthylamine, Aniline, and *o*-Toluidine in Certain Food Dyes

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IN THE manufacture of the food dyes Yellow AB (benzeneazo-2-naphthylamine) and Yellow OB (tolueneazo-2-naphthylamine), it is possible that small quantities of the intermediates used may be present in the finished product. Since these intermediates, 2-naphthylamine, aniline, and *o*-toluidine, are more or less toxic, an accurate and rapid method for their estimation is needed.

The methods based upon diazotization and coupling of the intermediates to produce colored compounds were not investigated, as the method recorded here seemed more convenient as a routine method.

It has been found possible, by a further extension and modification of the classical hypochlorite method for estimating aniline, to determine 2-naphthylamine, as well as *o*-toluidine or aniline, in the same solution.

According to Elvove (*1*), the color produced by aniline in the presence of calcium hypochlorite is intensified by the addition of alkali. Upon this fact is based his colorimetric method for the determination of small quantities of aniline. The authors have observed that *o*-toluidine also produces a yellow color in alkaline solution and that either of these intermediates, whether present in large or small amounts, produces only a faint trace of color in acid solution. They have also found that 2-naphthylamine produces a yellow color in acid solution which may also be quantitatively estimated. This intermediate, if not present in amounts exceeding 0.5 mg. in a volume of 30 cc., produces only a faint trace of color in alkaline solution. The effect of these interfering traces of color, that produced by aniline or *o*-toluidine in acid solution and by 2-naphthylamine in alkaline solution, may be neutralized by using standards containing approximately the same amounts of each amino compound as the unknown sample. On these observations is based the method recorded here for the quantitative evaluation of aniline or *o*-toluidine and 2-naphthylamine in the same solution.

The amount of calcium hypochlorite used should be sufficient, but not excessive, as too large an amount tends to destroy the color. About 3 drops, or 0.1 to 0.2 cc. of the freshly made solution, containing about 1 per cent of available chlorine, were found suitable.

The amount of alkali added to destroy the color due to 2-naphthylamine and bring out the color due to aniline or *o*-toluidine was found to be a controlling factor in the time of appearance of the maximum color. About 1.5 cc. of 10 per cent sodium hydroxide in excess of that necessary to neutralize the acid present were found to produce the maximum color in a convenient period of time, such as 5 minutes.

A much larger excess of alkali brings out the color at once, but the color also tends to fade sooner. In the presence of a very slight excess, the maximum color may not appear at all.

It was found possible to detect 0.0075 mg. in 30 cc. or 1 part in 4 million of 2-naphthylamine or *o*-toluidine, and 0.005 mg. or 1 part in 6 million of aniline.

Reagents

A standard solution containing 50 p. p. m. of 2-naphthylamine is prepared as follows:

Dissolve 0.25 gram of the pure compound in 100 cc. of benzene in a separatory funnel. Extract the amino compound by shaking with four 100-cc. portions of hydrochloric acid (1 to 3). Then wash once with 100 cc. of water and dilute the combined extracts and the wash water to 1 liter in a volumetric flask, adding 150 cc. of hydrochloric acid to make the acid concentration 1 to 3. Dilute 100 cc. of this solution to 500 cc.

A standard solution containing 50 p. p. m. of aniline or *o*-toluidine is prepared by dissolving the pure amino compound in hydrochloric acid (1 to 19).

A calcium hypochlorite solution containing approximately 1 per cent of available chlorine is prepared by shaking 5 grams of the fresh $Ca(OCl)_2$ with 25 cc. of distilled water at intervals for about 10 minutes, filtering, and washing with 50 cc. of water.

Method

Dissolve 10 grams of dye in 100 cc. of benzene. Extract the intermediates by shaking with hydrochloric acid (1 to 19) heated

TABLE I. ANALYSIS OF SAMPLES CONTAINING KNOWN AMOUNTS OF INTERMEDIATES

	2-Naphthylamine			Aniline			*o*-Toluidine		
No.	Present	Found	Difference	Present	Found	Difference	Present	Found	Difference
	%	%	%	%	%	%	%	%	%
1[a]	0.009	0.010	+0.001	...	...	...	0.011	0.012	+0.001
2[a]	0.010	0.011	+0.001	...	...	...	0.012	0.012	0
3	0.0135	0.012	−0.0015	...	...	...	0.0085	0.009	+0.0005
4	0.06	0.06	0	0.02	0.02	0	...	...	...
5	0.017	0.017	0	0.04	0.04	0	...	...	...
6	0.015	0.015	0	0.0425	0.04	−0.0025	...	...	...
7	0.045	0.044	−0.001	0.008	0.007	−0.001	...	...	...
8	0.09	0.09	0	0.01	0.01	0	...	...	...
9	0.01	0.01	0	0.05	0.048	−0.002	...	...	...
10	Trace	0.001 Trace	...	Trace	0.0006	...	...	...	...
11	0.04	0.04	0	0.04	0.037	0.003	...	...	...
12	0.076	0.08	+0.004	...	...	...	0.012	0.011	−0.001
13	0.10	0.095	−0.005	...	...	...	0.001	Trace	...
14[a]	0.04	0.04	0	...	...	...	0.04	0.04	0
15[a]	0.046	0.05	+0.004	...	...	...	0.046	0.05	+0.004
16[a]	0.010	0.011	+0.001	...	...	...	0.01	0.01	0
17	0.009	0.010	+0.001	...	...	...	0.009	0.009	0
18	0.0115	0.011[a] 0.012	±0.0005	...	...	...	0.0095	0.009[a] 0.010	±0.0005

[a] Amounts added known to analyst.

to 60° C. Shake for 2 minutes with one 50-cc. portion and two 25-cc. portions, successively, then with 50 cc. of distilled water, draining the extracts into another funnel. Wash the combined extracts with 25-cc. portions of benzene until the benzene is colorless. Each benzene portion should be washed with a few cubic centimeters of water to remove acid extract adhering to the side of the funnel, and this wash water should be added to the main acid extract. Dilute the washed acid extract to 200 cc. in a volumetric flask.

Make a preliminary estimation of the per cent of each amino compound present, as follows:

Pipet 10 cc. of the acid extract into a Nessler or suitable test tube and dilute to 30 cc. with distilled water. Prepare a series of standards containing known amounts of the amino compounds to be estimated, and dilute to 30 cc. Add to these and the tube containing the unknown, 0.1 to 0.2 cc. of calcium hypochlorite solution, mix, and compare at once, estimating approximately the amount of 2-naphthylamine present. Then add to each tube about 1.5 cc. of 10 per cent of sodium hydroxide in excess of that required to neutralize the acid in each tube. Mix and let stand 4 or 5 minutes. By comparing the tubes, estimate the approximate amount of aniline or *o*-toluidine present. Knowing the approximate amounts of each intermediate present, make a more accurate estimation as follows:

Take another 10-cc. portion of the acid extract and dilute to 30 cc. Prepare standards containing known amounts of the two intermediates, approximating those present in the unknown as just determined. Add to each tube calcium hypochlorite as before, mix, and compare at once. Determine the per cent of 2-naphthylamine. Then add to each tube 1.5 cc. of 10 per cent sodium hydroxide in excess of that necessary to neutralize the acid present, mix, and let stand 4 to 5 minutes. Estimate the per cent of aniline or *o*-toluidine present. Using 10 cc. of the acid extract, 1 cc. of the standard is equivalent to 0.01 per cent of amino compound. (If the quantity of amino compound present exceeds 0.02 per cent, a smaller volume of the acid extract should be used.)

Application of Method

To test the accuracy of this method, known amounts of the amino compound were added to a benzene solution of 10 grams of Yellow OB from which any amino compound originally present had been previously removed by repeated extraction with warm, dilute hydrochloric acid (1 to 19). The results obtained are shown in Table I. The amounts added were not known to the analyst except as noted.

The maximum error of 12 per cent is not considered excessive in view of the small quantities determined.

The 2-naphthylamine and *o*-toluidine content of Nos. 14 and 15 could easily be distinguished. Referring to Nos. 16, 17, and 18, it was possible to distinguish the 2-naphthylamine content of these and the *o*-toluidine content of No. 16, as compared with the other two, but Nos. 17 and 18 could not be differentiated.

Summary

A colorimetric method is described for determining the free intermediates in the oil-soluble food dyes, Yellow AB and Yellow OB. The method is based upon the observation that in the presence of calcium hypochlorite 2-naphthylamine produces a yellow color in acid solution, and aniline or *o*-toluidine produces a yellow color in alkaline solution. The results obtained on samples containing known amounts of the intermediates showed that the maximum error was 12 per cent.

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Volumetric Determination of Bromide

After Oxidation to Bromate in the Presence of Much Chloride

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IN THE course of certain experimental work, it became necessary to make several hundred bromide determinations in the presence of much chloride. After a critical and experimental survey (for a review see Zorkin, *6*), the method originating with van der Meulen (*2*) was selected, in which the bromide is oxidized to bromate with a solution of hypochlorite and the bromate is determined iodometrically after removal of the excess hypochlorite. The procedure was modified by D'Ans and Höfer (*1*), and by Szabo (*4*). The directions given by D'Ans and Höfer are as follows:

> The sample in a volume of 35 ml. is treated with 3 grams of sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), 10 ml. of 0.3 *N* sodium hypochlorite, and 10 grams of sodium chloride and heated slowly (5 to 10 minutes) to 90° C.; 2 ml. of a half saturated solution of sodium formate are added, and the solution is cooled. Then, 0.3 gram of potassium iodide and 25 ml. of 2 *N* hydrochloric acid are added and the solution is allowed to stand a short time and titrated with 0.1 *N* thiosulfate.

The authors believe that this procedure is preferable to that of van der Meulen, which gave good results but was difficult to use because of the uncertainty as to the time of complete removal of hydrogen peroxide (used by van der Meulen instead of formate to reduce the excess of hypochlorite) by boiling in the presence of nickel salts or osmium tetroxide to decompose the excess peroxide. It is likewise more rapid and convenient to use than that of Szabo, which involves evaporation to dryness with hypochlorite (spattering) and an empirical correction depending upon the amount of bromide found. Since D'Ans and Höfer give rather meager data in support of their method, the authors wish to describe briefly the results it has given in their hands and a slight modification of their procedure. In the following experiments the above procedure was followed except that 1 *N* hypochlorite was used and 5 ml. of a solution containing 0.5 gram of sodium formate per ml. were substituted for the half-saturated solution of the same salt. The waiting period between addition of acid and the titration was eliminated by the addition of one drop of 0.5 *N* ammonium molybdate as a catalyst.

Materials Used

Sodium Hypochlorite Solution. The *N* hypochlorite solution was prepared according to van der Meulen (*2*) by dissolving 71 grams of chlorine in 1500 ml. of water containing 88 grams of sodium hydroxide. This was diluted to 2 liters to give a solution *N* in hypochlorite and 0.1 *N* in hydroxide.

Potassium Bromide. Chloride-free bromide was prepared by thermal decomposition of pure potassium bromate. An approximately 0.01 *M* solution was prepared. It was standardized gravimetrically, and also by potentiometric titration with pure silver nitrate. The molarities found were 0.00997 and 0.00996, respectively.

Other chemicals used were of c. p. grade.

Experimental

In the first place it was ascertained that formate does not reduce bromate on boiling under the experimental conditions.

No reduction was found upon boiling a standard bromate solution in the presence of the phosphate and formate (no chloride or hypochlorite added) for various periods of time.

D'Ans and Höfer do not report experiments concerning the amounts of phosphate and hypochlorite necessary under various conditions. In Table I are reported the results of experiments carried out according to the procedure given above but with varying amounts of these reagents. It may be inferred that 1 gram of sodium dihydrogen phosphate and 5 ml. of *N* hypochlorite are sufficient for the quantitative oxidation of 10 ml. of neutral 0.01 *M* bromide.

Table I. Effect of Amounts of Phosphate and Hypochlorite

0.00997 *M* KBr	Phosphate	*N* NaOCl	0.02089 *N* $Na_2S_2O_3$	$Na_2S_2O_3$[a] after Correcting for Blank	Molarity of KBr Found	Error
Ml.	*Grams*	*Ml.*	*Ml.*	*Ml.*		%
10.02	3	10	29.20	28.68	0.00997	0.0
			29.21	28.69	0.00997	0.0
			29.20	28.68	0.00997	0.0
			28.97	28.45	0.00989	− 0.8
5.02	3	10	14.88	14.36	0.00996	− 0.1
			14.93	14.41	0.01000	+ 0.3
10.02	1	5	28.92	28.65	0.00996	− 0.1
	2	5	28.90	28.63	0.00995	− 0.2
	3	5	28.75	28.48	0.00990	− 0.7
10.02	1	1	13.27	13.12	0.00456	−54
	2	1	12.15	12.00	0.00417	−56
	3	1	9.77	9.62	0.00334	−66
5.02	1	5	14.56	14.29	0.00991	− 0.6
	1	5	14.58	14.31	0.00992	− 0.5

[a] The total titration volume must be corrected by subtracting a blank run on the reagents. In the above cases it amounted to 0.52 ml. for 3 grams of phosphate, 10 ml. of NaOCl; 0.27 for 1 gram of phosphate, 5 ml. of NaOCl; and 0.15 ml. for 1 gram of phosphate, 1 ml. of NaOCl.

The addition of large amounts of sodium chloride, specified by van der Meulen (*2*), was found to be disadvantageous in the determination of very small amounts of bromide. Even the c. p. grades of sodium chloride contain bromide, necessitating the application of a relatively large blank. Moreover, the high salt concentration makes the starch-iodine end point much less distinct, especially when thiosulfate as dilute as 0.001 *N* is used. The following experiments were carried out with 0.001 *M* bromide by the described procedure using 1 gram of phosphate and 5 ml. of *N* hypochlorite, but without the addition of sodium chloride.

Table II. Determination of 0.001 *M* Bromide without Addition of Sodium Chloride

0.000997 *M* KBr Taken	0.01090 *N* Thiosulfate Used	Thiosulfate after Correcting for Blank	Molarity of KBr Found	Error
Ml.	*Ml.*	*Ml.*		%
10.02	6.23	5.46	0.000990	−0.7
	6.27	5.50	0.000997	0.0
25.00	14.41	13.64	0.000991	−0.6
	14.50	13.73	0.000998	+0.1
50.00	26.62	25.85	0.000939	−5.8
	27.18	26.41	0.000960	−3.7

Apparently, the addition of sodium chloride can be omitted in the determination of 25 ml. of 0.001 *M* bromide or less; for larger amounts its presence is necessary, as shown by van der Meulen.

The following procedure has yielded good results:

To a suitable (25 ml. or less) volume of the neutral bromide solution add 1 gram of sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$), 10 grams of sodium chloride, and 5 ml. of *N* sodium hypochlorite, heat just to boiling and add 5 ml. of sodium formate solution (= 2.5 grams of the solid). After cooling, dilute to 150 ml. and add 1.0 gram of potassium iodide, 25 ml. of 6 *N* sulfuric acid, and 1 drop of 0.5 *N* ammonium molybdate. Titrate immediately with standard thiosulfate, adding starch solution just before the end point. A blank should be run under identical conditions, substituting an equal volume of water for the bromide solution. The blank is subtracted from the volume of thiosulfate required in the test.

The addition of 10 grams of sodium chloride may be omitted in the test and in the blank when the sample contains less than 25 micromoles of bromide.

The procedure was applied to the determination of bromide in Mallinckrodt's reagent sodium chloride. As will be seen from Table III, the method gives quite reproducible results.

Table III. Bromide Determination in c. p. Sodium Chloride

Sodium chloride taken, grams	10	20
0.01013 *N* thiosulfate (corrected for blank[a]), ml.	1.65, 1.66	3.35, 3.36

[a] Blank = 0.82 ml. of 0.01013 *N* thiosulfate.

The figures in Table III correspond to a sodium bromide content of 0.0029 per cent. According to the colorimetric procedure of Stenger and Kolthoff (*3*) a sodium bromide content of 0.0032 per cent was found by Stenger.

Several hundred analyses have been made (*5*) using the modified procedure with satisfactory results. The procedure was also applied to the analysis of mixtures of silver chloride and bromide. The precipitate was digested with 10 ml. of a saturated solution of sodium chloride for a few hours, after which the modified procedure was used. The results agreed within 0.5 per cent with the theoretical values.

Attempts were made to apply the method in the presence of easily brominated organic matter. However, the presence of appreciable amounts of such substances as dyes or gelatin gave erratic results. The dyes, apparently, became brominated, causing low results. Gelatin gave a yellow gelatinous precipitate when hypochlorite was added, which apparently was not reduced by formate, but reacted with iodide and caused high results. Very small amounts of indicators, added in a neutralization, for instance, were harmless. In order to determine bromide in the presence of relatively large amounts of dye or gelatin, the following procedure was successfully used: The sample was evaporated to dryness in a nickel crucible and fused at a low temperature with sodium peroxide. The residue was taken up in hot water and filtered. The filtrate was evaporated to a small volume and neutralized with hydrochloric acid to methyl red, and the modified procedure applied. The results of experiments in which known amounts of bromide were added to gelatin or wool violet agreed within 0.5 to 1 per cent with the theoretical values.

Summary

The modified procedure of van der Meulen and D'Ans and Höfer given in this paper, in which bromide is oxidized to bromate and the latter determined iodometrically, gives accurate, precise, and rapid results. With 10 ml. or more of 0.01 *M* bromide the accuracy was found to be within 0.3 per cent, and with 10 ml. of 0.001 *M* bromide within 1 per cent. The procedure is useful for the determination of bromide in commercial chlorides.

Directions are given for the determination of bromide in mixed silver chloride and bromide, and in the presence of dyes and gelatin.

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Determination of Sulfate, Calcium, and Magnesium in Salt Samples of High Purity

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TO THE authors' knowledge the only published methods for salt analysis are those outlined by the Association of Official Agricultural Chemists (*1*). These methods were presumably designed for the analysis of salt of "average" purity, and experience has shown that when they are applied directly to the analysis of salt of high purity (above 99.90 per cent sodium chloride), dependable results are not obtained. The procedures used in this laboratory, which are presented below, were designed primarily for the analysis of such high-purity salt and have recently been subjected to rigorous investigation and further refinement.

The methods adopted are modifications of the standard procedures for the gravimetric determination of sulfate as barium sulfate, the volumetric determination of calcium by means of ammonium oxalate and potassium permanganate, and the volumetric determination of magnesium by means of 8-hydroxyquinoline (*4*). The modifications have been developed for the purpose of reducing errors to a practical minimum. It was found, however, that in maintaining sufficient speed and facility, the errors involved for certain ranges of composition could not be entirely eliminated. The procedures were therefore "calibrated" by applying them to the analysis of samples covering a range of known compositions.

In the procedures given below the absence of acid-insoluble material and of trivalent metals has been assumed. In case their presence is suspected, standard procedures should be followed for their removal.

Sulfate

SOLUTIONS REQUIRED. Barium chloride dihydrate solution (10 per cent), 1 per cent silver nitrate test solution, and methyl orange indicator solution.

PROCEDURE. Dissolve 50 grams of the salt to be analyzed in 250 cc. of distilled water, add 2 drops of methyl orange indicator, and add hydrochloric acid a drop at a time until the solution is pink colored; then add 1 cc. of acid in excess. Heat the solution almost to boiling and add, all at one time while stirring, 10 cc. of the barium chloride solution. Cover the solution with a watch glass and digest at a temperature slightly below the boiling point until the supernatant liquid is clear. This digestion usually requires about 1 hour.

Allow the solution to cool to about 50° C. and filter through a Whatman No. 42 (or equivalent) filter paper or a well-prepared Gooch crucible. Transfer the precipitate completely to the filter paper by scrubbing the inside of the beaker with a rubber policeman, and wash the precipitate on the filter with distilled water until no cloudiness is produced when the filtrate is tested with the silver nitrate solution. When the washing is complete, transfer the filter paper and its contents to a crucible which has been ignited to constant weight, warm until the paper is dry, and then increase the temperature until the paper is burned and the ash is white. Then heat the crucible in the flame of a Bunsen burner or the upper part of the flame of a Meker burner for about 15 minutes, cool in a desiccator, and weigh as barium sulfate.

Weight of barium sulfate × 1.166 = per cent of sulfate as calcium sulfate. When necessary, apply the correction indicated in Figure 1.

Calcium

SOLUTIONS REQUIRED. Ammonium oxalate solution (4 per cent), saturated calcium oxalate solution, 0.05 *N* potassium permanganate solution, and phenolphthalein indicator solution.

PROCEDURE. Dissolve 50 grams of the salt to be analyzed in 225 cc. of distilled water in a 400-cc. beaker (the Griffin or low form is preferable). Add 2 drops of phenolphthalein indicator and make the solution alkaline, if not already so, by the addition of 1 to 5 ammonium hydroxide solution. Heat the solution almost to boiling and add, while stirring, 25 cc. of the ammonium oxalate solution. Stir for about 0.5 minute more to obtain complete mixing. Cover the beaker with a watch glass and digest the solution at a temperature slightly below the boiling point for 1 hour; then cool rapidly to about 25° C.

Within 3 hours after the precipitation, filter through a Whatman No. 40 (or equivalent) filter paper. Wash the precipitate on the filter paper with 150 cc. of cold 0.2 per cent ammonium oxalate solution by placing the wash liquid 30 or 40 cc. at a time in the beaker in which the precipitation took place, rinsing off the inside of the beaker, and then passing the liquid through the filter paper. (It is not necessary to remove the precipitate completely from the beaker, as this vessel will be used for the subsequent titration.) Reserve the filtrate and washings obtained thus far for the determination of magnesium.

In order to remove the ammonium oxalate remaining in the beaker and on the precipitate and filter paper, wash as above described with 75 cc. of the saturated calcium oxalate solution. Discard the filtrate from this washing.

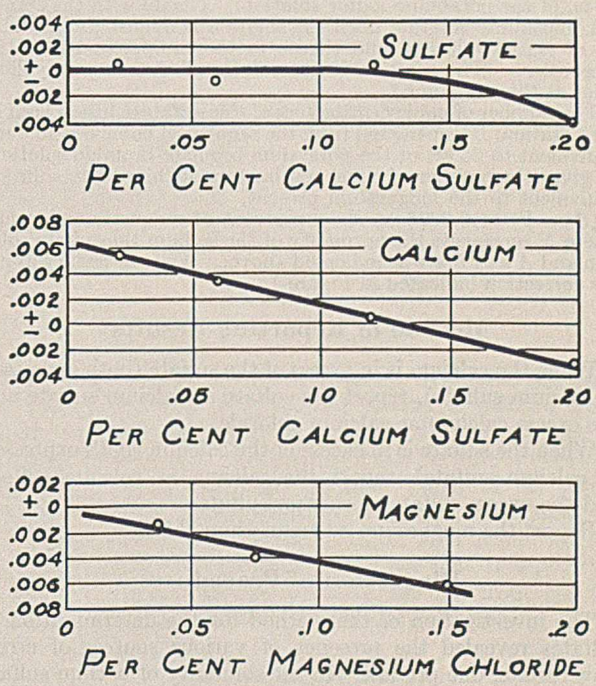

FIGURE 1. CORRECTION CURVES FOR USE WITH STANDARDIZED PROCEDURES

When the washing is completed, transfer as much as possible of the precipitate to the beaker in which the precipitation took place (the most convenient method of transferring the precipitate is to puncture the folded filter paper at its apex with a pointed glass rod, wash off the glass rod into the beaker, and then wash the precipitate down the stem of the funnel into the beaker with a small stream of water from a wash bottle), add 100 cc. of distilled water and 10 cc. of 1 to 1 sulfuric acid, heat to about 90° C., and titrate with 0.05 *N* potassium permanganate solution. When near the end point, add the filter paper and continue the titration, taking as the final end point the first pink color which persists for 0.5 minute.

Cc. of permanganate solution × normality × 0.136 = per cent calcium as calcium sulfate. When necessary, apply the correction indicated in Figure 1.

Magnesium

Solutions Required. Acetic acid solution of 8-hydroxyquinoline (2.5 per cent). Dissolve 25 grams of 8-hydroxyquinoline in 60 cc. of glacial acetic acid. When solution is complete, dilute to a volume of 1 liter with cold distilled water.

Potassium iodide solution (25 per cent).

Starch indicator solution. Dissolve 5 grams of soluble starch and 2.5 grams of salicylic acid in 1 liter of water.

Sodium thiosulfate solution (0.2 *N*).

Potassium bromate-bromide solution (0.2 *N*). Dissolve 20 grams of potassium bromide and 5.57 grams of potassium bromate in 200 cc. of water and dilute to 1 liter. The titer ratio of this solution to the sodium thiosulfate solution is obtained as follows: To 200 cc. of cool water in a 400-cc. beaker add 10 cc. of the potassium iodide solution and exactly 25 cc. of the potassium bromate-bromide solution. Add quickly, while stirring, 40 cc. of 1 to 1 hydrochloric acid and titrate with the standard sodium thiosulfate solution until nearly colorless. Add 2 cc. of the starch indicator and titrate to the disappearance of the blue color.

Procedure. The filtrate and washings retained from the calcium determination should have a volume of about 400 cc. Heat this solution to 60° or 70° C. and add 16 cc. of ammonium hydroxide (sp. gr. 0.90) and 20 cc. of the 8-hydroxyquinoline solution. Heat to boiling and set aside to cool for about 1 hour, or longer if required for the precipitate to settle.

Transfer the precipitate completely to a Whatman No. 40 (or equivalent) filter paper and wash with 200 cc. of hot 1 to 50 ammonium hydroxide solution. Dissolve the precipitate on the filter with 50 to 75 cc. of hot 1 to 10 hydrochloric acid, dilute the resulting solution to 200 cc., add 15 cc. of concentrated hydrochloric acid, and cool to 25° C. Add exactly 25 cc. of the standard potassium bromate-bromide solution and then immediately 10 cc. of the potassium iodide solution. Titrate with the standard thiosulfate solution until the solution is almost clear, add 2 cc. of starch solution, and titrate to the disappearance of the blue color. (The solution is not colorless but is a pale yellow color at the end point.)

The number of cubic centimeters of thiosulfate solution used in the titration, *B*, subtracted from the number of cubic centimeters equivalent to 25 cc. of the potassium bromate-bromide solution, *A*, gives the number of cubic centimeters of thiosulfate solution equivalent to the magnesium present.

$(A - B) \times 0.0238 \times N =$ per cent of magnesium chloride, where *N* represents the normality of the sodium thiosulfate solution and *A* and *B* are as indicated above. When necessary apply the correction indicated in Figure 1.

Method of Reporting Results

When the calcium is in excess of the sulfate (both expressed as calcium sulfate), report the sulfate as calcium sulfate and the excess calcium as calcium chloride.

When the sulfate is in excess of the calcium (both expressed as calcium sulfate), report the calcium as calcium sulfate and the excess sulfate as sodium sulfate.

Report the magnesium as magnesium chloride.

Discussion of Procedures

The investigation of the method for the determination of sulfates revealed the presence of various sources of error. Low results, due primarily to the solubility of barium sulfate in the sodium chloride solution from which it is precipitated, were found to occur when the barium chloride solution was added slowly. On the other hand, high results, due primarily to the occlusion of barium chloride by the precipitate, were found to occur when the barium chloride solution was added quickly. Also, higher results were obtained in the presence of hydrochloric acid. In designing the procedures, the influence of these factors has been fixed by specifying the volume of solution, the amount of barium chloride added, the rate of addition, etc. As indicated by the curve for sulfates in Figure 1, these factors are very well balanced for percentages of calcium sulfate below 0.12. Above this value a slight negative correction is necessary.

Preliminary experiments concerning the calcium determination indicated that negative errors result from the solubility of calcium oxalate in the sodium chloride solution. A solubility as high as 36 mg. of calcium oxalate per liter of 10 per cent sodium chloride solution at 20° has been reported by Maljaroff and Gluschakoff (*3*). On the other hand, positive errors result from the occlusion of ammonium oxalate. In developing the standard procedure for this determination, these variables have been fixed by specifying the volume of solution, the amount of ammonium oxalate added, the period of digestion, the temperature of filtration, etc. To counteract the appreciable solubility of calcium oxalate in water, the precipitate is washed with a dilute ammonium oxalate solution and the ammonium oxalate solution remaining on the filter is removed with a saturated calcium oxalate solution. Errors due to the occlusion of magnesium by the calcium oxalate were found to be negligible, which is perhaps due to the fact that the increased solubility of magnesium oxalate in the sodium chloride solution reduces its tendency to precipitate with the calcium. A second precipitation was therefore deemed unnecessary.

The correction curve for calcium (Figure 1) indicates that for low percentages the solubility factors predominate, while for high percentages they are outweighed by the occlusion factors. Clarke and Wooten (*2*) also found that incomplete recovery of small amounts of calcium was obtained in the determination of calcium in lead-calcium alloys by the oxalate-permanganate method.

Table I. Constant Error and Precision Data

No. of Determinations	Added	Mean of Values Found	Probable Error of Mean	Average Deviation from Mean
	%	%	%	%
		Sulfates (as $CaSO_4$)		
4	0.0217	0.0210	±0.0002	±0.0004
4	0.0617	0.0625	±0.0004	±0.0008
5	0.1217	0.1210	±0.0003	±0.0007
5	0.2017	0.2057	±0.0004	±0.0009
		Calcium (as $CaSO_4$)		
8	0.0200	0.0148	±0.0004	±0.0012
8	0.0600	0.0566	±0.0004	±0.0011
8	0.1200	0.1196	±0.0003	±0.0010
8	0.2000	0.2033	±0.0004	±0.0010
		Magnesium (as $MgCl_2$)		
4	0.0156	0.0169	±0.0002	±0.0004
4	0.0312	0.0355	±0.0004	±0.0007
8	0.0625	0.0686	±0.0003	±0.0009

The predominating source of error in the determination of magnesium was found to be the occlusion of 8-hydroxyquinoline. A negative correction (Figure 1) is therefore necessary for all percentages of magnesium chloride. The occlusion of 8-hydroxyquinoline has already been noted by Redmond and Bright (*4*).

Constant-Error Determinations

In order to determine the constant errors, if any, involved in the procedures presented above, determinations were made on samples of known composition which were prepared from the following materials:

C. P. (Baker's analyzed) sodium chloride was used as the basis of all "known" samples. In order to eliminate the possibility of interference from impurities in this salt, a portion of it was recrystallized three times from distilled water with about 50 per cent recovery in each crystallization. It was found that determinations made on samples prepared from the recrystallized salt were the same (within the limits of precision of the methods) as those made on samples prepared from the original material. The C. P. salt was therefore used without recrystallization in the remainder of the error determinations.

A saturated solution of C. P. (Baker's analyzed) calcium sulfate in distilled water was used as the source of sulfate. The sulfate content of this solution was determined by precipitating as barium sulfate and weighing. Independent standardizations checked to within 1 per cent error.

A solution containing about 10 mg. of C. P. (Baker's analyzed) calcium chloride per cubic centimeter was used as the source of calcium. This solution was standardized by precipitating as calcium oxalate, igniting to calcium oxide, and weighing. Independent standardizations checked to within 1 per cent error.

A solution of c. p. magnesium sulfate containing about 1.5 mg. per cc. was used as a source of magnesium. This solution was standardized by precipitating as magnesium ammonium phosphate, igniting to magnesium pyrophosphate, and weighing. Independent standardizations checked to within 1 per cent error.

The results of determinations made on the known samples are given in Table I, and the correction curves (Figure 1) were plotted from these results. The computed values for the probable errors of the means in all cases justify the constant errors indicated by Figure 1.

The error in the determination of calcium was found to be independent of the presence of magnesium up to 0.06 per cent as magnesium chloride, and the error in the determination of magnesium was found to be independent of the presence of calcium up to 0.20 per cent as calcium sulfate.

Precision of the Methods

The precision to be expected from a single determination made according to these procedures may be calculated from the indicated values (Table I) of the average deviation from the mean. The largest average deviations obtained were 0.0009, 0.0012, and 0.0009 per cent for sulfate, calcium, and magnesium, respectively. The chances are about one in a thousand that a deviation will occur which is greater than four times this average. Therefore, an almost certain precision of ±0.0048 per cent for calcium and ±0.0036 per cent for sulfate and magnesium should be obtained in any single determination.

For any series of determinations the expected precision can be determined by dividing the value given for a single determination by the square root of the number of determinations made.

TABLE II. TYPICAL ANALYSES

Determination No.	Calcium Sulfate	Calcium Chloride	Magnesium Chloride
	%	%	%
1	0.020	0.018	0.013
2	0.021	0.019	0.012
3	0.020	0.018	0.013

The results of three separate analyses of the same sample of salt are given in Table II. In this case the maximum deviation is only 0.001 per cent.

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Applications of Confined Spot Tests in Analytical Chemistry

Preliminary Paper

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THE use of paper impregnated with suitable reagents in establishing the presence of chemical constituents is probably one of the earliest developments in the art of analytical chemistry. Thus, as early as 23 to 79 A. D., Pliny records a method for detecting the presence of ferrous sulfate in verdigris using a test paper saturated with an extract from gallnuts.

> Rhodian verdigris is subject to sophistication with powdered marble, pumice, or gum. The most successful adulterant, however, is shoemaker's black (ferrous sulfate), for the others can be detected by the gritty feel when ground between the teeth. To detect adulteration with shoemaker's black, place a portion on papyrus previously steeped in extract of gallnuts which blackens immediately in the presence of the adulterant (*1*).

The diverse chemical reactions resulting in the production of characteristic color phenomena have in recent years received considerable study by Gutzeit (*4*), Feigl (*3*), Tananaeff (*7*), and numerous other workers who have developed the methods for the detection of the elements by making use of the capillary properties of filter paper in enhancing the color reaction. Systems of qualitative analysis have been developed by Engelder (*2*), van Nieuwenburg (*6*), and Hynes (*8*) embodying these tests for the final identification of the different ions. These *Tüpfelreaktionen* or spot tests are made by adding a drop of the solution of the sample to a specially retentive paper (C. S. S. 601) impregnated with a suitable reagent. The presence of a given constituent is made manifest by the formation of an irregular colored area, or a series of colored zones on the test paper.

The writer has found it advantageous to confine the spot test within the compass of a uniform area of definite cross section, with the aid of a water-repellent barrier embedded in the fibers of the paper. By means of this technic it becomes possible to execute the tests on filter paper of the usual porosity without loss in sensitivity owing to the spreading of the spot over a large surface. Also, as a result of the uniformity both in the area and tint of the spot, it is possible to approximate the concentration of the ion from the intensity of coloration produced by the drop of solution.

Embedding of Rings

A large number of substances such as waxes, resins, and the cellulose esters can be employed in the formation of water-repellent zones on filter paper. Paraffin wax is recommended in this work, owing to its general inertness to chemical reagents and to the ease with which it can be embedded in diverse patterns on the paper. The paraffin rings are formed by warming the metal tube of the tool, *A* (Figure 1), over a small flame until the edge nearest the wooden handle becomes warm to the touch; the hot end is then brought to the surface of a slab of paraffin and the adhering film of molten wax is transferred to the sheet of filter paper. This method produces rings of sufficient uniformity for qualitative spot tests.

To make a series of enclosures of practically identical cross-sectional area, immerse a thin sheet of absorbent tissue paper in a bath of liquid paraffin, drain, cool, and lay the

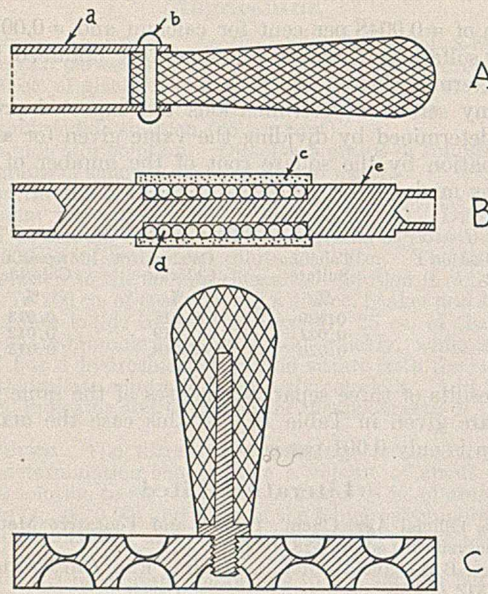

Figure 1. Tools for Making Confined Areas

a. Brass or aluminum tube, 4 × 1.27 cm.
b. Copper bolt
c. Rubber tubing
d. Asbestos cord
e. Brass rod with 0.95- and 0.63-cm. holes

waxed sheet over the filter paper to be inscribed. By momentarily pressing the hot edge of the metal tube against successive parts of the waxed tissue, paraffin rings enclosing areas of uniform diameter are printed through the filter paper. The pressing operation is facilitated by supporting the filter and waxed sheets on a smooth pad of writing paper.

By means of tool *C* (Figure 1), it is possible to embed the paraffin so as to leave a series of confined absorbent areas on the filter paper in one printing operation. This instrument is made by drilling holes of the desired size in both sides of a flat piece of brass or aluminum measuring about 10 × 5 × 1.3 cm. (4 × 2 × 0.5 inches), and polishing the drilled surfaces so as to leave smooth printing faces. Provision should be made in the center of the slab for the location of a removable wooden handle. The tool is operated by warming the plate in a drying oven to about 70–80° C.; the handle is then inserted and the hot plate is pressed against a paraffined tissue as described above. The print made with this tool on the filter paper is represented in Figure 2.

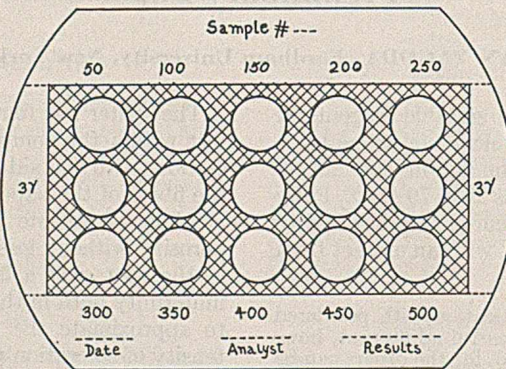

Figure 2. Paraffined Print Made by Tool *C*

The exact size of the area confined by the paraffin varies with the temperature of the printing tool, the pressure, the time of contact, and the porosity of the filter paper. The diameter of the absorbent region is usually somewhat smaller than the dimension of the printing tool. Thus, in making a series of rings with the cylindrical tube, *A* (Figure 1), the confined areas measure between 12.7 and 12.2 mm. in diameter. In preparing test papers for quantitative analyses, it is advantageous to employ the metal slab, for though the abovementioned variables are still present, the inward flow of the paraffin is the same for all the areas printed.

It is convenient to locate the rings on circular sheets of filter paper within a region bordered by an inscribed square, as shown in Figure 3. By folding the paper along the edges of the square the sides form a support for the region containing the absorbing spots. The resulting unit resembles a porcelain drop plate in appearance. Papers prepared in this fashion and impregnated with the proper reagents can be employed advantageously in determining the end points of volumetric processes that necessitate the use of external indicators.

Deposition of Reagent in the Test Papers

The filter paper employed in this method of analysis should be of a readily absorbent texture and when used for a quantitative analysis the surface should be as smooth as possible. The entire sheet of paper may be impregnated with a solution of the reagent and dried previous to the formation of the rings, or a definite volume of the reagent is permitted to evaporate within the confined areas on the untreated sheet. The latter procedure has the advantage that the amount of reagent deposited within a given area can be accurately determined from the volume and concentration of the solution permitted to evaporate within it. When the entire sheet is steeped in a solution, the reagent is deposited more uniformly over the surface of the dried paper, and this is an important factor in obtaining spots of uniform tint.

In making analyses by the confined spot method, the amount of reagent deposited within the absorbent area should be in sufficient excess to complete the reaction with the substance in the drop taken for analysis. When the entire paper is steeped in solution and dried, it is not possible to gage the surface concentration of the solid reagent by weighing the paper before and after the deposition because the sheet cannot be dried to constant weight. This quantity can be approximated by application of the following rule: The volume of liquid imbibed by a filter paper after being immersed in it and permitted to drain is approximately equal to the volume of the paper. Circular sheets of filter paper measuring 12.5 cm. in diameter and 0.020 cm. in thickness have a volume of 2.45 cc. Experiments revealed that the volume of water absorbed by such sheets averaged 2.35 ± 0.01 cc., which is in fair agreement with the theorem. After immersion in alcohol only 1.96 cc. of the liquid were found to be absorbed. This deviation from the rule is partly due to the evaporation of the alcohol during the weighing of the wet paper, but chiefly to the low viscosity and surface tension of the liquid which permit its more complete drainage from the paper.

This formulation is probably also valid for dilute solutions whenever the solute does not markedly alter the surface tension of the solvent. In working with the 1 per cent solutions of the reagents commonly used in spot analysis, it can be assumed that filter paper of 0.020-cm. thickness will retain after drying 160 γ or 180 γ of the solute per sq. cm., depending upon whether the paper is wetted with an alcoholic or an aqueous solution. A more exact value of this quantity can be ascertained from the weight of solution absorbed by several sheets of the paper.

Test Portions of Fixed Volume

The volume of small test portions taken from a solution can be ascertained by counting the number of separate drops delivered by a clean pipet of calibrated volume. When filled with water or dilute aqueous solutions, the standard 1-cc. pipets deliver drops having an average volume of about 0.05 cc. which are suitable for making qualitative spot tests. To gage the concentration of a solution by the method described it is desirable to work with large drops in order to secure greater accuracy and to avoid irregularities in the tint of the spot. Such test portions can be obtained either through the use of calibrated micropipets, or by the diverse types of stalagmometers employed for the determination of the surface tension of liquids. Previous investigations (*5*) reveal that the volume of drops falling from an orifice can be ascertained with great accuracy by means of these special dropping pipets, but the elaborate precautions necessary for their dependable operation are not in harmony with the simplicity of the present method of analysis.

The simple stalagmometer shown at *A* (Figure 4) can be made by reconstructing a Folin-Wu pipet. The tube can be employed to obtain large drops of constant volume, provided the dropping surface is kept clean and the operator has a steady hand. The chief difficulty in its application is that often the drop will fall from the orifice before it has grown to equilibrium size as a result of too rapid formation or mechanical vibration. The capillary pipet illustrated at *B* is recommended for general use in transferring test portions of solution to the reacting areas. It is operated by filling to the mark with the solution and blowing the contents on to the circular area, keeping the tip at right angles about 2 to 3 mm. above the center of the spot. At the point where the contents are nearly emptied, the tip of the pipet should touch the globule of solution deposited on the absorbent spot, and should be withdrawn from the liquid on the appearance of the first air bubble. The pipet is calibrated by weighing the water delivered by it to a piece of filter paper printed with a confined area supported in a wide-mouthed weighing bottle, using the same technic as that described above. Several such determinations made with a 0.1-cc. pipet showed that the volume delivered could be reproduced with an accuracy of 0.3 per cent.

Limits of Discernibility

In order to obtain colored spots of sufficient uniformity of tint to permit the estimation of the quantity of the ion present in the test sample, the solution must be diluted to a point where the area of the confined spot contains a considerable excess of reagent over that necessary to complete the chemical reaction with the ion in question, and the quantity of the colored product formed must be large enough to be readily noticeable to the eye. With the two metals investigated in the present report, nickel and copper, it was found that a range of concentration between 100 and 10 γ per cc. was suitable. In making a series of test spots over this range of concentration a difference of 10 per cent in the concentration of two test solutions of equal volume could be readily discerned by the change in color intensity of two adjacent spots of equal area.

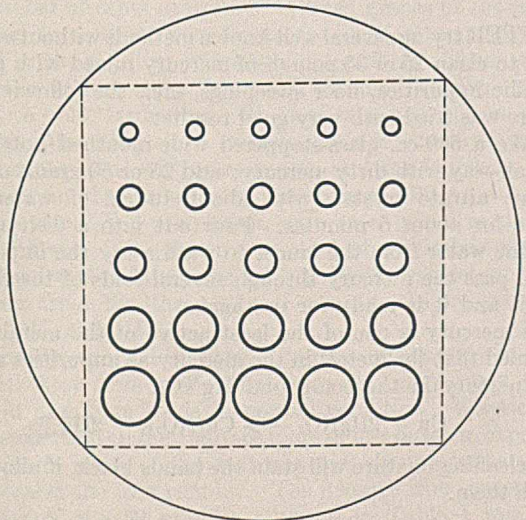

FIGURE 3. PARAFFINED RINGS FORMED WITH TOOLS *A* AND *B*

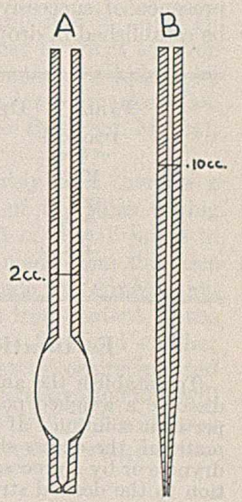

FIGURE 4. PIPETS FOR DELIVERING LARGE-SIZED DROPS

There are several methods for adopting these properties to the estimation of the concentration of dilute solutions. In the first, the color made by a test portion of the sample is compared with the colors made by test portions of several solutions containing known quantities of the element being investigated. This method, though direct in the interpretation of the results, necessitates the preparation and storage of numerous solutions. Another possibility is to take advantage of the fact that the minimum quantity of an element detectable on a spot of fixed area is a fairly reproducible constant for a given observer. By diluting the solution in successive stages until the vanishing point is reached, the total quantity of an ion present in it can be calculated from the final volume and known concentration at that point. The method selected for investigation in the present report is a compromise between the two methods just mentioned, in that the solution being analyzed is diluted to a point where a test portion produces a spot which matches in color an adjacent spot produced with a standardized solution of the element.

The colors of adjacent spots are best compared after the test portions become dry. Small differences in the shade of intensely colored spots are readily discerned in transmitted light. The spots resulting from dilute solutions can be compared by a reflected light, as the precipitate is almost entirely deposited on the upper surface of the filter paper. In working at the dilutions necessary for the successful operation of this method of analysis, it is safe to assume that there will be no appreciable change in volume as a result of the mixing of the solution with solvent and that the final volume of the mixture will be equal to the sum of the component liquids.

Detection of Metallic Ions

The several salts of nickel and copper employed in these investigations were purified by crystallization. In the case of hydrates the crystals were permitted to dry at room temperature until the crop attained constant weight. Standard stock solutions of nickel and copper were prepared by dissolving weighed quantities of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ in water and diluting the solutions to definite volume. Gravimetric analyses of these solutions showed that they possessed the same metal content as that calculated from the weight of the dissolved salts, proving that standard solutions can be prepared for this work by dissolving known amounts of a pure salt of the metal in question.

The minimum quantities of the metals that can be detected on spots of varying area were determined by diluting portions of the stock solution and transferring 0.029-cc. test portions to the absorbent areas. The test papers were impregnated with 1 per cent alcoholic solutions of dimethylglyoxime and α-benzoinoxime for use with nickel and copper, respectively. The results of these dilution experiments, recorded in Table I, show that by decreasing the diameter of the spot the presence of successively smaller amounts of the metals can be established in droplets of the same volume.

Table I. Detection of Nickel and Copper

Diameter of Spot *Mm.*	Ni^{++} γ	Cu^{++} γ
12.7	0.090	0.32
9.5	0.067	0.26
6.3	0.050	0.17
4.8	0.036	0.12
3.2	0.021	0.075

Estimation of Nickel and Copper

To establish the amount of an element present in a sample, dissolve a weighed portion in water so as to make about a 0.1 per cent solution. If acid is employed to effect solution of the material, the excess should be removed by evaporation to near dryness or by a process of neutralization before diluting the solution to the desired strength. Prepare a test paper as shown in Figure 2, transfer a 0.1-cc. test portion of the solution to the first area on the top row, and pipet 50 cc. of the remaining solution to a dry 600-cc. beaker. Deposit test portions of known strength on the center row of spots containing either 2 or 3 γ of the element sought. The color of the spot made by the first test portion should be considerably darker than the standard spots. Dilute the solution pipetted into the beaker with successive 50-cc. portions of water, transferring test portions of each dilution product to the remaining areas on the paper. It is convenient to make the markings of the spots numerically equal to the total volume of the solution from which the test sample was taken. When the paper dries, compare the tint of the spots made at the successive dilutions with the color of the standards, noting at which dilution the intensities match.

The percentage of the element in the sample is then computed by means of the relationship:

$$P = \frac{v_0Vc}{10\, v_dw}$$

In this expression v_0 represents the volume of the solution containing the sample, v_d the volume of the aliquot taken for dilution, V the volume at which the test spot matches the standard spot, w the weight of the sample in milligrams, and c the concentration of the standard solution expressed in γ units of the element per cc. If v_0 is 100 cc., v_d is 50 cc., and c is 30 γ per cc., as in the case of the experiments recorded below, the above expression simplifies to $P = 6V/w$.

Table II. Determination of Nickel and Copper

Salt	Reagent	c	w	P	Error %
$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (%Ni = 14.86)	Dimethylglyoxime	30	124.9	14.4	
		20	114.5	14.4	
		20	81.3	14.8	
			Av.	14.5 ±0.2	2.0
$CuSO_4.5H_2O$ (%Cu = 25.5)	α-Benzoinoxime	30	103.6	26.1	
		30	97.1	24.7	
		30	84.2	25.0	
			Av.	25.3 ±0.6	0.8
$Cu(C_2H_3O_2)_2 \cdot H_2O$ (% Cu = 31.9)	α-Benzoinoxime	30	88.8	30.4	
		30	80.8	31.6	
		30	69.8	31.0	
			Av.	31.0 ±0.4	2.8

In Table II are recorded the results of several analyses of pure nickel and copper salts arrived at by following the above procedure. The difference between the observed and calculated figures is in the range of 1 to 3 per cent. This limits the applications of the method to analyses where speed is of greater importance than accuracy, or to circumstances where only minute fragments of a sample are available. It may be possible to reduce the error to about 1 per cent by making the test on porous filter paper of a smoother finish than that manufactured at present for filtration purposes.

The results obtained for copper indicated that the method can be used to determine the end point of an electrolytic copper determination by removing a test portion from the electrolyte and comparing the color of the spot with one of known copper content. If the test indicates that an appreciable amount of the metal is still in solution, the amount removed in the test sample can be corrected for if it is found to exceed the error in the weighing of the electrode.

Summary

By confining spot tests to regions of uniform area it is possible to approximate the amount of an ion present in a solution from the tint of the colored spot. By means of this technic it has been possible to determine the metal content of pure nickel and copper salts with an accuracy of 1 to 3 per cent. Work is in progress in the refinement of this method of analysis and its application to the determination of pH, the direct analysis of the mineral content of drinking waters, and the assaying of ores and alloys. This technic should also prove useful in biological analyses of the composition of blood and urine.

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Rapid Cleaning of Mercury

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After trying several well-known methods without success, to clean 25 or 35 pounds of mercury mixed with grease, metallic impurities, floor sweepings, etc., the following procedure was tried with very good results:

Take a 500-cc. glass-stoppered wide-mouthed bottle and fill half-way with dirty mercury; add 25 or 50 grams of mercurous nitrate crystals with about 10 cc. of water, and shake for about 5 minutes. Pour out into a dish and allow the water from the faucet to wash away the impurities. Then pass the mercury through several folds of toweling to dry it and it is ready for use again.

As mercury is one of the least active of the metals, it is assumed that the metals in the mercury as impurities replace the mercury in the compound $HgNO_3$:

$$Cu + 2HgNO_3 \longrightarrow Cu(NO_3)_2 + 2Hg$$

The cleaning mixture will stain the hands black, if allowed to touch them.

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The Iron Content of Grapes and Wine

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IN ALL wine-making regions of the world wine often becomes hazy or cloudy owing to the formation of a finely divided, colloidal precipitate caused by the presence in the wine of an excess of iron salts. The problem is of considerable economic importance in California and is one to which much attention has been given in this laboratory.

von der Heide (*5*), until his death a member of the staff of the Geisenheim Enological Station in Germany, has published an excellent review of the literature and knowledge of the iron problem in relation to wine making. He states that grapes and the wines made from them contain small amounts of iron naturally, but does not indicate the amounts normally present. He calls attention to the fact that considerable iron may be dissolved by the must from dust and soil adhering to the grapes at the time of crushing.

de Castella (*2*) of Australia in a bulletin on the casse of wine states that wine normally contains in the neighborhood of 10 parts per million of iron and that when this proportion is much exceeded clouding is apt to occur. Brown (*1*) found that normal California grape juice contained from 5 to 10 p. p. m. of iron. He reports grape juices made in California containing as much as 150 p. p. m., evidently dissolved by contact with iron equipment. Mathieu (*7*) and Grandchamp (*4*) as well as many other authors on wine, discuss the "iron problem" and various methods of solving it, but give very little information concerning the normal iron content of grapes and wine. Sherman (*10*) gives the iron content of whole grapes (variety not stated) as 0.0013 per cent or 13 p. p. m. Fabre and Bremond (*3*) give the normal iron content of wines made from Carignane grapes in Algeria as 10 to 12 p. p. m. Wine that came in contact with iron equipment or was stored in concrete tanks greatly increased in iron content attaining as much as 60 p. p. m.

Marotta (*6*) reports that juice of grapes of the Herault district of France contained from 1 to 4 p. p. m. of iron and that the iron content of grapes is unaffected by the nature of the soil. Wines made commercially from the same grapes contained 5 to 39 p. p. m. of iron, indicating that much iron was dissolved by the must and wine during vinification.

In the present investigation samples of grapes from several of the important grape-growing districts of California were collected. The must of each was analyzed for iron content by wet-ashing a 2-cc. sample with perchloric and sulfuric acids, followed by determining the iron present colorimetrically, using *o*-phenanthrolene in the presence of hydroxylamine hydrochloride. The details are given by Saywell and Cunningham (*9*).

A number of other samples of crushed grapes or the juices expressed from them were fermented in glass and the iron content of the resulting wines was determined. These wines were made in four ways from each sample: One was made with juice only, fermented with pure wine yeast; one with juice only, plus 100 p. p. m. of sulfur dioxide; one by fermentation on the skins with pure yeast; and the fourth by fermentation on the skins in the presence of 100 p. p. m. of sulfur dioxide. For comparison with these wines made out of contact with iron, the iron content of a number of new commercial wines of the same vintage (1935) was determined. The data from the three sets of samples are presented in Tables I, II, and III.

The juices reported in Table I varied considerably in iron content; those from grapes that were obviously dusty were higher in iron than those in normal condition. Practically all grapes contain on their surface more or less dust; in expressing the juice some of the dust unavoidably enters the juice and increases the iron content. The average iron content of the juices of the 59 samples reported in Table I was 8.6 p. p. m.; of the additional 16 samples reported in Table II, it was 9 p. p. m. Locality did not appear to affect the iron content of the juice in any consistent manner, as judged by the limited number of samples available for comparison (see particularly analyses of Zinfandel, Alicante Bouschet, Muscat, and Thompson seedless).

The data of Table II show conclusively that there is a very striking decrease in iron content of the juice during fermentation. The average iron content of the 16 juices in Table II was 9.0 p. p. m., of the wines made from the juice alone, 1.9 p. p. m., and of the wines made by fermentation on the skins, 1.7 p. p. m. The average iron content of the whole grapes was 11.9 p. p. m. It was not determined whether the iron was utilized by the yeast in its tissues, or precipitated as an insoluble salt; this point is under investigation and will be reported upon later. Whether or not sulfur dioxide was used apparently did not affect the iron decrease during fermentation.

TABLE I. IRON CONTENT OF JUICES OF FRESH CALIFORNIA GRAPES

(Arranged according to variety. 1935 season)

Sample Number	Grape Variety	Locality	Iron *P. p. m.*
18	Zinfandel	St. Helena	12.0
19	Zinfandel	St. Helena	12.0
20	Zinfandel	St. Helena	12.5
21	Zinfandel	St. Helena	6.0
22	Zinfandel	St. Helena	9.0
24	Zinfandel	St. Helena	3.0
1	Zinfandel	Lodi	8.5
29	Zinfandel	Lodi	5.0
33	Zinfandel	Lodi	10.0
3	Alicante Bouschet	Lodi	8.5
23	Alicante Bouschet	St. Helena	10.0
52	Alicante Bouschet	Fresno	3.0
62	Alicante Bouschet	Fresno	8.5
63	Alicante Bouschet	Fresno	12.0
64	Alicante Bouschet	Fresno	7.5
2	Carignane	Lodi	5.0
5	Sultana	Lodi	6.0
43	Sultana (dusty)	Tulare	16.0
44	Sultana (dusty)	Tulare	15.0
11	Semillon	Livermore	5.5
12	Semillon	Livermore	8.0
16	Semillon	Geyserville	1.5
6	Muscat	Lodi	9.0
54	Muscat	Fresno	8.0
55	Muscat	Fresno	3.0
57	Muscat	Fresno	5.0
58	Muscat	Fresno	7.0
61	Muscat	Fresno	6.0
25	Thompson seedless	Lodi	11.5
28	Thompson seedless (dusty)	Lodi	23.0
30	Thompson seedless (dusty)	Lodi	8.0
32	Thompson seedless (dusty)	Lodi	23.0
34	Thompson seedless	Lodi	9.0
36	Thompson seedless	Lodi	17.0
37	Thompson seedless	Lodi	4.0
38	Thompson seedless	Lodi	5.0
39	Thompson seedless	Kingsburg	7.0
40	Thompson seedless	Kingsburg	13.0
41	Thompson seedless	Kingsburg	17.0
59	Thompson seedless	Fresno	3.0
10	Golden Chasselas	Livermore	2.5
17	Golden Chasselas	Geyserville	3.5
26	Golden Chasselas	Lodi	11.0
27	Tokay	Lodi	12.0
31	Tokay	Lodi	14.0
35	Tokay	Lodi	7.0
49	Malaga	Fresno	4.0
50	Malaga	Fresno	4.0
53	Malaga	Fresno	4.0
60	Malaga	Fresno	12.0
13	Pinot	Asti	9.5
14	Pinot	Asti	9.5
15	Pinot white	Asti	8.5
7	Petite sirah	Livermore	10.0
8	Sauvignon blanc	Livermore	5.0
9	Sauvignon blanc	Livermore	8.0
42	Ribier	Kingsburg	10.0
51	Ribier	Fresno	4.0
45	Salvatore (dusty)	Tulare	17.0
Average			8.6

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[1] Present address, Pacific Can Company, San Francisco, Calif.

Table II. Iron Content of Grapes and Wines Made from Them in Glass

Grape Type and District	Iron Content					
	Juice	Wine from juice alone		Juice + seeds + skins, whole grapes	Wine from juice + seeds + skins	
		SO₂	No SO₂		SO₂	No SO₂
	P. p. m.					
Carignane, Lodi	12.0	2.5	1.9	11.5	2.0	2.1
Zinfandel, Lodi	15.7	3.3	2.1	26.6	2.5	2.7
Tokay, Lodi	1.0	1.5	1.5	1.5	1.0	0.8
Mission, Lodi	6.0	1.6	1.6	6.0	1.3	1.7
Semillon, Livermore	9.5	1.0	1.5	10.5	1.8	1.6
Burger, Livermore	14.0	1.1	4.5	23.0	1.0	1.6
Mourastel, Livermore	6.5	1.7	1.3	10.5	0.8	1.4
Zinfandel, Geyserville	12.1	2.9	3.6	11.0	2.0	2.1
Grand Noir, Geyserville	2.5	2.8	2.4	12.0	2.1	2.2
Alicante, Napa	14.0	2.1	2.0	15.4	2.5	2.1
Alicante, Fresno	13.4	2.2	1.7	17.7	2.1	2.2
Thompson, Fresno	9.8	1.7	1.5	13.0	2.0	1.7
Sultana, Fresno	10.0	1.9	1.7	12.0	2.0	1.7
Muscat, Fresno	7.0	1.7	1.7	7.5	1.2	1.0
Muscat, Fresno	5.0	1.0	1.0	6.8	1.0	1.5
Carignane, Fresno	6.0	2.0	1.0	6.5	1.5	1.2
Average	9.0	1.9	1.9	11.9	1.7	1.7

In Table III is given the iron content of a number of "natural" new wines—i. e., those that had not been fortified by the addition of brandy—and also of a similar number of fortified new wines including sherries, muscatel, port, and angelica types. Most of the wines had received no treatment beyond normal fermentation, or fermentation and fortification. A few had been clarified with bentonite (*8*). Evidently some of the unfortified new wines had dissolved from contact with the metal equipment of the winery considerable to large amounts of iron, one sample containing 35 p. p. m. The average iron content of the 55 samples was 5.4 p. p. m., which is about 3 times that of the wines made out of contact with iron, as reported in Table II. Iron pickup during vinification is indicated. The fortified wines were considerably lower in iron than were the unfortified. Fortified wines of the Fresno-Tulare-Kingsburg district are much lower in acidity than the unfortified wines of the Geyserville district and on this account they may have exerted less solvent effect on the iron of crushers, pipe lines, etc. However, the principal conclusion to be drawn from comparison of the data of Tables II and III is that wines made under commercial conditions have on the average several times the iron content of wines made out of contact with iron.

Table III. Iron Content of Some Californian Commercial Wines

(1935 vintage)

Sample	Type	District	Iron	Treatment
			P. p. m.	
1	White, dry	Geyserville	6.0	None
2	White, dry	Geyserville	3.0	None
3	Sherry material	Geyserville	2.5	None
4	White, dry	Geyserville	5.0	None
5	Red, dry	Geyserville	20.0	None
6	White, dry	Geyserville	2.0	None
7	Muscat	Geyserville	2.0	None
8	Port	Geyserville	6.0	None
9	Red, dry	Geyserville	17.0	None
10	Angelica	Geyserville	1.5	None
11	Red, dry	Geyserville	25.0	None
12	Port	Geyserville	7.0	None
13	Port	Geyserville	8.0	None
14	Red, dry	Geyserville	35.0	None
15	Sherry	Geyserville	6.0	None
16	Red, dry	Geyserville	25.0	None
17	White, dry	Geyserville	1.0	Fined with bentonite
18	Sherry material	Geyserville	6.0	Fined with bentonite
19	Red, dry	Geyserville	2.5	Fined with bentonite
20	Red, dry	Geyserville	7.0	Fined with bentonite
21	Red, dry	Geyserville	2.3	Fined with bentonite
22	Red, dry	Geyserville	2.0	Fined with bentonite
23	White, dry	Geyserville	1.5	None
24	White, dry	Geyserville	1.5	Fined with bentonite
25	Red, dry	Geyserville	7.0	Fined with bentonite
26	Red press	Geyserville	8.0	Fined with bentonite
27	Red, dry	Geyserville	5.0	Fined with bentonite
28	Red, dry	Geyserville	8.0	Fined with bentonite
29	Red, dry	Geyserville	2.0	Fined with bentonite
30	Malaga	Fresno	6.0	None
31	Thompson	Fresno	3.0	None
32	Muscat	Fresno	1.5	None
33	Sherry material	Fresno	2.0	None
34	Muscat	Fresno	2.5	None
35	Thompson	Fresno	1.2	None
36	Sherry material	Fresno	4.0	None
37	Sherry material	Fresno	1.0	None
38	Angelica	Fresno	1.0	Racked
39	Port	Fresno	4.0	Fined with bentonite
40	Muscat	Fresno	1.5	Fined with bentonite
41	Angelica	Fresno	1.5	Fined with bentonite
42	Muscat	Fresno	1.5	Fined with bentonite
43	Port	Fresno	2.0	Racked
44	Sherry material	Fresno	2.5	None
45	Muscat	Kingsburg	1.0	None
46	Muscat	Kingsburg	1.5	None
47	Alicante	Kingsburg	1.5	None
48	Muscat	Kingsburg	1.3	None
49	Sherry material	Kingsburg	2.5	None
50	Alicante	Tulare	7.5	None
51	Sherry material	Tulare	3.5	None
52	Sherry material	Tulare	5.5	None
53	Muscat	Tulare	6.5	None
54	Muscat	Tulare	3.0	None
55	Angelica	Tulare	1.4	None
Average			5.4	

In most California wineries the crushed grapes, unfermented juice, and wine come in contact with iron in such equipment as crushers, stemmers, pipe lines, etc., a fact that would account for the higher iron content of the commercially made wines reported upon in Table III.

It has been observed that California wines vary markedly in respect to the minimum iron concentration required to cause clouding. White wines such as sauterne, Chablis, and Riesling types will usually develop "iron casse" (cloudiness due to precipitated iron compounds) at considerably less than the 10 p. p. m. minimum mentioned by de Castella (*2*) for Australian wines. Clouding has been observed at 5 p. p. m. of iron in such wines. The stability of red wines such as claret and Burgundy types is apparently relatively unaffected by the concentration of iron normally encountered in California wines.

Excess iron can be removed by fining the affected wine with casein or with potassium ferrocyanide. When used in excess the latter remains in the wine and in part decomposes to liberate hydrocyanic acid. On this account its use is not to be encouraged and is prohibited in most wine-producing countries. The addition of a small amount of citric acid to white wines will usually prevent iron casse and is the standard preventive measure in France.

Summary

The iron content of the juice of California grapes ranged from 1.5 to 23 p. p. m., depending upon the degree of contamination with dust or soil.

The iron content markedly decreased during fermentation, e. g., from an average of 9.0 p. p. m. to an average of 1.8 p. p. m. Addition of sulfur dioxide before fermentation did not affect the decrease in iron during fermentation.

The average iron content of commercially made wines was approximately three times that of wines made in the laboratory in glass, indicating solution of iron by the juice and wine from iron equipment.

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The Principle of the Suspended Level

Applications to the Measurement of Viscosity and Other Properties of Liquids

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AS A PHYSICAL constant of substances and because of its relation to the theory of liquids, viscosity has become increasingly important both in industry and in scientific research. Viscometers for its determination have not kept pace with the need for exactness. Examined critically, even the best instruments in use possess inherent defects which cannot be eliminated. As a result, many viscosity data now in the literature are erroneous and true values or corrections are practically impossible to estimate. In industry various empirical units measured by a variety of devices have come into use, but these values do not meet present requirements for accuracy and convenience.

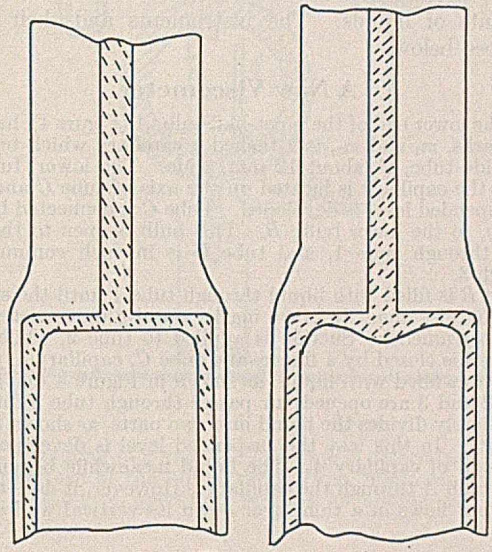

FIGURE 1

A phenomenon heretofore unnoticed—namely, the suspended level—has made it possible to remedy this by refining to an extraordinary degree the measurement of properties of liquids and a simple and accurate type of viscometer has been developed employing it. The application of this principle opens new possibilities in the determination of static and dynamic surface energy as well as viscosity, and sheds new light on other problems of flowing films, important alike in colloid chemistry and biology and in the lubrication of bearings.

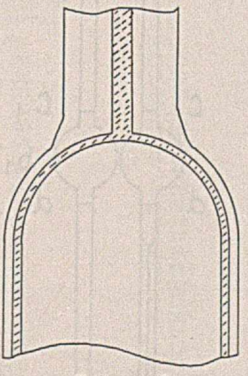

FIGURE 2

In viscometers, it has been customary to allow the liquid under examination to flow through a capillary tube discharging either into the air or into a mass of liquid. In each of these situations the effective pressure driving the liquid through the capillary is influenced by the surface tension of the film lying on the surface of liquid at the higher level, and by the surface tension effect either on the stream emerging from the capillary or on the surface of the liquid in the lower reservoir. These effects have introduced indeterminate errors into the calculation of viscosity from the time of flow. Further uncertainty has been introduced by failure to recognize and correct for the kinetic energy of the flowing liquid.

Application of the Suspended Level

Application of the principle of the suspended level allows one to balance corrections for these factors against each other and to design an instrument whose dimensions are so proportioned as to avoid others. The suspended level is the term used to designate the hanging surface of a liquid. This film has been formed with a plane surface (Figure 1, left), a domed surface, convex downward (Figure 1, right), and a hemispherical surface, concave downward (Figure 2). It is formed at the point where a vertical capillary expands into a relatively large tube by the layer of liquid spreading upon the interior surface of this junction. The suspended level is so called to distinguish it from the recumbent level formed by the film lying on the surface of a liquid.

The suspended level becomes an ideal auxiliary for hydrodynamic and hydrostatic measurements. Applied to viscometers it yields an entirely new type of apparatus in which the customary recumbent surface lying on the liquid is replaced by a suspended one. If this suspended level is made to take the form of a hollow hemisphere, even corrections for surface tension become unnecessary. This frees viscometers of their hitherto inescapable defect, inaccurate adjustment of level, and by the use of a simple air inlet tube for producing the film at will creates an instrument of unsurpassable simplicity and outstanding accuracy.

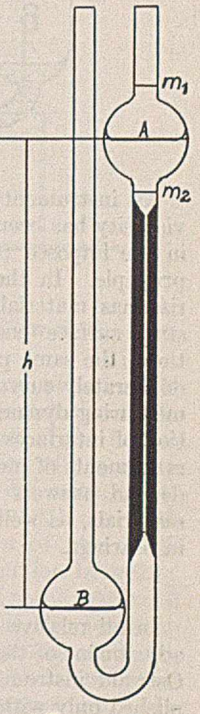

FIGURE 3

Correction for the kinetic energy of flow, necessary in all previous instruments, must be applied. This correction has usually been neglected, although this may introduce errors far exceeding all others and may occasionally make the instruments practically useless. This neglect can be understood when the difficulty in applying the correction is realized. The elimination of these defects was accomplished by a new proportioning of dimensions which determines the magnitude of the correction and allows the corrected time of flow to yield kinematic viscosity directly in centistokes when merely multiplied by a power of ten—that is, by the mere insertion of a decimal point. To construct viscometers for this purpose requires an accuracy of dimension in glass within 0.01 mm. The resulting instrument is so easily used and so free from error that no excuse remains for doubtful values of viscosity.

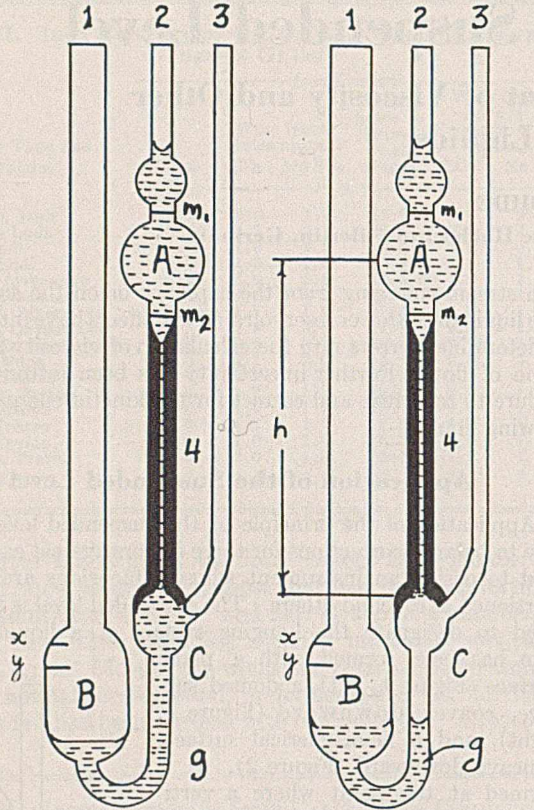

FIGURE 4

An instrument for the direct determination of dynamic viscosity has been built which avoids error from fluctuations in the imposed pressure by employing the suspended level principle. In the same way the measurement of capillary rise has materially increased the accuracy of determining static surface tension. On the basis of theoretical considerations, the same principles have been applied to form layers deliberately curved and a new method has been obtained for measuring dynamic surface tension. This permits examination of interfaces for the formation of layers, anisotropic arrangements of molecules, and allied phenomena, upon which depend answers to problems of biology and structure of materials, as well as the very practical problems of friction in bearings.

Viscometers

In all relative viscometers the main difficulty lies in the adjustment of the liquid column to a precise height. In the Ostwald instrument (Figure 3) this adjustment is accomplished only with difficulty, and with some liquids is impossible. The effective height of the liquid column is indefinite in pipet instruments as well as in viscometers adjusted by overflow. In all such devices the source of error lies primarily in the lower level as well as in the varying effect of surface tension. Attempts at refinement of these devices already undertaken appear to introduce complications without achieving the desired results; hence, further effort at improvement may well be abandoned.

With a plane suspended level, surface tension acts perpendicularly to the vertical capillary, which is the direction of flow, and hence does not affect the height of the liquid column. In every viscometer a second liquid surface exists in the upper bulb in which surface tension acts on the height of the column. Since all liquids wet the walls of this upper bulb, the meniscus formed exerts an upward pull against the vessel walls because of surface tension, and thus tends to diminish the effective height of the liquid column. Theoretical considerations, which have been amply proved by experiment, lead to the conclusion that by properly curving the surface layer at the suspended level, an amount of traction can be there developed acting in the direction opposite to the tension on the surface of the liquid in the upper bulb and balancing it.

These considerations may be summarized as follows:

1. The suspended level, regardless of whether plane or curved, assures the development of a suspended layer of liquid at the same location independent of kinematic viscosity, specific gravity, and other properties of the liquid.
2. By using a plane suspended level the effect of surface tension at the foot of the column can be eliminated.
3. By forming the suspended level in a hemispherical layer, such an amount of traction can be applied through surface tension as to balance that exerted at the upper meniscus.

The foregoing conclusions have been subjected to careful mathematical and hydrodynamic analyses and have been proved by experiment. From them has been developed a practical form of apparatus for measuring the properties of liquids, particularly viscosity, surface tension, and related constants of liquids. The instruments and their use are described below.

A New Viscometer

At the lower end of the pipet-like bulb, *A* (Figure 4), having the two marks, m_1 and m_2, is attached a capillary which terminates in a wide tube, *C*, about 12 mm. wide. The lower, funnel-like end of the capillary is located on the axis of tube *C* and on this the suspended level is developed. Tube *C* is connected by a bent tube, *g*, to the lower bulb, *B*. This bulb is open to the atmosphere through tube 1, and tube *C* is in such communication through 3.

Bulb *B* is filled with liquid through tube 1 until the surface of the liquid lies about between marks *x* and *y* (not marked on the glass instrument). Suction is applied to tube 2, while the top of tube 3 is closed by a finger, and tube *C*, capillary 4, and bulb *A* are thus filled with liquid, as shown in Figure 4 (left). When tubes 2 and 3 are opened, air passes through tube 3 into *C* and immediately divides the liquid into two parts, as shown in Figure 4 (right). In this way the suspended level is developed on the lower end of capillary 4. The liquid meanwhile begins to flow out of bulb *A* through the capillary. However, it does not again fill *C*, but flows in a thin layer down its vertical wall and joins

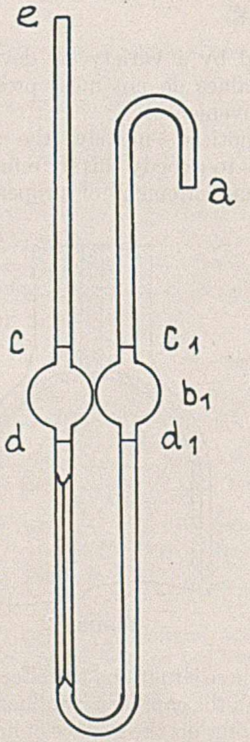

FIGURE 5

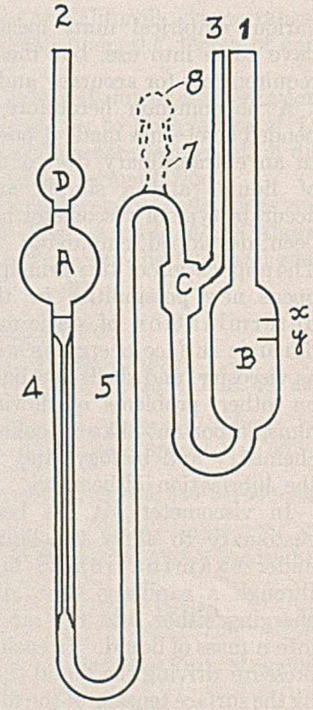

FIGURE 6

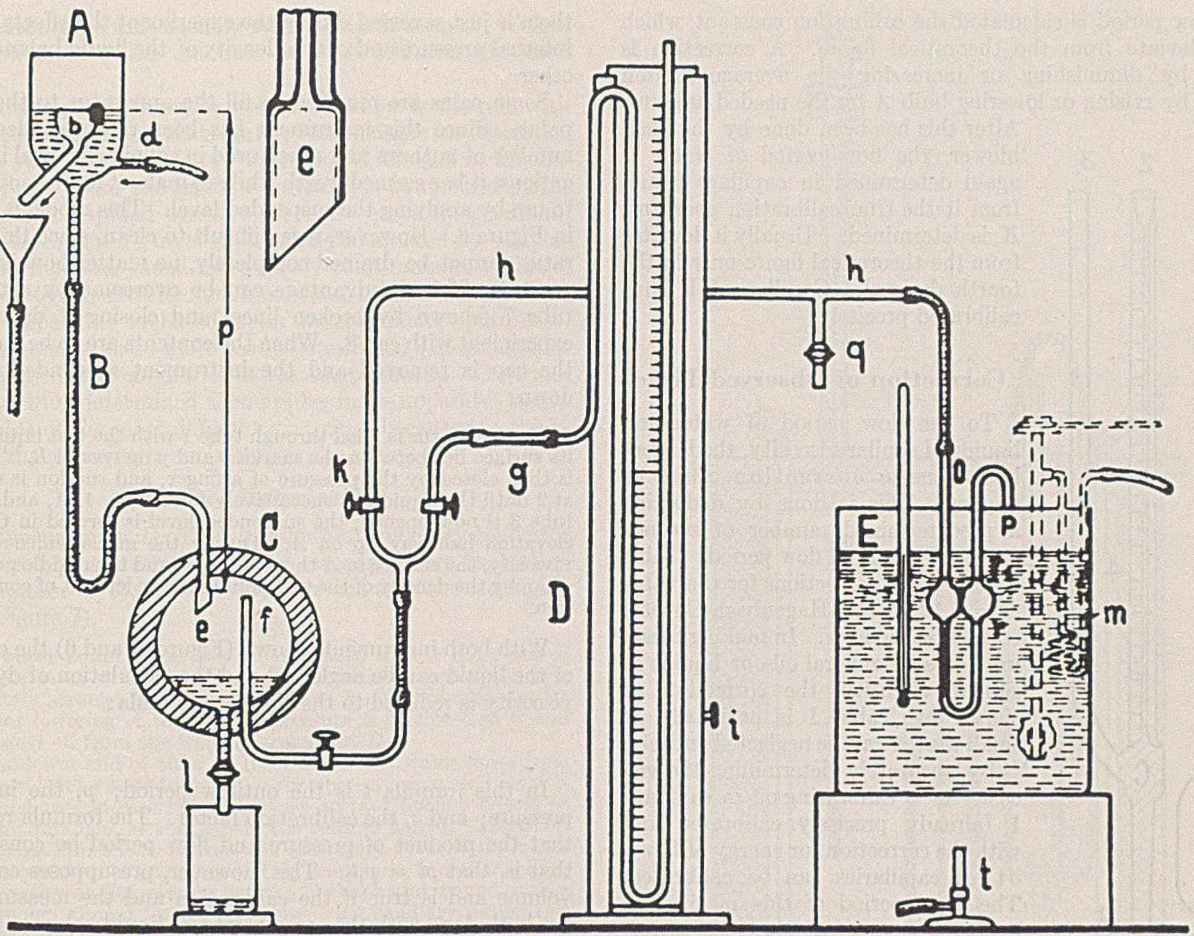

FIGURE 7

the liquid remaining in g and B. The time is determined during which the surface of the liquid drops from mark m_1 to mark m_2. The method of operation is thus as simple as can be imagined.

The viscometer (*9*) greatly resembles the diagrammatic representation, except that it is more compact, since the three tubes are arranged in a triangle instead of in a plane. The glass body is enclosed in a cage comprised of two circular sheets and three rods of metal, to protect it as far as possible against breakage.

Capillaries of three different diameters are supplied, the dimensions being so selected that the flow period measured need only be multiplied by a power of 10 to yield the kinematic viscosity directly. These are supplied with the calibration factor etched on.

For a capillary 9 cm. long, a volume of 5.67 cc. in bulb A, and an average column height of 13 cm., the calibration constant $K = 0.01$ requires the radius of capillary I to be 0.0318 cm. For capillary II with $K = 0.01$, this radius is 0.0565 cm., and for capillary III with $K = 1.0$, 0.1005 cm.

Since small deviations from the theoretical radius of the capillary appear as the fourth power in the calculated viscosity, they are made by the KaPeG process of the firm of Schott & Gen., Jena, which forms capillaries with a radius up to 0.05 cm. with an accuracy of ±0.001 cm. The production of the hemispherical junction between 4 and C on which the suspended level forms is also based on the KaPeG process and can, only in exceptional cases and with the greatest pains, be made with a blast lamp. Manual production requires very careful selection of product and produces an excess of rejects.

TABLE I. CORRECTIONS FOR ENERGY OF FLOW

(Corrections apply to capillaries I, II, and III having calibration constants $K = 0.01$, 0.10, and 1.0, respectively. The table also applies when K deviates somewhat from these figures.)

Flow Period Observed	Seconds to Be Deducted from Flow Period for Capillaries I	II	III
Sec.	*Sec.*	*Sec.*	*Sec.*^{a}
20	(14.1)	(1.41)	0.14
25	(11.2)	(1.12)	0.11
30	(9.34)	(0.93)	0.1
35	(8.1)	0.81^b	0.08
40	(7.0)	0.7^b	0.07
45	(6.27)	0.63^a	0.06
50	(5.6)	0.56^a	0.06
55	(5.1)	0.51^a	0.05
60	(4.68)	0.47^a	0.05
70	(4.01)	0.4^a	0.04
80	3.5^b	0.35^a	0.04
90	3.1^b	0.31^a	0.03
100	2.8^b	0.28^a	0.03
120	2.34^a	0.23^a	0.02
140	2.00^a	0.20^a	0.02
160	1.75^a	0.18^a	0.02
180	1.56^a	0.16^a	0.02
200	1.4^a	0.14^a	0.01
250	1.12^a	0.11^a	
300	0.94^a	0.09^a	
350	0.80^a	0.08^a	
400	0.70^a	0.07^a	
450	0.63^a	0.06^a	
500	0.56^a	0.06^a	

[a] Error does not exceed 0.2 per cent.
[b] Error does not exceed ±0.1 per cent.
Figures in parentheses are doubtful (*6*).

Calibration

The calibration of these viscometers is conducted at a temperature of 20° ± 0.001° C. in a thermostat of greatest precision. The time of flow of the purest water through capillary I (theoretical calibration constant of 0.01) is determined. From this flow period is calculated the calibration constant, which may deviate from the theoretical figure. A correction is made by diminishing or increasing the average column height by raising or lowering bulb *A* by the needed amount. After this has been done by the glass blower, the flow period of water is again determined in capillary I, and from it the true calibration constant, *K*, is determined. Usually it deviates from the theoretical figure only in the fourth decimal. Capillary I is thus calibrated precisely.

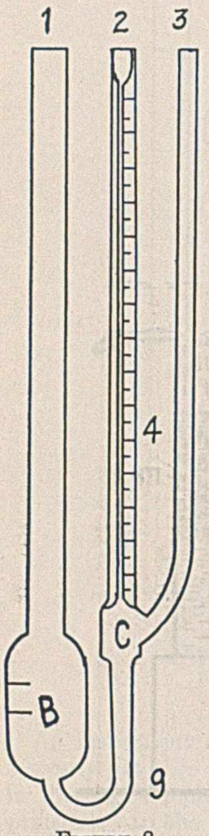

FIGURE 8

Correction of Observed Time

To the flow period of water and liquids of similar viscosity, the Hagenbach-Couette correction must be applied. This is done by deducting a predetermined number of seconds from the observed flow period. Table I shows such corrections for the value $m = 1.12$ in the Hagenbach-Couette correction member. In making measurements on mineral oils or liquids of similar viscosity, the correction as shown by Table I is ordinarily so small that it can be neglected entirely.

By accurately determining the viscosity of a calibrating oil in capillary I (already precisely calibrated and with the correction for energy of flow), other capillaries can be calibrated. The flow period of this oil in this capillary is so great that the correction for energy of flow can be neglected. Capillary II is now calibrated accurately (as above) with this calibrating oil. This procedure is repeated with capillary III, using an oil of still greater viscosity.

Once a sufficient number of the calibrating oils have been precisely calibrated, it naturally is unnecessary to repeat the original calibration with water. Thus even with capillary I the correction for energy of flow is avoided in the determination of the calibration constant, *K*.

The principal errors which may occur in the precise calibration of viscometers are caused by small fluctuations of temperature. These so affect the viscosity of the various calibrating liquids that marked errors may occur in the values determined. In order to prevent these errors as far as possible, the author has built and used a thermostat which can be kept for any desired time at 20° ± 0.001° C.

Determination of Dynamic Viscosity

As a rule it is advantageous to determine the kinematic viscosity ν directly, and by multiplying it by the density, to calculate the dynamic viscosity, η. For this purpose the apparatus described above, functioning under its own pressure, can be used with materially greater accuracy than the following forms, which are complicated by employing outside pressure sources. Only where it is necessary to determine dynamic viscosity directly or to investigate displacement elasticity is the use of instruments with outside sources of pressure unavoidable.

The author's older double-bulb apparatus (*1*, *7*) is filled with the test liquid until it initially reaches from *C* to d_1 (Figure 5). Excess pressure is then applied to *C*, the liquid being thus forced into the other bulb. Since both bulbs are located at the same height, and the difference in level between them is just reversed during the experiment the effects of the internal pressure and of the density of the liquid balance each other.

Some pains are required to fill the apparatus to the exact point. Since this instrument has been recommended by a number of authors and much used in colloid chemical investigations, it has seemed worth while to make it more convenient to use by applying the suspended level. This model is shown in Figure 6. However, it is difficult to clean, since the apparatus cannot be drained completely, no matter how it is suspended. This disadvantage can be overcome by attaching tube 7 (shown by broken lines) and closing it during the experiment with cap 8. When the contents are to be emptied, the cap is removed and the instrument suspended upside down.

The apparatus is filled through tube 1 with the test liquid until its surface lies between the marks *x* and *y* on vessel *B*. Tube 3 is then closed by the pressure of a finger, and suction is exerted at 2 until the liquid has successively filled *C*, 5, 4, *A*, and *D*. If tube 3 is now opened, the suspended level is formed in *C* at an elevation half-way up on *A*. During the measurement of the viscosity, the surface in *A* then varies around the middle position, whereby the density of the test liquid may be left out of consideration.

With both instruments shown (Figures 5 and 6) the density of the liquid can be neglected and the calculation of dynamic viscosity is reduced to the simplest formula:

$$\eta = ptk$$

In this formula *t* is the outflow period; *p*, the imposed pressure; and *k*, the calibration factor. The formula requires that the product of pressure and flow period be constant—that is, that $pt = p_1t_1$. This, however, presupposes constant volume and is true if the calibration and the measurement are both done with the same height of liquid column.

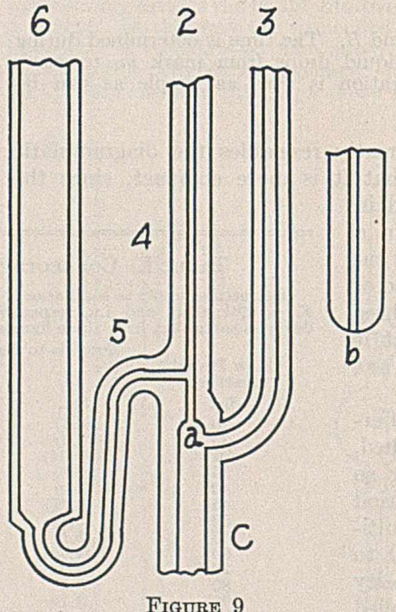

FIGURE 9

In the literature (*1*) the opinion has been widely expressed that a greater residue of highly viscous than of less viscous liquids remains in the viscometer vessel and that this affects the accuracy of the determination. This view is not supported by the facts. From the author's calculations it can be deduced that the volume remaining, V_2, is equally large with liquids of varying viscosity if the outflow period is proportional to the kinematic viscosity—that is, when $\frac{V}{t}$ is constant. This occurs in all instruments which operate without imposed pressure or at constant pressure. Omitting the theoretical derivation, we shall cite a practical experiment. Use was made in the experiments of an apparatus like that in Figure 6, except that it had a very short capillary and the liquid was allowed to flow out under its own pressure. Two very different oils were examined: a very light gas oil and a lubricating oil of fifteen times greater viscosity. At the instant when the surface of the liquid reached the mark m_2 the apparatus was laid horizontal so that nothing more could flow out. Weighing showed that like amounts of both oils had remained behind.

In working with changing pressure—which is the rule with these instruments and is absolutely unavoidable for determining the structural elasticity—more liquid remains in the viscometer the more the outflow period, *t*, is diminished by increasing the imposed pressure, *p*. The quantity remaining in the viscometer, V_2, must therefore be eliminated by calculation. V_2 increases much more slowly than pressure *p*, but it is difficult to calculate its numerical value because the constant of the apparatus is based upon indeterminate quantities. The correction can be more easily determined experimentally by calibrating the capillaries at various pressures. The function of *p* thus determined then applies in the apparatus tested for liquids of the most different viscosities because the thickness of the adhering layer is always the same.

Pressure Regulation

For the instruments shown in Figures 5 and 6 any generator of imposed pressure may be used, among others that cited by the author (*1*, *7*), which is also provided with the suspended level (Figure 7).

The water admitted at *d* is so regulated that it flows out of the upper level vessel, *A*, through the small overflow, *b*, in a moderately strong stream. Cocks *l* and *k* are kept closed. By raising or lowering *A* the desired pressure is produced in *C* and can be read off from the water manometer, *D*.

At the lower end of tube *e*—from which the water flows from the upper level vessel into the lower one—a suspended level is formed (shown in insert). Otherwise surface tension effects at this point produce fluctuations in the column height. The overflow, *b*, sometimes fails to function uniformly because the water wets the overflow edge poorly. This trouble is, however, eliminated by suspending a wire, bent to U-shape and wound with a thick woolen thread, in the overflow. By capillary action this usually keeps the upper level constant.

Interfacial Tension by the Capillary Rise

The usual instruments for the determination of the capillary constant by the height of ascent method resemble the Ostwald viscometer. The capillary rise is determined by measuring the height of the meniscus in the capillary above the surface in the vessel. Here are obviously encountered the same difficulties as in the determination of the viscosity. Michaelis (*4*) recommended, instead of determining the difference in height between the capillary meniscus and the level surface, immersing two capillaries of different diameter in the liquid to be examined and reading off the difference in height, which is proportional to the surface tension. The difficulties can, however, be more easily obviated by the suspended level. A suitable instrument (Figure 8) differs from the viscometer (Figure 4) in that the large bulb, *A*, above the capillary is eliminated and the narrower capillary carries a millimeter scale beginning at zero.

The instrument is filled to a point between the two marks, *x* and *y*, on the lower vessel, tube 3 is closed by a finger, and at 2 the liquid is sucked up into the capillary. The finger is then removed from tube 3 with simultaneous release of suction at 2, allowing the meniscus in the capillary to drop. The position of the meniscus is then read off on the scale, and from it the capillarity constant α is calculated by the formula:

$$\alpha = \frac{1}{2} hr\gamma$$

Here *h* represents the capillary rise in cm.; *r*, the radius of the capillary in cm. (engraved on vessel *B*); and γ, the specific gravity at the experimental temperature.

In executing the measurement it is better to proceed as follows:

Tube 3 is closed with the finger and the liquid is forced by pressure applied through tube 1 into the capillary until a small drop appears at its top. This drop is carefully removed with a bit of filter paper. Tube 3 is then opened, the liquid breaks loose at the shoulder forming the suspended level, and the column adjusts itself. Depending upon the viscosity of the liquid used, this may require a prolonged period, but equilibrium is easily determined with a microscope or a reading lens.

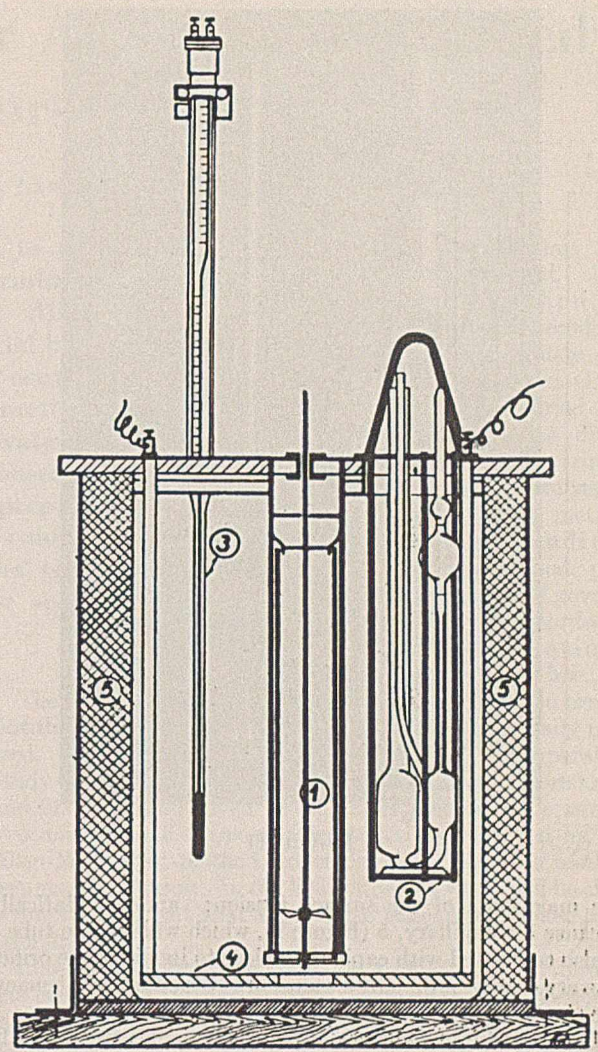

FIGURE 10

With the viscometers of Figure 4, α can be determined before or after the determination of the viscosity, but the capillaries are usually too wide to yield satisfactory results.

Dynamic Surface Tension

In the foregoing, liquids are considered as though their molecules were uniformly distributed throughout the entire mass. In the present discussion, however, hydrodynamics gives way to interfacial effects which occur through orientation and are brought about by molecular fields of force. This formation of layers influences time of drainage, and also changes the surface tension. Lenard (*2*, *3*) has treated these phenomena thoroughly from the theoretical standpoint.

The author's dynamic method presents a new means for this determination. The doming of the surface, and hence its pressure effect, can be reinforced by giving the discharge surface suitable form and size. The speed of the formation of the surface can also be varied by changing the size of the surface and the flow velocity. The tension can be measured in two ways: (1) dynamically, because the counterpressure, and with it the outflow period, must change according to

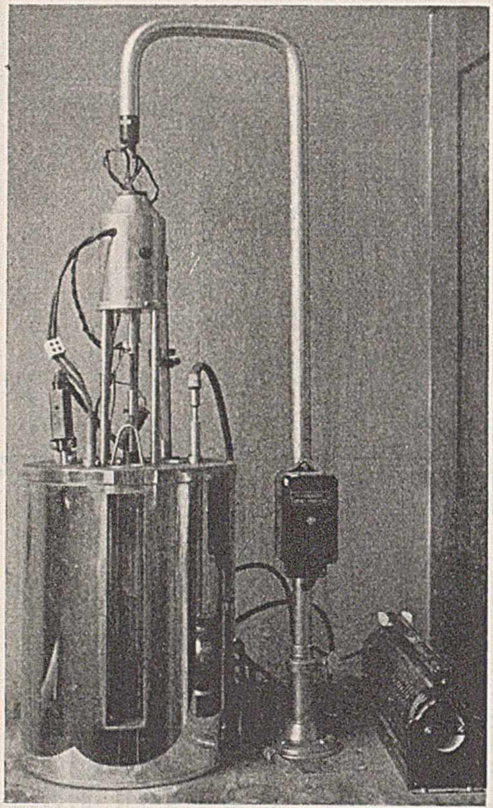

FIGURE 11

the magnitude of the surface tension; and (2) statically, because if a capillary, 5 (Figure 9), which widens into tube 6, is also connected with capillary 4 close to its discharge orifice, *a*, every change of the surface tension at the end, *a*, must change the static pressure in tube 6.

It is therefore possible simultaneously to measure statically and dynamically. The concave discharge face (*a*, Figure 9) would produce traction, while a convex one (*b*, Figure 9) would produce pressure. The respective forms of such instruments must depend upon the material to be tested and the purpose of the test. With suitable curvatures the effects can also be treated mathematically. Only when the flowing film becomes so thin that the effect of the molecular fields of force at the interfacial surface "liquid-solid" predominates does the problem become very complicated.

The instruments can be readily calibrated for a surface equal to zero. The concave or convex discharge face must either be replaced by another which is flat and therefore possesses no pressure action, or the curved discharge face can be robbed of its pressure action by immersion in liquids. If desired, tube 3 can be omitted, wide tube *C* being ground obliquely at its lower end. In this case the suspended level is produced by air entering *C* below as the end of the tube is withdrawn from the liquid in a vessel placed below.

The new measuring method could perhaps be utilized for the study of anisotropic surface tension in the Ostwald sense (*5*). With rodlet dispersoids or mesomorphic forms, rodlet-shaped molecules, after flowing through the capillary, could spread out in the suspended layer parallel to its surface, and thus show one type of surface tension, while other methods yield other types.

With mineral oils the surface tension may be of special interest because of its relationship to the internal pressure, compressibility, absorption velocity, dielectric constant, and related factors, and might open up new insights into semidry friction (also a problem of the flowing film). The author will shortly communicate more on this question which he broached (*8*) previously.

Thermostats

In conclusion, mention is made of the thermostats for practical use with all the instruments mentioned.

The first thermostat, shown in Figures 10 and 11, is intended for measurements at any temperature desired. It consists of an insulated water bath provided with electric heating, and by means of a contact thermometer can be adjusted to any temperature. A motor provides for vigorous stirring of the liquid. The suspended instruments, for which three openings are provided, can be observed through windows in the jacket.

If the measurement need not be made at predetermined temperatures—such, for example, as in the determination of the viscosity with the aid of viscosity-temperature tables—use is advantageously made of the ebullition thermostat shown in Figure 12 which operates with certainty and simplicity. Here the viscometer is suspended in the vapor space, while the thermostat liquid is heated to vigorous boiling. In the critical interval—that is, along the capillaries—the use of constant-boiling liquids yields a temperature accuracy of at least ±0.1° C. To avoid unnecessary condensation on the walls, the glass vessel is surrounded by insulation, in which windows are cut to permit the making of observations.

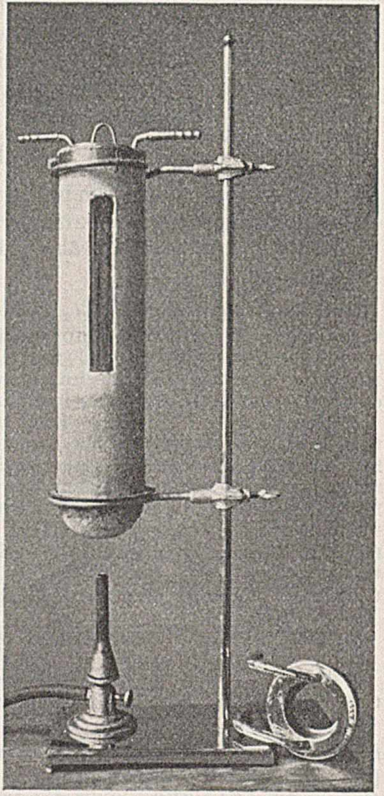

FIGURE 12

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RECEIVED December 19, 1936. This paper is an abstract prepared from a more extensive dissertation on this subject appearing in *Oel und Kohle*, containing a complete theoretical and experimental analysis of the subjects here treated. Dr. Ubbelohde is represented in the United States by the Fish-Schurman Corp., 250 East 43rd St., New York, N. Y.

Determination of Higher Alcohols in Distilled Liquors

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Attention is directed to defects in the various methods of determining fusel oil in distilled liquors. The Allen-Marquardt procedure, which is official in this country, reports only 60 to 70 per cent of the correct amount. Colorimetric methods are shown capable of giving accurate results when certain precautions are observed. Detailed directions are given for preparing the sample and carrying out the color reaction. In the opinion of the authors, the colorimetric method is unrivaled for speed, accuracy, and sensitivity.

A DISTILLED liquor may be regarded as an ethanol-water solution containing small quantities of certain secondary constituents (*2*) which usually amount to less than 1 per cent of the whole.

The secondary constituents, which impart to the beverage its characteristic flavor and bouquet, may be divided into three groups: (a) substances derived from the original grain or other starting material by the processes of fermentation, distillation, etc.; (b) reaction products formed during aging, particularly as a result of esterification and oxidation; (c) flavor-producing substances added or extracted from wood.

The first group—i. e., the flavor-producing materials which are inherent in the freshly distilled liquor—consist chiefly of the higher alcohols and their esters. The higher alcohols are grouped together under the collective designation fusel oil, which in analytical practice includes not only the free alcohols but also those portions which are esterified, the esters being decomposed by saponification before the higher alcohols are determined.

Fusel oil content furnishes one of the principal criteria for judging the type, quality, and purity of a distilled liquor, and for this reason its determination is of importance in the chemical examination of such a beverage. The various methods of fusel oil determination depend either upon an approximate separation of the higher alcohols from the ethanol-water solution by means of extraction, or on colorimetric reactions exhibited by the higher alcohols but not by ethyl alcohol. The available methods are defective in various ways, results varying not only with the method used but also to some extent with the analyst applying the method.

It is the purpose of the present paper to point out defects in the existing methods and to present what is believed to be an approach to a more satisfactory procedure.

Extraction Methods

In the Rose-Herzfeld procedure (*13, 18*) the sample is shaken with a measured volume of chloroform and the higher alcohols are estimated from the increase in volume of the extractant. This method usually gives results of the correct order or magnitude. Difficulties cited by Schidrowitz (*21*) in applying the method to whisky are easily avoided in practice. The Rose-Herzfeld method is, however, subject to the limitation that the different higher alcohols are distributed differently between the two phases and the result is therefore dependent upon fusel oil composition.

The same objection applies with greater force to the Beckmann-nitrite (*4*) and Allen-Marquardt (*1, 2, 3, 5, 14, 15*) procedures, in which a partial separation of the higher alcohols is effected by successive extractions with carbon tetrachloride, the extract is purified by washing, and the higher alcohols are then estimated chemically. The Beckmann method has been tested experimentally by a number of workers (*5, 17, 22*) but has never been widely used. The Allen-Marquardt method, on the other hand, is the mode of determination most widely employed both here and in Great Britain, and when carried out in accordance with the directions of the Association of Official Agricultural Chemists (*3*) constitutes the official method in this country. Findings obtained by this method, particularly in the hands of government chemists, are accorded a respect which is sometimes equivalent to weight of law.

The method has long been known to be subject to errors, but the magnitude of these errors has not been generally realized. For example, Dudley (*7*) after making a comparative study of the Allen-Marquardt and Rose-Herzfeld procedures, and finding results given by the latter method to be two to two and one half times greater than those obtained by the Allen-Marquardt method, concluded that the Rose method was greatly in error. In the light of results which will be cited below it is evident that the reverse conclusion should have been drawn.

In the present work the accuracy of the A. O. A. C. method has been tested in various ways, the results being presented in Tables I and II. In all cases the official procedure has been followed strictly, and the results calculated to amyl alcohol.

TABLE I. ERRORS IN A. O. A. C. METHOD OF FUSEL OIL DETERMINATION

(Ethyl alcohol; 50 per cent by volume)

No.	Higher Alcohols	Total Concentration of Higher Alcohols Present	Found	Yield
		Grams/100,000 cc.		%
1	Mixture of isoamyl and isobutyl in ratio of 4 to 1	41	32	78
2	Mixture of isoamyl and isobutyl in ratio of 4 to 1	81	46	57
3	Mixture of isoamyl and isobutyl in ratio of 4 to 1	163	89	55
4	Mixture of isoamyl and isobutyl in ratio of 4 to 1	244	127	52
5	Mixture of isoamyl and isobutyl in ratio of 4 to 1	325	142	45
6	Mixture of isoamyl and isobutyl in ratio of 4 to 1	410	172	42
7	Isopropyl	40	11	28
8	*n*-Propyl	39	11	28
9	*n*-Butyl	40	21	52
10	Rye fusel oil	100	69	69
11	Rye fusel oil	300	194	65

The figures of Table I indicate that the errors in the A. O. A. C. method vary both with the composition and concentration of fusel oil, and hence no single correction factor can be applied to all cases. The percentage accuracy with rye fusel oil is somewhat larger than with the synthetic mixture of isoamyl and isobutyl alcohols. Apparently the method may be expected to report on the average about 60 per cent of the total fusel oil actually present, though under certain conditions the accuracy may be as low as 40 per cent.

The data of Table II were obtained by adding weighed quantities of the higher alcohols to carbon tetrachloride and oxidizing with the bichromate–sulfuric acid mixture according to the A. O. A. C. Percentage yields here are larger than for the whole process. This indicates that the errors in the method occur partly in the oxidation stage and partly in the extraction stages. Errors in the extraction stage of the Allen-Marquardt method have been demonstrated by Bedford and Jenks (*5*) and by Mitchell and Smith (*16*). The last-named investigators also proposed the use of alkaline permanganate instead of the bichromate mixture for oxidizing the higher alcohols. From time to time various other changes in procedure have been suggested, as, for example, oxidation in closed tubes or at carefully controlled temperatures (*14*). While it is possible that some of these modifications might result in a more nearly quantitative conversion of the higher alcohols to acids, there would remain the rather large and variable errors which occur in the extractive stages of the method.

TABLE II. ERRORS IN OXIDATION OF HIGHER ALCOHOLS TO ACIDS BY A. O. A. C. METHOD

Concentration of Higher Alcohols Present	 Found	Yield
Grams/100,000 cc.		%
163	144	
163	139	87
325	260	
325	245	79

The A. O. A. C. method is materially affected by variations in technic and by uncontrolled factors, such as the temperature at which the extraction steps are carried out. This probably accounts for the well-known fact that when identical samples are analyzed by different operators, both observing the letter of the method, divergent results are sometimes reported. Table III shows a comparison of results obtained by this laboratory and another on a series of six samples of distilled liquors. It will be noted that in two cases the corresponding figures differ by as much as 20 per cent. Much larger discrepancies were found in a series of coöperative tests carried out under the auspices of the A. O. A. C. (*23*), although in this case amyl was the only higher alcohol used. Figures reported by eleven different laboratories ranged from 42 to 145 per cent of the total amyl alcohol actually present. The method employed differs slightly from the present form.

TABLE III. COMPARISON OF A. O. A. C. RESULTS FROM TWO LABORATORIES

No.	Fuel Oil by A. O. A. C. Method Laboratory A	 Laboratory B
1	116	103
2	102	99
3	148	117
4	134	105
5	96	81
6	53	61

Despite the above-mentioned defects the Allen-Marquardt method is capable of giving fairly reproducible results, when carried out by the same operator, using the same equipment, duplicate determinations usually agreeing to within 5 grams per 100,000 cc. The figures so obtained may be regarded as a rough comparative index of fusel oil content, and are therefore of some practical utility in the control of plant operations.

Colorimetric Methods

Colorimetric methods of fusel oil determination utilize the so-called Komarowsky reaction (*11*) by which colored products are formed through the interaction of higher alcohols with cyclic aldehydes in the presence of concentrated sulfuric acid. In the earliest form of the method (*20*) the sample was treated with sulfuric acid alone. The resulting color was due largely to the small and variable quantities of furfural occurring naturally in the liquor and hence failed to furnish a reliable measure of fusel oil content.

The Komarowsky reaction has been studied extensively by Swiss and German chemists (*6, 8, 12, 19*). Aldehydes which have been employed as reagents include the following: salicylaldehyde, benzaldehyde, *p*-dimethylaminobenzaldehyde, furfural, veratric aldehyde, and vanillin. In one study (*10*) the last-named reagent was given a special use as a precipitant.

The work of von Fellenberg indicates that the higher alcohols are converted by the action of sulfuric acid into unsaturated hydrocarbons, which then combine with the cyclic aldehyde to form colored products (*9*). (This investigator after an extensive study finally abandoned the colorimetric method of fusel oil determination, for reasons which the writers have not found to be conclusive. In fact, difficulties cited by this worker have been of value to the present authors in pointing the way to optimum reaction conditions.) The color reaction is therefore not peculiar to the higher alcohols but is exhibited in general by (a) unsaturated hydrocarbons and their derivatives; (b) substances which on treatment with concentrated sulfuric acid are converted into unsaturated hydrocarbons. This group includes aldehydes and ketones but not acids. Other interfering substances which may occur in liquors include acetals and terpenes (*2, 21*). All interfering substances must, of course, be eliminated or reduced to negligible proportions before the sample is subjected to the colorimetric methods.

In the present work the sample has been prepared by a treatment which decomposes acetals and terpenes and fixes all but a negligible portion of aldehydes. This treatment embodies features used by various other workers.

Various reagents and treatments have been employed for the removal of aldehydes. These include *m*-phenylene diamine hydrochloride (*1*), which Schidrowitz and Kaye (*22*) found to be less effective than phenylhydrazine *p*-sulfonate; *p*-nitrophenylhydrazine; and saponification with silver oxide catalyst. In the present work, the last-named treatment has been found to be the most effective.

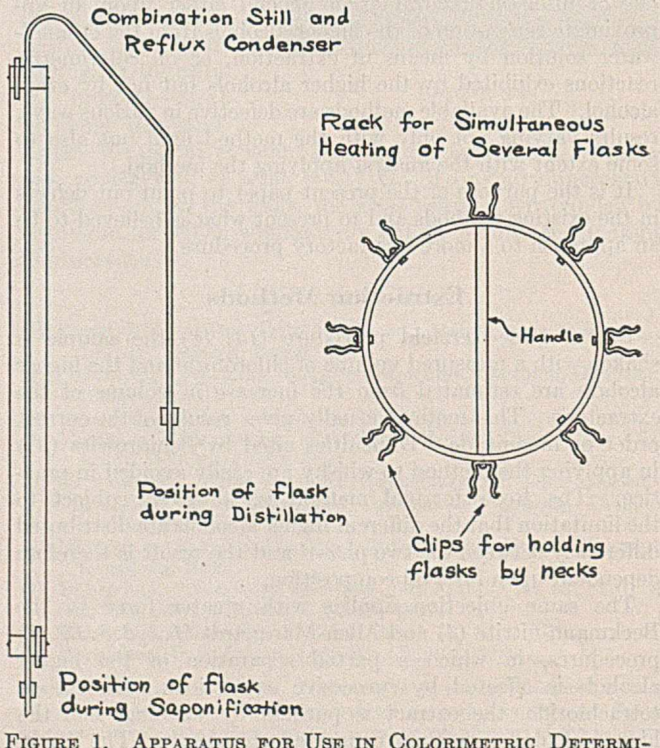

FIGURE 1. APPARATUS FOR USE IN COLORIMETRIC DETERMINATION OF FUSEL OIL

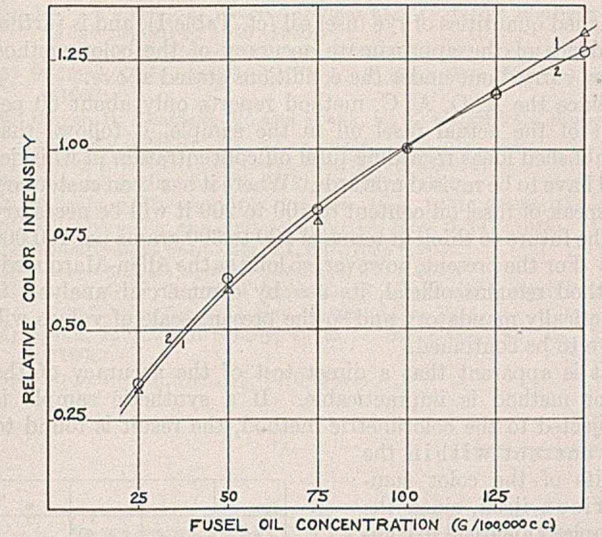

Figure 2. Relation between Fusel Oil Concentration and Color Intensity

Preparation of Sample. Place 25 cc. of sample in a 500-cc. round-bottomed flask. Add 0.5 gram of silver sulfate and 1 cc. of (1+1) sulfuric acid, and make the total volume up to 110 cc. Reflux gently for 15 minutes. Make the solution alkaline with 5 cc. of (1+1) sodium hydroxide solution, and reflux for 30 minutes. Bumping can be prevented by the addition of small quantities of granulated zinc. If foaming occurs, this can be reduced by adding 15 grams of sodium chloride. The addition of salt results in a partial conversion of silver oxide to silver chloride, but this fact does not appear to affect the efficiency of the silver as a dealdehyding agent.

After the saponification the sample is distilled, 75 cc. of distillate being collected. This distillate contains all of the higher alcohols originally present in the sample. The concentration has been reduced to one-third that of the sample. This reduction in concentration is made necessary by the extreme sensitivity of the color reagents.

General Direction for the Color Reaction. In carrying out the color reaction it is necessary to select proportions and other conditions which will result in a clear solution whose color intensity is suitable for examination in the colorimeter. The following factors must be controlled: (1) amount of sample, (2) amount of reagent, (3) amount of concentrated sulfuric acid, (4) concentration of ethyl alcohol, (5) temperature and time of heating to develop the color, (6) amount of diluent added after terminating the reaction, and (7) concentration of sulfuric acid in the diluent solution.

The reaction is not allowed to go to completion but is arbitrarily stopped after a definite length of time by chilling the reaction mixture and diluting. It is therefore necessary to run standards and sample side by side under exactly similar conditions.

Different color reagents demand slightly different conditions for optimum results. The reagents and procedures which the authors have found most useful are given below.

Procedure with *p*-Dimethylaminobenzaldehyde or Salicylaldehyde. Place 2.00 cc. of the distillate, obtained as directed above, in a 125-cc. Florence flask. Add 20.0 cc. of concentrated sulfuric acid, swirling the flask in a bath of cold water during the addition. Then add 2.00 cc. of a solution of the reagent in 95 per cent ethyl alcohol (10 mg. per cc.), again swirling the flask in cold bath.

Prepare a similar flask containing 2.00 cc. of a standard fusel oil solution, acid, and reagent.

Place the flasks simultaneously in a bath of vigorously boiling water. After 20 minutes transfer the flasks to the cold bath. When cool add 25 cc. of (1+1) sulfuric acid and mix thoroughly by swirling. The solutions are then ready for comparison in the colorimeter.

Procedure with Vanillin. Proceed as directed above for the other two reagents, except for the following differences: (a) use only 10 cc. of concentrated sulfuric acid in making up the reaction mixture; (b) the vanillin solution contains 17.5 mg. of reagent per cc. of 95 per cent ethyl alcohol.

Reagents and Apparatus. The aldehydes and other reagents used in the colorimetric work were of c. p. grade not further purified.

c. p. alcohol containing only a trace of fusel oil should be used in making up standard solutions, etc.

No specialized apparatus is required either for the preparation of sample or for the color reaction. Figure 1 shows simplified equipment which has been found convenient in the present work. The colorimeter used was of the Duboscq type.

Relation between Fusel Oil Concentration and Color Intensity. When the above procedure is applied to a series of solutions of varying fusel oil content, the resulting color intensities are nearly but not quite proportional to fusel oil concentration. Calibration curves for the three reagents are shown in Figure 2. The color intensities are of course only relative, that for 100 grams per 100,000 cc. being taken as unity.

With increasing concentration of fusel oil there is a slight shift in color tone from red towards purple. This fact makes it desirable in practice to compare the sample with a standard of approximately equal fusel oil content.

Standard Fusel Oil Solutions. The success of the colorimetric method depends upon the use of accurate and reliable color standards. The most satisfactory standard is a solution containing a weighed quantity of actual fusel oil of the same type as that contained in the sample.

The standard fusel oil used in the present work was obtained from a sweet-mash rye whisky of the Maryland type. The process of obtaining the fusel oil is itself capable of use as an analytical method with moderate-sized samples (1 liter). When applied to larger samples, fusel oil is obtainable in amounts sufficient for fractional distillation to determine the amounts of each alcohol present. Work of this nature is now in progress, and is expected to be presented in a forthcoming publication.

Where a standard fusel oil is not available, a satisfactory working standard for colorimetric work can be prepared by mixing isoamyl (b. p. 132) and isobutyl alcohols in the ratio of 4 to 1. The resulting color shades match fairly closely those given by sweet-mash rye fusel oil. When the reaction is carried out as described above, the synthetic mixture is slightly weaker than fusel oil, the ratio being 0.95 for *p*-dimethylaminobenzaldehyde or salicylaldehyde and 0.90 for vanillin. In using a synthetic standard, the colorimeter reading should in each case be multiplied by the appropriate factor.

The percentage of ethyl alcohol in the standard should be approximately the same as in the prepared sample, or 15 per cent by volume in the case of liquors originally 90- to 100-proof. A convenient fusel oil concentration for the standard has been found to be 100 grams per 100,000 cc.

Color Reactions of Individual Higher Alcohols. When tested separately, the various higher alcohols exhibit very different color intensities, isobutyl being strongest when either vanillin or *p*-dimethylaminobenzaldehyde is used as reagent. With salicylaldehyde the strongest color intensity is given by *n*-amyl alcohol. The relative color intensities are shown in Figure 3, which was obtained by carrying out the color reaction on 0.100 per cent solutions of each of the higher alcohols and comparing the resulting color intensities with that given by isoamyl.

Errors due to differences between the individual alcohols are largely eliminated by the use of real fusel oil as standard, or by the accurate calibration of the working standard against actual fusel oil. Where an accurate fusel oil standard is not available, either salicylaldehyde or *p*-dimethylaminobenzaldehyde is preferable to vanillin, since for the higher alcohols

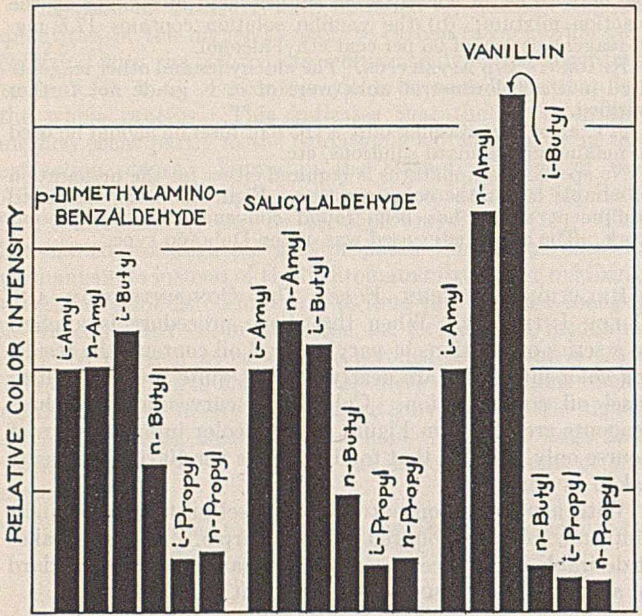

Figure 3. Relative Color Intensities Given by Individual Higher Alcohols

which make up the greater part of fusel oil, more nearly equal color intensities are given by the first two reagents. In general the use of two or more reagents on the same sample is desirable because a comparison of the results gives information as to the type of fusel oil, and abnormal samples may be detected.

The individual higher alcohols differ also in the exact shade of color produced. Amyl alcohol gives a slightly redder shade, while butyl and propyl alcohols tend more towards purple. Variation in color shade thus furnishes an indication as to type of fusel oil.

Comparison of A. O. A. C. and Colorimetric Methods

Fusel oil has been determined in a considerable number of whiskies by both the A. O. A. C. and colorimetric methods, the results being shown in Figure 4. The open circles represent actual whisky samples while the black circles refer to synthetic solutions containing weighed quantities of isoamyl and isobutyl alcohols in the ratio of 4 to 1. In the case of the latter points the ordinates represent actual content of higher alcohols. These points thus afford a rough calibration of the A. O. A. C. method. It will be noted that they fall well within the area over which the actual whisky points are spread. This is an indication that the colorimetric results are at least approximately correct.

A further comparison of the two methods is shown in Table IV where A. O. A. C. results on three rye whiskies are compared with the results given by three colorimetric reagents.

Table IV. Fusel Oil Content of Three Rye Whiskies (White) by A. O. A. C. and Colorimetric Methods

(Grams per 100,000 cc. of 100-proof spirits)

Sample No.	A. O. A. C. Method	Colorimetric Method		
		Vanillin	p-Dimethyl-aminobenz-aldehyde	Salicyl-aldehyde
175985	133	192	198	201
175996	123	197	194	206
176144	168	267	255	276

The A. O. A. C. figures are 62 to 67 per cent of the colorimetric. This ratio agrees well with the percentage yields obtained when the A. O. A. C. method is applied to solutions containing weighed quantities of rye fusel oil (cf. Table I), and is further evidence of the approximate accuracy of the color method when carried out under the conditions stated above.

Since the A. O. A. C. method reports only about 60 per cent of the actual fusel oil in the sample, it follows that established ideas regarding fusel oil concentration in whiskies will have to be revised upwards. Where it has been customary to speak of fusel oil content of 100 to 200 it will be necessary in the future to think in terms of 200 to 300 grams per 100,000 cc. For the present, however, so long as the Allen-Marquardt method remains official, its use by commercial analysts is practically mandatory and so the present scale of values will have to be continued.

It is apparent that a direct test of the accuracy of the color method is impracticable. If a synthetic sample is subjected to the colorimetric method, the result is found to be correct within the limits of the color comparison itself, since the sample is identical in composition with the standard used in the color reaction. The only possible discrepancy would be due to loss of fusel oil during the preparatory treatment of sample (saponification, distillation, etc.). By trial it has been found that no such loss occurs. Maximum errors due to inaccuracies in the volume measurements and the color comparison should not total over 2.5 per cent of the final result.

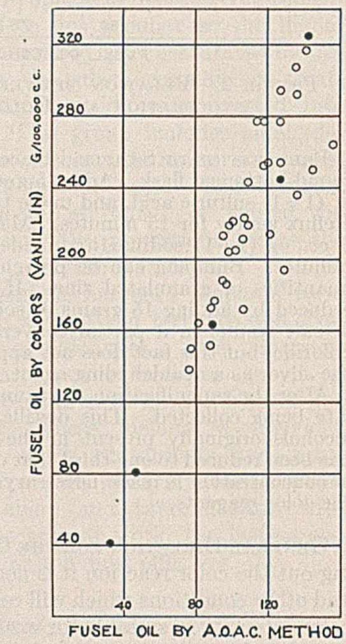

Figure 4. Comparison of Colorimetric and A. O. A. C. Methods of Fusel Oil Determination

The colorimetric method offers the following advantages:

The time required for the determination is less than by any other method.

The sensitivity of the method is far greater than that of any other. By virtue of its sensitivity the colorimetric method is applicable to low-proof beverages, such as wines and beers, in which fusel oil has not hitherto been determined.

Abnormal or unusual samples are readily detected by off-shades of color and by the use of two or more color reagents on the same sample.

The method yields results of the correct order of magnitude.

The colorimetric method possesses the following disadvantages:

The sample must be given a rigorous pretreatment to eliminate interfering substances.

For accurate work it is desirable to use as the colorimetric standard a sample of actual fusel oil of the same type as that contained in the sample.

The individual alcohols exhibit different color intensities, and the result is therefore dependent on composition of fusel oil. This source of error is very largely, though not entirely, eliminated by the use of fusel oil standards.

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Support for Perforated Platinum Crucibles

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THE need has long been felt for a holder that would support both the cap and the receptacle proper of the Gooch filtering crucible (*1*) during a high-temperature ignition. If a triangle be selected to accommodate the cap, the small system is somewhat lacking in stability; whereas, if a larger triangle be chosen, the hot cap (especially during the early stages of the heating) may fall to the work table. Using two rings, placed one above the other, becomes impracticable for small crucibles, since with ordinary rings the upper and lower triangles are located too far apart.

The contrivance here depicted, after a design by one of the authors (J. G. S.), has been found to serve admirably and permits the treatment of perforated crucibles differing considerably in size.

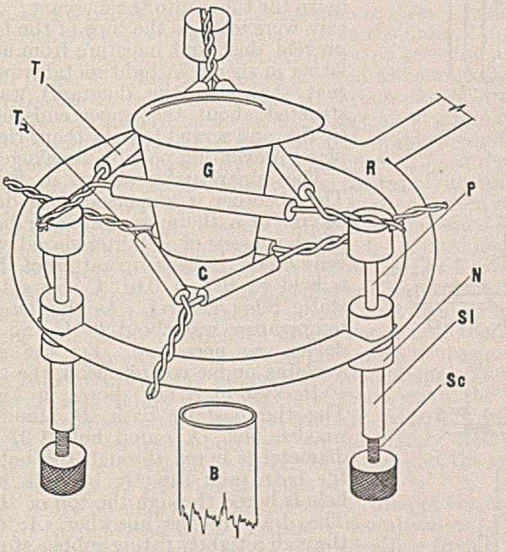

FIGURE 1. DIAGRAM OF APPARATUS

P, total length, 37 mm.; diameter, 3.5 mm.; height of head, 7 mm.; diameter of head, 9 mm.; diameter of groove, 3.5 mm.; depth of groove, 2.5 mm.

Sl, total length, 35 mm.; external diameter, 5 mm.; internal diameter (exclusive of threaded portion), 3.75 mm.; height of head, 4 mm.; diameter of head, 9 mm.; height of supporting nut *N*, 5 mm.; diameter of nut, 9 mm.

Sc, total length, 40 mm.; diameter (exclusive of grooved head), 3 mm.; height of knurled nut, 7 mm.; external diameter of nut, 9 mm.; internal diameter of nut, 7 mm.; depth of cylindrical cup in nut, 3 mm.

Construction

An 8.3-cm. (3.25-inch) cast-iron ring, *R*, is notched at three places equidistant from one another, preferably at the points where the little projections extend inward, so as to produce six level spaces about 5 by 10 mm. each—three above and three below. At the approximate center of each of these rudely rectangular areas a hole is drilled and subsequently threaded, and into this opening sleeve *Sl*, the upper and slightly larger third of which (exclusive of the cylindrical head) is reciprocally threaded, is fitted by turning downward until the head rests snugly upon the flattened part of the ring, where it is firmly held by tightening nut *N*.

The slender rod, *P*, with grooved head rests loosely in the sleeve and naturally falls to the lowest level permitted by screw *Sc*. This long thin screw is without taper, terminates in a rounded and grooved head, is threaded throughout its length, and a knurled nut is attached to it by virtue of its own threads. Sleeve *Sl*, starting at its lower end, is threaded for a short distance, where its internal diameter is a little less than that of the remaining portion; these threads control the up-and-down movements of screw *Sc*.

The rod, sleeve, and screw were machined from mild steel.

Manipulation

The smaller triangle, T_2, lies on ring *R* and the twisted ends of the larger triangle, T_1, rest in the grooves of the three rods, *P*. By turning the screws, *Sc*, triangle T_1 can be brought into a horizontal plane parallel to the one defined by ring *R*, and can be raised or lowered to any desired level. It is thus easy to set triangles T_2 and T_1 just tangent at three points to cap *C* and crucible *G*, respectively, rendering the entire apparatus stable.

Triangles made of nichrome wire covered with fused-silica ("vitreosil") tubes, the one measuring 3.8 cm. (1.5 inches) and the other 5.1 cm. (2 inches) on a side, are well suited to a 20-ml. perforated platinum crucible of the usual form, and when properly adjusted stand about 15 mm. apart.

The steel parts of the outfit have not as yet been observed to burn, even when the full power of the Tirrill burner, *B*, was being utilized. Rusting may be prevented by coating them with light machine oil when not in use.

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Precise Determination of Carbon Dioxide in Air

Hand-Operated Apparatus

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IN SOME investigations on the photosynthetic or respiratory activity of leaves, using the absorption or excretion of carbon dioxide by the leaf as the criterion of activity, it was necessary to construct a hand-operated apparatus which would determine the carbon dioxide content in 2.5 liters of air whose carbon dioxide content ranged from 65 to 125 per cent of that of ordinary air with a maximum error of 2 per cent and an average error of approximately 1 per cent of the atmospheric concentration, and allow of 2 or 3 determinations an hour. Because certain field conditions were unsuitable for the operation of the apparatus for determining the carbon dioxide, the air samples were collected in containers, transported into the laboratory, and determined at leisure. This apparatus, while not having the advantages and possibilities of an automatic apparatus such as that of Thomas (*9*), is cheaper and easier to construct. Besides being almost entirely assembled from standard laboratory equipment, it could be adapted to various problems involving the measurement of carbon dioxide, and should prove useful in the investigation of air pollution, animal respiration, and other biological problems, especially where small quantities of carbon dioxide are involved.

In the development of the apparatus, the method of Rideal and Taylor (*7*) was considered, but because of difficulty in controlling the rate of flow of alkali and the time-lag factor involved in obtaining readings it was rejected. Some experiments were made to increase the accuracy of the potentiometric method of Wilson, Orcutt, and Peterson (*11*), but errors caused by drift of the glass electrode and electrical leakage were much in excess of the accuracy demanded. The method of Heinicke and Hoffman (*2*) is readily adapted to measurements on large volumes of air, but the error inherent in titration and manipulation becomes too large when small volumes of air are used. Thomas (*9*) describes an absorber capable of removing all the carbon dioxide from a stream of normal air moving at a rate of 350 cc. per minute by means of 40 cc. of 0.0052 *N* sodium hydroxide with 0.4 per cent *n*-butyl alcohol. His absorber includes a fritted glass plate to break the air stream into fine bubbles, and a small amount of butyl alcohol in the dilute sodium hydroxide solution to depress the surface tension of the solution, allowing the bubbles to persist and thereby increasing efficiency of absorption. The maximum error of the total concentration of the carbon dioxide in the air was found to be less than 1 per cent. A hand-operated apparatus as outlined by Thomas (*9*) seemed most promising, and the apparatus described below is in large part based on it.

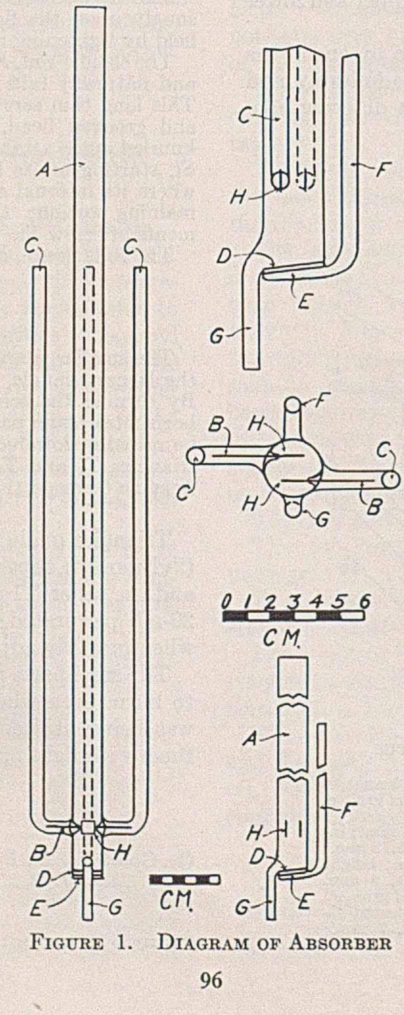

FIGURE 1. DIAGRAM OF ABSORBER

Description of Apparatus

The apparatus developed for measuring the carbon dioxide content of the air consists primarily of an absorber, as shown in Figure 1, which is designed to hold dilute alkaline solutions for the absorption of carbon dioxide and to measure the electrical conductivity of the solutions.

The absorber is made entirely of Pyrex glass and consists essentially of a glass tube, *A*, 75 cm. long, having an inside diameter of 25 mm. The absorber is provided with a fritted-glass plate at *D*, sealed in at an angle of about 10 degrees to the horizontal. The plate is made of 80-mesh glass according to the method of Bruce and Bent (*1*), and is 4.5 mm. thick. Below the fritted-glass plate is a small septum, *E*, into which a tube, *F*, of 6-mm. outside diameter is sealed. A drain, *G*, made of 6-mm. glass tube and 4 cm. long, is sealed into the absorber just above the fritted plate, so that the absorber can be drained of solution, except for a small residual amount of less than 1 cc.

The electrodes, *H*, are platinized-platinum plates 1 cm. square and are welded to tungsten shanks, *B*, about 0.7 mm. in diameter and 2.5 cm. long. The electrodes are parallel, in a vertical plane, and 1 cm. apart. The welding of the platinum plates to the tungsten shanks is accomplished by welding platinum beads to the ends of the shanks in the oxy-gas flame, and electrically spot-welding the platinum plates to the beads. The shanks are sealed in the glass tube and are covered with a coating of glass as far as the plates. The other ends of the shanks extend into 1-cm. glass tubes, *CC*. In order to obtain electrical connection with the plates, tubes *CC* were filled with mercury to a depth of 3 cm. and copper wires run down the tubes into the mercury. Rubber caps were fixed on the tops of the tubes to prevent dust and moisture from accumulating in them. A light metal framework (not shown in the diagram) was constructed about the upper ends of tubes *CCFA*, and served to hold them rigidly in place, preventing possible breakage.

The apparatus is shown in Figure 2. The absorber is immersed to a depth of 30 cm. in a thermostatic water bath, *B*, which consists of a 19-liter glazed earthenware crock. The temperature of the bath is held to 30° ± 0.01° C. by a thermostatic relay control. As the laboratory temperature was about 26° C., no cooling device was necessary. For the sake of avoiding undue complication, the thermostatic system is not shown in Figure 2. The thermostatic bath, *B*, stands on a wooden box. A round hole 1.27 cm. in diameter is bored through the bottom of the bath, and directly beneath another hole is bored through the top of the box. The drain of the absorber, *A*, extends through a tightly fitting rubber stopper in the bottom of the bath. A short length of rubber tubing provided with a clamp is fitted on the drain at *C* so that the absorber can be drained at will, and a beaker is used to collect drained solutions.

The absorbing solution, consisting of 0.00488 *N* sodium hydroxide with 0.4 per cent *n*-butyl alcohol, is stored in a 19-liter bottle, *E*, which is provided with a soda-lime U-tube, *F*, to prevent the solution

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from absorbing carbon dioxide from the air. The solution is measured into the absorber by means of a 50-cc. refill pipet, *D*, which is provided with a soda-lime U-tube, *G*, to prevent carbon dioxide absorption. A rubber stopper is tightly fitted in the top of the absorber, and the delivery tube of the pipet extends through this stopper into the absorber. A water suction pump, *M*, provides vacuum for aspirating the air through the absorber. A water trap, *L*, consisting of a 1-liter Erlenmeyer flask, prevents possible sucking back of water into the absorber if the water pressure falls. A three-way stopcock at *I* is used to regulate the suction as desired. When the suction is stopped, air passes through the soda-lime U-tube, *H*, is freed of carbon dioxide, and equalizes the pressure in the absorber with the atmospheric pressure. In this way a small continued flow of air through the absorber due to a remaining partial vacuum in the absorber, which might disturb the conductivity measurements, is prevented. The air intake of the absorber is at *Q*, which leads to a three-way stopcock, *J*. A long soda-lime tube, *N*, provides carbon dioxide–free air for the absorber when desired. A float-valve which prevents water from entering the absorber, but permits air to pass, is provided at *O*. The bend, *S*, prevents condensed water from draining into the absorber, and a short side tube, *R*, with a short length of rubber tubing and a clamp, collects the water and can be periodically drained.

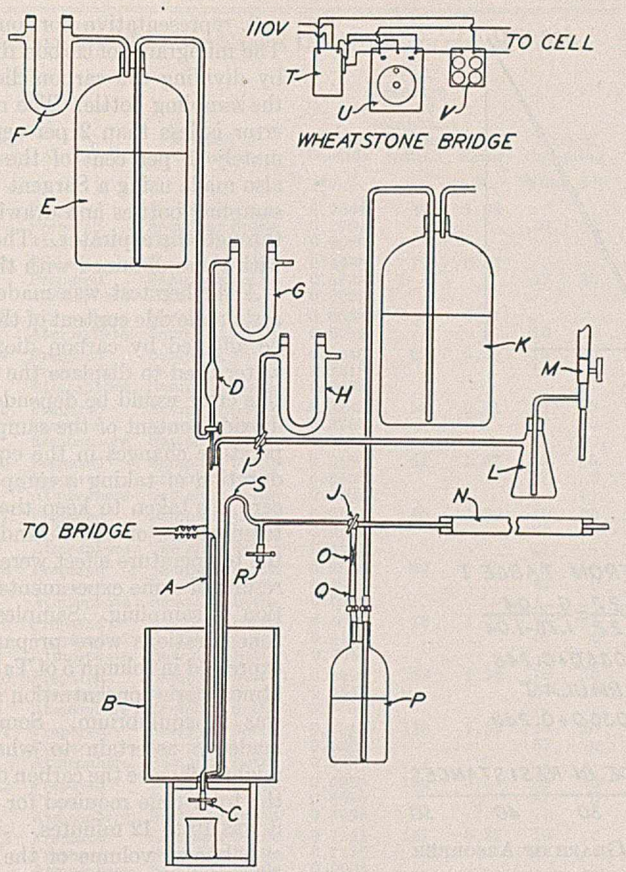

FIGURE 2. APPARATUS FOR DETERMINING CARBON DIOXIDE IN AIR

Manipulation of Apparatus and Analyses

In making a determination, the absorber is given a preliminary rinsing with the absorbing solution. Then the drain, *C*, is closed and 50 cc. of absorbing solution are pipetted into the absorber by refill pipet, *D*. The solution is allowed to come to the temperature of the thermostatic bath, and carbon dioxide–free air is passed through the solution for about 30 seconds at a rate of about 300 cc. per minute to stir the solution and establish equilibrium. This is done by turning the three-way stopcock, *J*, so that air is drawn through the soda-lime tube, *N*, and then applying suction by turning the three-way stopcock, *I*. The suction is then removed by turning stopcock *I*, and the resistance of the quiescent solution is measured by applying the Wheatstone bridge and taking a reading when a steady value is reached, which occurs in a few minutes. Samples of air are collected in 2.5-liter Baker Chemical Co. bottles, *P*, which are fitted with rubber stoppers and two glass tubes. One tube extends to the bottom of the bottle and the other is flush with the stopper. The outside ends of the tubes are fitted with short lengths of rubber tubing and screw clamps. The rubber stoppers are also tightly tied with cord to the necks of the bottles, so that they cannot work out to let leakage occur. The volumes of the bottles ("sampling bottles") are accurately determined. A sample of air is obtained as described below, and the sampling bottle sealed off by screwing the clamps tight.

When ready for analysis, the short glass tube of the sampling bottle, *P*, is connected to the intake of the absorber at *Q*, and the long glass tube is connected to a tube leading from a 19-liter bottle, *K*, which is filled with distilled water whose carbon dioxide content is maintained in equilibrium with that of the outside atmosphere by leading air in from outside and bubbling through the water. Then the three-way stopcock, *J*, is turned so that the sampling bottle, *P*, is connected to the intake of the absorber. The clamps of the bottle are released and suction is applied by turning *I*. The air is aspirated through the absorber at a rate of 350 cc. per minute, and is replaced by distilled water from *K*. As soon as the sampling bottle is filled with water, *J* is turned so that air remaining in the tube is washed through the absorber by carbon dioxide–free air from *N*. The carbon dioxide–free air is allowed to aspirate 30 seconds and the suction removed. The final resistance of the solution is measured as before. The difference between the initial and final resistances of the solution is obtained, and the amount of carbon dioxide absorbed is obtained from a calibration curve which gives the relation between the differences in initial and final resistance and the carbon dioxide absorbed.

The construction of the calibration curve and calculation of carbon dioxide are discussed below. For the Wheatstone bridge a 110-volt, 60-cycle alternating current was used as a source of electrical energy. A diagram of the bridge is given in the upper right-hand corner of Figure 2. It consists of Leeds and Northrup equipment, an alternating current galvanometer with lamp and scale, a Kohlrausch slide wire with auxiliary resistances, and a 4-dial noninductive resistance box. The bridge is similar to one described by Leeds and Northrup (*5*).

Calibration of Absorber

A rough calculation for the absorber indicated that the absorption of the carbon dioxide of 2.5 liters of ordinary air (approximately 1.4 mg.) in 50 cc. of the absorbing solution would produce a change of approximately 30 ohms. This proved useful in ascertaining by electrical measurement when, for the construction of a calibration curve, appropriate amounts of carbon dioxide had been absorbed by the solution. The titration method of Walker, Bray, and Johnston (*10*) was used to calibrate the absorber, and the technic is similar to that employed and described by Thomas (*9*). A calibration curve was plotted using the ohms difference in resistance as abscissa and the milligrams of carbon dioxide absorbed as ordinate. The calibration curve is given in Figure 3 and is seen to be almost linear. Consequently, small variations in the initial resistances of the solutions will not introduce a significant error, since it is the difference in initial and final resistances that is considered, and a small variation in initial resistance will not sensibly change the relation between the difference in resistance and the amount of carbon dioxide absorbed. The amounts of carbon dioxide absorbed may now be obtained from the calibration curve by finding the point on the curve corresponding to the difference in resistance obtained and reading off on the ordinate the amount of carbon dioxide absorbed. This method, however, is tedious and subject to visual errors involved in obtaining the amounts of carbon dioxide absorbed. Another method is to derive a formula from the curve, relating the difference in resistance and the carbon dioxide absorbed. The method of deriving the formula is developed below.

On the basis that ordinary air contains approximately 0.55 mg. of carbon dioxide per liter, 2.5 liters will contain about 1.4 mg. In the photosynthesis and respiration studies, the carbon dioxide content of the air seldom deviated more than 30 per cent above or below the normal concentration. Therefore the portion of the curve between 1.0 and 1.8 mg. of carbon dioxide was sufficient for determinations. If a straight line is drawn joining

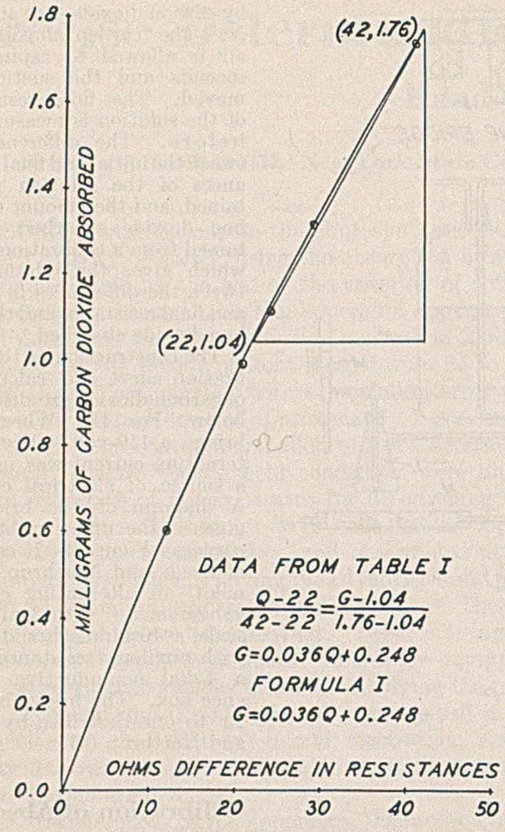

Figure 3. Calibration Graph of Absorber

the points (22, 1.04), (42, 1.76) as in Figure 3, the straight line and the curve within the interval of the points do not differ appreciably. Values may therefore be taken along the straight line without appreciable error. From analytical geometry, it is known that a straight line can be represented by a linear function. Using the two-point formula (*8*) for deriving the equation of a straight line, we obtain $G = 0.0360\ Q + 0.248$ for the equation, where G is the milligrams of carbon dioxide absorbed, and Q is the difference in resistances expressed in ohms. This formula may now be used in place of the graph. By mathematical methods it is possible to obtain more complicated formulas which would approximate the curve more closely, but the straight-line function was sufficient for the author's purpose.

Precision of Apparatus

In testing the precision of the apparatus, it was decided to make duplicate determinations on ordinary air. Two sampling bottles filled with equilibrium water were clamped in inverted positions on ringstands, which with the bottles were taken outside and placed on the roof of the Plant Science building, an elevation over 20 meters (60 feet) above the ground. The bottles were within 60 cm. (2 feet) of each other, the air circulation was very good, and there were no sources of carbon dioxide in the vicinity which might disturb the tests. The operator withdrew and the bottles were allowed to stand several minutes to dissipate any carbon dioxide from the breath of the operator. Then, holding his breath, the operator approached, unscrewed the clamps on the bottles, and immediately withdrew again. The water ran out into collecting vessels and air entered the bottles. The sampling bottles were allowed to stand in position for 30 minutes until they had reached air temperature. Then they were sealed off by screwing the clamps tight, and were taken into the laboratory where they were analyzed. Besides the samples taken on the elevation, a few samples were taken in the greenhouse and orchard. The water in the collecting vessels was poured back into the 19-liter bottle, *K*, Figure 2, and used over again.

A representative portion of the data is given in Table I. The milligrams of carbon dioxide per liter of air are obtained by dividing the carbon dioxide absorbed by the volume of the sampling bottle. The results indicate that the maximum error is less than 2 per cent and the average error approximately 1 per cent of the total concentration. Tests were also made using a Sargent wet-test gas meter in place of the sampling bottles and drawing 2.5-liter samples of outside air through the aspirator. The results (not given) are in accord with those obtained with the sampling bottles.

A further test was made to ascertain to what extent the carbon dioxide content of the air in the sampling bottles might be affected by carbon dioxide absorbed or evolved by the water used to displace the air in the bottles. The extent of this error would be dependent on the variation of the carbon dioxide content of the sample from that of ordinary air, temperature changes in the equilibrium water, and the time or duration of taking a sample. In the author's experiments, care was taken to keep the equilibrium water at a constant temperature of 25° C. and consequently no experiments on the temperature effect were made. In Table II are given the results of some experiments on the effect of the time or duration of sampling. Samples of air of various carbon dioxide concentrations were prepared, and these concentrations are expressed in column 5 of Table II as percentages of the normal atmospheric concentration at that time with which the water was in equilibrium. Some preliminary experiments were made to ascertain to what extent the equilibrium water might influence the carbon dioxide content of the sample when the total time required for taking the sample and aspirating it was 10 to 12 minutes.

A known volume of the sample (2268 cc.) was aspirated through the absorber, using a calibrated bulb with mercury to measure the volume of the sample. A second portion of the same sample was collected in a sampling bottle by the usual procedure and aspirated through the absorber. In both cases the air was saturated with water vapor, so that no correction was necessary. The concentration of carbon dioxide is given in column 4. In column 7 is given the total time required for taking a sample and aspirating it through the absorber. Since the time of aspiration was always 7 minutes, the actual time taken for collecting a sample may be obtained by subtracting 7 minutes from the total time. The intervening time between sampling and aspirating, during which the sample was not exposed to the water, is not taken into account. The percentage error given in column 6 is

Table I. Test of Precision of Apparatus

Time		Carbon Dioxide Absorbed	Volume of Sampling Bottle	Carbon Dioxide	Error of Samples
Date	Hour	*Mg.*	*Cc.*	*Mg./l.*	%
11/4/34	12 N.	1.409	2500	0.5636	
		1.403	2510	0.5590	0.82
11/4/34	3 P. M.	1.410	2500	0.5640	
		1.400	2510	0.5578	1.11
11/6/34	8 A. M.	1.344	2510	0.5355	
		1.347	2510	0.5367	0.22
11/6/34	12 N.	1.331	2475	0.5378	
		1.331	2465	0.5400	0.41
11/7/34	9 A. M.	1.354	2510	0.5394	
		1.354	2510	0.5394	0.00
11/7/34	12 N.	1.321	2465	0.5359	
		1.311	2475	0.5297	1.17
11/8/34	9 A. M.	1.412	2510	0.5625	
		1.396	2510	0.5562	1.13
11/8/34	12 N.	1.402	2475	0.5665	
		1.390	2465	0.5639	0.46
11/9/34	9 A. M.	1.419	2510	0.5653	
		1.416	2510	0.5641	0.21
11/9/34	12 N.	1.372	2500	0.5718	
		1.372	2500	0.5718	0.00
11/10/34	9 A. M.	1.359	2500	0.5436	
		1.369	2500	0.5476	0.74
11/10/34	12 N.	1.393	2510	0.5550	
		1.403	2510	0.5590	0.72

calculated by obtaining the difference in carbon dioxide concentrations per liter of air given in column 4 for the two procedures, and expressing this difference as a percentage of the concentration in atmospheric air at the time of sampling.

The data given in tests 1 to 3 indicate that for intervals of sampling and aspiration involving 10 to 12 minutes, with carbon dioxide concentrations as low as 47 per cent of normal, the error is less than 2 per cent. In tests 4 to 13 are given the results of samplings of various durations and carbon dioxide concentrations compared with samplings of 10 to 12 minutes. The results indicate (with one exception) that with a range of carbon dioxide concentration from 63 to 127 per cent of normal atmospheric concentration and 67 minutes for sampling and aspirating, the error in carbon dioxide concentration is less than 2 per cent of the concentration in normal air. For samples of briefer duration, the range of carbon dioxide concentration may very likely be increased without loss in precision, but the above range was sufficient for the author's purpose. It may be possible to reduce this error still further by the use of a sodium sulfate–sulfuric acid solution (*6*) to reduce the solubility of carbon dioxide or by some other liquid in which carbon dioxide is relatively insoluble. However, no tests on these methods were made.

TABLE II. TEST OF ERROR DUE TO EQUILIBRIUM WATER

Test No.	Air Used	Method of Collection	Carbon Dioxide	Percentage of Atmospheric Concentration	Error	Time of Sampling	
			Mg./l.		%	*Min.*	*Sec.*
1	Prepared	Hg apparatus	0.2844	47	1.98	..	..
	Prepared	Sampling bottle	0.2964			10	50
	Atmosphere	Hg apparatus	0.6066			..	..
2	Prepared	Hg apparatus	0.4685	77	0.87	..	..
	Prepared	Sampling bottle	0.4738			12	30
	Atmosphere	Hg apparatus	0.6066			..	..
3	Atmosphere	Hg apparatus	0.6066	100	0.87	..	..
	Atmosphere	Sampling bottle	0.6013			10	0
4	Prepared	Sampling bottle	0.3840	69	0.39	10	30
	Prepared	Sampling bottle	0.3818			17	0
	Atmosphere	Sampling bottle	0.5603			..	..
5	Prepared	Sampling bottle	0.3243	58	0.21	10	30
	Prepared	Sampling bottle	0.3255			37	0
	Atmosphere	Sampling bottle	0.5603			..	..
6	Prepared	Sampling bottle	0.3406	61	1.07	10	30
	Prepared	Sampling bottle	0.3466			37	0
	Atmosphere	Sampling bottle	0.5603			..	..
7	Prepared	Sampling bottle	0.3551	63	1.22	10	30
	Prepared	Sampling bottle	0.3620			67	0
	Atmosphere	Sampling bottle	0.5658			..	..
8	Prepared	Sampling bottle	0.3855	69	2.20	10	45
	Prepared	Sampling bottle	0.3979			67	0
	Atmosphere	Sampling bottle	0.5624			..	..
9	Prepared	Sampling bottle	0.4066	73	1.67	10	45
	Prepared	Sampling bottle	0.4159			67	0
	Atmosphere	Sampling bottle	0.5584			..	..
10	Prepared	Sampling bottle	0.4920	88	1.36	10	30
	Prepared	Sampling bottle	0.4844			67	0
	Atmosphere	Sampling bottle	0.5598			..	..
11	Prepared	Sampling bottle	0.6340	113	1.34	10	30
	Prepared	Sampling bottle	0.6265			67	0
	Atmosphere	Sampling bottle	0.5603			..	..
12	Prepared	Sampling bottle	0.6929	122	0.58	10	30
	Prepared	Sampling bottle	0.6896			67	0
	Atmosphere	Sampling bottle	0.5658			..	..
13	Prepared	Sampling bottle	0.7141	127	0.37	10	0
	Prepared	Sampling bottle	0.7120			67	0
	Atmosphere	Sampling bottle	0.5603			..	..

Methods of Obtaining Air Samples

In Figure 4 is illustrated the apparatus for obtaining the air samples.

M represents a leaf on which the experiments are made and *K* its cup chamber (*3*) for drawing air over the leaf. The inlet of the cup chamber is fitted with a tube, *T*, which leads to outside air. A suction pump is attached at *J* for drawing air over the leaf and the rate of air flow is determined and adjusted by means of a Sargent wet-test gas meter, *I*, which is accurate to 28 cc. The leaf is subjected to the appropriate external conditions, side tube *E* on T-tube *G* is shut off, and the three-way stopcock turned so that air is drawn through the cup-chamber, *K*, through *L*, through *G* and *H* to the gas meter, *I*, and out at *J*.

The method of taking samples was as follows: A sampling bottle, *A*, was clamped in an inverted position in the ringstand, *F*. The side tube, *E*, was attached to the long tube of the sampling bottle and a small tube, *C*, drawn out to a jet was attached to the short tube of the sampling bottle. This small tube was adjusted to allow the water to run out at an appropriate rate, and consequently determined the rate of flow of air into the sampling bottle. Tubes were made which gave rates of air flow from 5 to 80 liters per hour, and where more accurate data were required, stopwatch readings were taken. In some cases when the sample was taken, the suction was shut off from the cup chamber by turning *H*, and the air flowed over the leaf directly to the sampling bottle. In other cases, suction was applied and a sample taken slowly over a long interval of time with a high rate of air flow over the leaf. In fact, a considerable number of variations were obtained, and records were kept of the temperature, barometric pressure, and other factors which might have their influence on the data. The method of taking the air check was very simple and consisted in attaching a sampling bottle to a tube which led air in directly from the outside. The difference in carbon dioxide content between the air that had passed over the leaf and the air check gave the amount of carbon dioxide absorbed or excreted by the leaf.

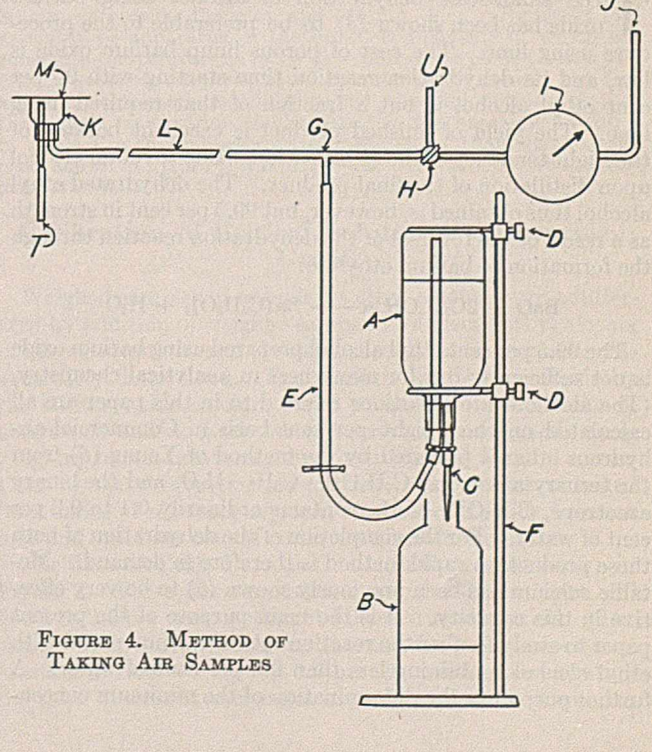

FIGURE 4. METHOD OF TAKING AIR SAMPLES

Suggested Modifications

Several modifications that might be suggested for the apparatus are as follows: By using an absorbing solution of one-half the concentration (0.0025 *N* sodium hydroxide) the accuracy for 2.5-liter samples of air would probably be increased and by using two or more absorbers and operating them alternately, greater rapidity of determinations could be obtained. While not done in the author's experiments, the apparatus could be assembled in a compact unit and adapted for transportation, a vacuum pump being used in place of the water-suction pump. It is not necessary to have the absorber of such excessive length, the length of the author's absorber being due to some tentative experiments made with high rates of air flow where a long absorber was necessary. Finally, the Wheatstone bridge circuit could probably be modified to reduce the current applied to the absorber and the effects of polarization reduced.

Summary

Hand-operated apparatus has been constructed for the precise determination of carbon dioxide in ordinary air. The apparatus will determine the carbon dioxide in a 2.5-liter sample of air whose carbon dioxide content ranges from 65 to 125 per cent of that prevailing in ordinary air with a maximum error of 2 per cent and an average error of 1 per cent of the atmospheric concentration, and will allow of 2 or 3 determinations an hour. Except for one or two parts, the apparatus is constructed from standard laboratory equipment and employs the electrical conductivity principle with an absorber capable of removing all the carbon dioxide from an air stream of 350 cc. per minute by means of 50 cc. of 0.0049 *N* sodium hydroxide with 0.4 per cent *n*-butyl alcohol. Efficient absorption of carbon dioxide is obtained by the use of a fritted-glass plate and the butyl alcohol to break the air stream into small bubbles and decrease surface tension, allowing the bubbles to persist. Samples of air for analysis are collected in 2.5-liter bottles, transported into the laboratory, and determined for carbon dioxide by the apparatus.

Acknowledgment

The author is indebted to A. J. Heinicke of the Department of Pomology, Cornell University, Ithaca, N. Y., in whose laboratory and under whose general direction this work was carried out; to M. D. Thomas of the American Smelting and Refining Co., Salt Lake City, Utah, for his helpful advice and suggestions; and to C. C. Murdock of the Department of Physics, Cornell University, for the use of electrical equipment.

Since completion of this work and prior to publication, an article by Holdheide, Huber, and Stocker (*4*) has appeared which in some repects is similar to the work reported here.

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Rate of Dehydration of Ethyl Alcohol Using Metallic Calcium

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THE small-scale dehydration of alcohol using barium oxide has been shown (*3*) to be preferable to the procedure using lime. The cost of porous lump barium oxide is low, and its dehydration reaction time starting with 95 per cent ethyl alcohol is but a fraction of that required using lime. The yield of finished product is excellent because of the slight tendency of the spent barium oxide to retain alcohol upon distillation of the final product. The dehydrated ethyl alcohol thus obtained is, however, but 99.5 per cent in strength as a result of the reversal of the dehydration reaction through the formation of barium ethylate:

$$BaO + 2C_2H_5OH \longleftrightarrow Ba(C_2H_5O)_2 + H_2O$$

The 99.5 per cent ethyl alcohol prepared using barium oxide is not sufficiently dry for many uses in analytical chemistry. (The alcohol-water solutions referred to in this paper are all calculated on the weight–per cent basis.) Commercial anhydrous ethanol prepared by the method of Young (*5*) from the ternary azeotrope, $C_2H_5OH—C_6H_6—H_2O$, and the binary azeotrope, $C_2H_5OH—C_6H_6$, contains ordinarily 0.1 to 0.2 per cent of water. For the completion of the dehydration of both these products, a rapid method is therefore in demand. Metallic calcium has been previously shown (*3*) to be very effective in this capacity. It is the main purpose of the present paper to study further the reaction rate of calcium metal with ethyl alcohol containing less than 0.5 per cent of water. A further purpose is the determination of the minimum concentration of water in ethyl alcohol which will negatively catalyze the exothermal reaction between ethyl alcohol and metallic calcium to form calcium ethylate with the vigorous evolution of hydrogen.

Reactions between Metallic Calcium and Ethyl Alcohol

Boiling ethyl alcohol containing small amounts of water when placed in contact with metallic calcium gives rise to the following reactions:

$$C_2H_5OH + 2H_2O \text{ (less than 0.5 per cent)} + Ca \longrightarrow Ca(OH)_2 + H_2 \quad (1)$$

$$2C_2H_5OH + H_2O \text{ (less than 0.2 per cent)} + Ca \longrightarrow Ca(C_2H_5O)_2 + H_2 \quad (2)$$

$$Ca(C_2H_5O)_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2C_2H_5OH \quad (3)$$

Reaction 1 is slow and is accompanied by the formation of gradually increasing amounts of calcium hydroxide which is practically insoluble in alcohol of the strength indicated. The evolution of hydrogen is so slight that ordinary qualitative tests for it are not effective. A large excess of metallic calcium in the form of 3-mm. wire or rough turnings will hasten the reaction, but provision must be made for its quick removal from the boiling alcohol when Reactions 2 and 3 set in. Reactions 2 and 3 are very rapid when the alcohol has reached the 99.8 per cent stage (0.2 per cent of water). The

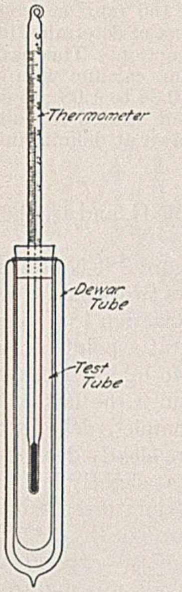

FIGURE 1. APPARATUS ASSEMBLY FOR DETERMINING CRITICAL SOLUTION TEMPERATURE

latter reactions are highly exothermal, and the rate of evolution of hydrogen in case of Reaction 2 is vigorous and can easily be followed by the usual qualitative explosion test, using an inverted test tube over the reflux condenser's drying tube ordinarily used to prevent return flow of atmospheric moisture to the reaction flask. Besides the noticeable development of heat due to Reaction 2 and the test for evolved hydrogen, there is also unmistakable evidence provided by the formation of a gelatinous precipitate which cannot be confused with the earlier formation of calcium hydroxide turbidities. Reaction 3 is without doubt the most rapid of the three. Calcium ethylate is sufficiently soluble in absolute ethyl alcohol to be used to dehydrate high-grade ethyl alcohol very effectively. Since solutions of calcium ethylate are easily prepared by use of Reactions 2 and 3, a more thorough study of them is much to be desired.

Application of Critical Solution Temperature Method

For the purpose of investigating the velocity of Reactions 1, 2, and 3, a rapid and accurate method for the determination of small amounts of water in ethyl alcohol is in demand. The use of small samples for this determination would be a distinct advantage. The critical solution temperature method of Crismer (*1*) is admirably adapted to fulfill both demands. This method has been investigated and found to be entirely satisfactory by Osborne, McKelvey, and Bearce (*2*). The method in brief consists in the determination of the consolute temperature of the conjugate system kerosene–absolute ethyl alcohol. (For use in connection with this method any type of kerosene may be used. The critical solution temperature with absolute ethyl alcohol may vary with samples from different sources, but if too high can be lowered by addition of petroleum ether.) The calibration of a graph relating the consolute temperature thus found with the change in critical solution temperature upon the addition of increasing small additions of water to the ethyl alcohol, completes the standardization required.

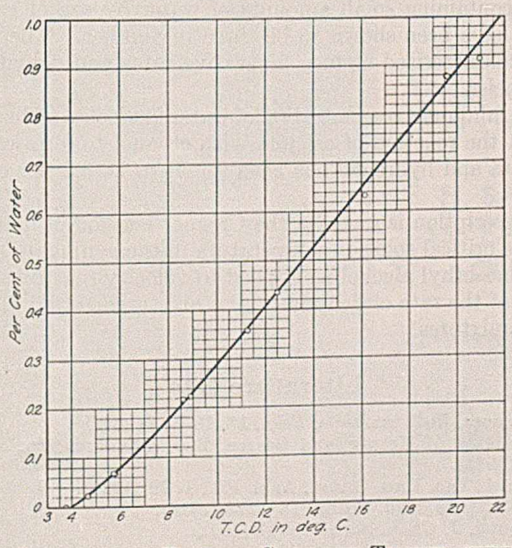

FIGURE 2. CRITICAL SOLUTION TEMPERATURE GRAPH FOR LOW-RANGE AQUEOUS ETHYL ALCOHOL

TABLE I. CALIBRATION DATA FOR CRITICAL SOLUTION TEMPERATURE DIAGRAM

(Low-range, aqueous ethyl alcohol)

Absolute Ethanol *Grams*	Ethanol 10.446 % H_2O *Grams*	Water Calcd. *%*	Critical Solution Temperature *° C.*
....	....	0.00	3.75
22.7516	0.0510	0.023	4.65
15.9680	0.1049	0.068	5.80
14.6930	0.3119	0.217	8.60
19.7553	0.5975	0.307	10.10
18.6657	1.2042	0.632	16.15
23.1732	0.5088	0.224	8.90
29.3854	1.2727	0.434	12.50
24.6240	2.3609	0.914	20.95
30.8745	2.4912	0.876	19.60
30.6852	2.8126	0.877	19.55
30.0951	0.3780	0.125	6.35
30.7653	0.1835	0.069	5.75
30.8642	0.9650	0.356	11.25

For the analysis of the unknown alcohol containing small amounts of water, the process is then reversed. The consolute temperature is determined for the system, kerosene–high-grade ethyl alcohol, and from the calibration graph the percentage of water is estimated. The determinations are easily made accurate to within 0.01 per cent of the true water content in the alcohol and require but a few minutes to be carried out, using 5 ml. or less of the samples of alcohol in question (*1*, *2*).

A drawing of the apparatus assembly is given in Figure 1.

The sample, 5 ml. of the alcohol, is placed in the test tube shown and 4.5 to 5.0 ml. of kerosene are added. The test tube is stoppered, using a close-fitting one-hole rubber stopper through which is inserted the specially designed thermometer. This thermometer is calibrated between the temperatures −10° and +60° C. with markings for each 0.05° which are 0.7 to 0.8 mm. wide. The lower half of the thermometer is uncalibrated and of such length that the bulb of the thermometer is just completely immersed in the mixture of kerosene and alcohol being examined. The sampling test tube is a stock article of Pyrex glass, 19 × 145 mm. with a flanged top and of 30-ml. capacity. The unsilvered Dewar jacket for minimizing temperature gradient between the sample tube and the surroundings is of Pyrex, baked and outgassed 6 to 8 hours at 500° C. It is 20 mm. in inside diameter, 30 mm. in outside diameter, and 145 mm. long. By use of this assembly of apparatus, if the mixed components of which the consolute temperature is to be determined are chilled below the critical solution temperature while outside the Dewar, the fine adjustment is more reasily obtained after the introduction of the sample tube within the Dewar. In the experiments listed in Table I, a thermometer of narrower range than that usually used, shown in Figure 1, was employed. It read directly to 0.02° instead of 0.05° C.

Calibration of Critical Solution Temperature Graph

Weighed samples of anhydrous ethyl alcohol were adulterated by addition of weighed samples of aqueous ethyl alcohol of known strength, and the critical solution temperature was accurately determined. The absolute alcohol was made by the barium oxide–calcium metal process (*3*), the samples of anhydrous and aqueous alcohols used were weighed, using weighing burets previously described (*4*), and vacuum corrections to the weighings were applied. The results obtained for a series of reference aqueous alcohols containing between 0.00 and 0.914 per cent of water are given in Table I.

The data of Table I are plotted with the results shown in Figure 2. For water concentrations under 0.9 per cent and down to 0.2 per cent, a straight-line relationship exists. The change in critical solution temperature for each 0.1 per cent of water is 1.66°+. Below 0.2 per cent water concentration the slope of the curve changes in such manner as to increase

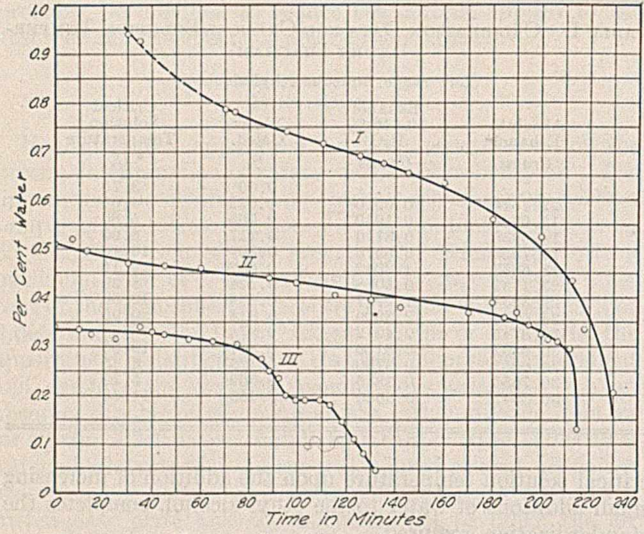

FIGURE 3. RATE OF DEHYDRATION OF ETHYL ALCOHOL

slightly the change in critical solution temperature for each fractional decrease in water down to absolute alcohol. An accuracy of 0.01° in determination of the critical solution temperature corresponds to an accuracy of 0.0006 per cent of water. Assuming temperature readings accurate to ±0.02°, an accuracy of ±0.001 per cent in the determination of water in ethyl alcohol is possible. Determinations in connection with the following experiments were considered accurate to the nearest tenth degree only since they were not filtered before the critical solution temperature was taken.

Velocity of Dehydration of 99.5 Per Cent Ethyl Alcohol

A 5000-ml. round-bottomed flask was suitably modified for the purpose by attaching a stopcock delivery tube near the bottom of the flask, approximately 25 mm. above the extreme bottom of the flask when in an upright position. The neck of the flask was fitted with a rubber stopper and 30-cm. (12-inch) reflux condenser through which a rapid stream of cold water was circulated. The top of the reflux condenser was provided with a drying tube with efficient desiccant to prevent return flow of moisture. Suspended through the reflux condenser was a tubular nichrome wire gauze hanging basket, 40 mm. in diameter and 150 mm. in length. By half filling the reaction flask for a given set of determinations, it could easily be lifted out of the field of reaction. This basket was charged with various amounts of 3-mm. calcium wire and the flask with 2500 ml. of ethyl alcohol of 0.34 to 1.08 per cent water content. The flask and contents were heated to boiling over an electric heater and samples withdrawn at definite intervals for analysis.

TABLE II. RATE OF DEHYDRATION OF 98.92, 99.49, AND 99.66 PER CENT ETHYL ALCOHOL

	98.92% Ethyl Alcohol[a]			99.49% Ethyl Alcohol[b]			99.66% Ethyl Alcohol[c]	
Time	Critical Solution Temperature	H_2O	Time	Critical Solution Temperature	H_2O	Time	Critical Solution Temperature	H_2O
Min.	° *C.*	%	*Min.*	° *C.*	%	*Min.*	° *C.*	%
0	24.9	...	0	13.9	0.51	0	11.0	0.34
10	23.8	...	7	14.1	0.52	10	10.9	0.335
30	21.0	0.940	13	13.7	0.495	15	10.7	0.325
35	20.7	0.925	30	13.5	0.47	25	10.6	0.315
70	18.5	0.785	45	13.2	0.465	35	11.0	0.34
74	18.4	0.780	60	13.15	0.46	40	10.8	0.33
95	17.7	0.740	88	12.75	0.44	45	10.7	0.325
110	17.3	0.715	99	12.6	0.43	55	10.6	0.315
125	16.9	0.690	115	12.2	0.405	65	10.5	0.31
135	16.7	0.675	130	11.95	0.395	75	10.4	0.305
145	16.4	0.655	142	11.8	0.38	85	9.9	0.275
160	16.1	0.635	170	11.5	0.37	88	9.4	0.25
180	14.8	0.560	180	11.9	0.39	92	9.1	0.235
200	14.2	0.525	185	11.3	0.36	95	8.5	0.20
213	12.7	0.435	190	11.5	0.37	99	8.3	0.19
218	11.9	0.335	195	11.1	0.345	103	8.3	0.19
230	8.6	0.205	200	10.7	0.325	109	8.3	0.19
...	....	...	203	10.55	0.315	113	8.1	0.18
...	....	...	207	10.5	0.31	118	7.4	0.145
...	....	...	212	10.2	0.295	123	6.7	0.11
...	....	...	215	7.1	0.13	127	6.1	0.08
...	....	...	...	...	...	132	5.1	0.045

[a] 2500 ml. of alcohol, 98 grams of calcium metal.
[b] 2500 ml. of alcohol, 25 grams of calcium metal.
[c] 2500 ml. of alcohol, 10 grams of calcium metal.

The data thus obtained are given in Table II, and are shown graphically in Figure 3.

From examination of Table II and Figure 3 it is observed that the dehydration of the alcohol follows two separate reaction speeds. The first stage represents Reaction 1. This reaction is complete to a sufficient extent (at a point between 0.2 and 0.3 per cent of water) no longer to inhibit Reactions 2 and 3. As a result of Reactions 2 and 3 the last of the water is rapidly reacted upon with the complete dehydration of the alcohol. Curve III, Figure 3, more clearly defines the point at which Reactions 2 and 3 set in, at slightly less than 0.2 per cent of water. The excess of calcium present in the experiments of Table II was calculated to be 315, 130, and 25 per cent, respectively. The failure of the experimental data to fall more closely upon a smooth curve is due to the fact that the samples taken from the reaction flask were not filtered before determination of the critical solution temperature. The suspension of insoluble matter made the determination of the consolute temperature difficult. The flat portion in curve III in the time interval between 95 and 115 minutes is probably due to the accumulation of insoluble matter on the unreacted calcium metal, only 2.5 grams of which remained at this stage of the reaction.

Use of Saturated Ethyl Alcohol Solution of Calcium Ethylate

A sample of anhydrous ethyl alcohol was allowed to react with metallic calcium until saturated with calcium ethylate. Samples of ethyl alcohol containing small amounts of water were treated by the addition of this saturated calcium ethylate, and allowed to digest at the boiling point 1 to 2 minutes, and a 5-ml. portion was then distilled out and analyzed. In all cases the alcohol so obtained was found to be anhydrous. The conclusions from the previous discussion relative to the speed of Reaction 3 were thus substantiated.

Summary

The reactions resulting from the dehydration of ethyl alcohol containing small amounts of water by use of calcium metal have been shown to be three in number. They have been characterized as to comparative rates and dehydration efficiencies.

The minimum concentration of water in alcohol sufficient to inhibit the reaction of calcium with ethanol to form calcium ethylate and hydrogen has been found to be 0.2 per cent of water.

A description is given of the Crismer method of determining the critical solution temperature in the conjugate system kerosene–ethyl alcohol as applied to velocity reactions in the study of the rate of dehydration of high-grade ethyl alcohol–water mixtures.

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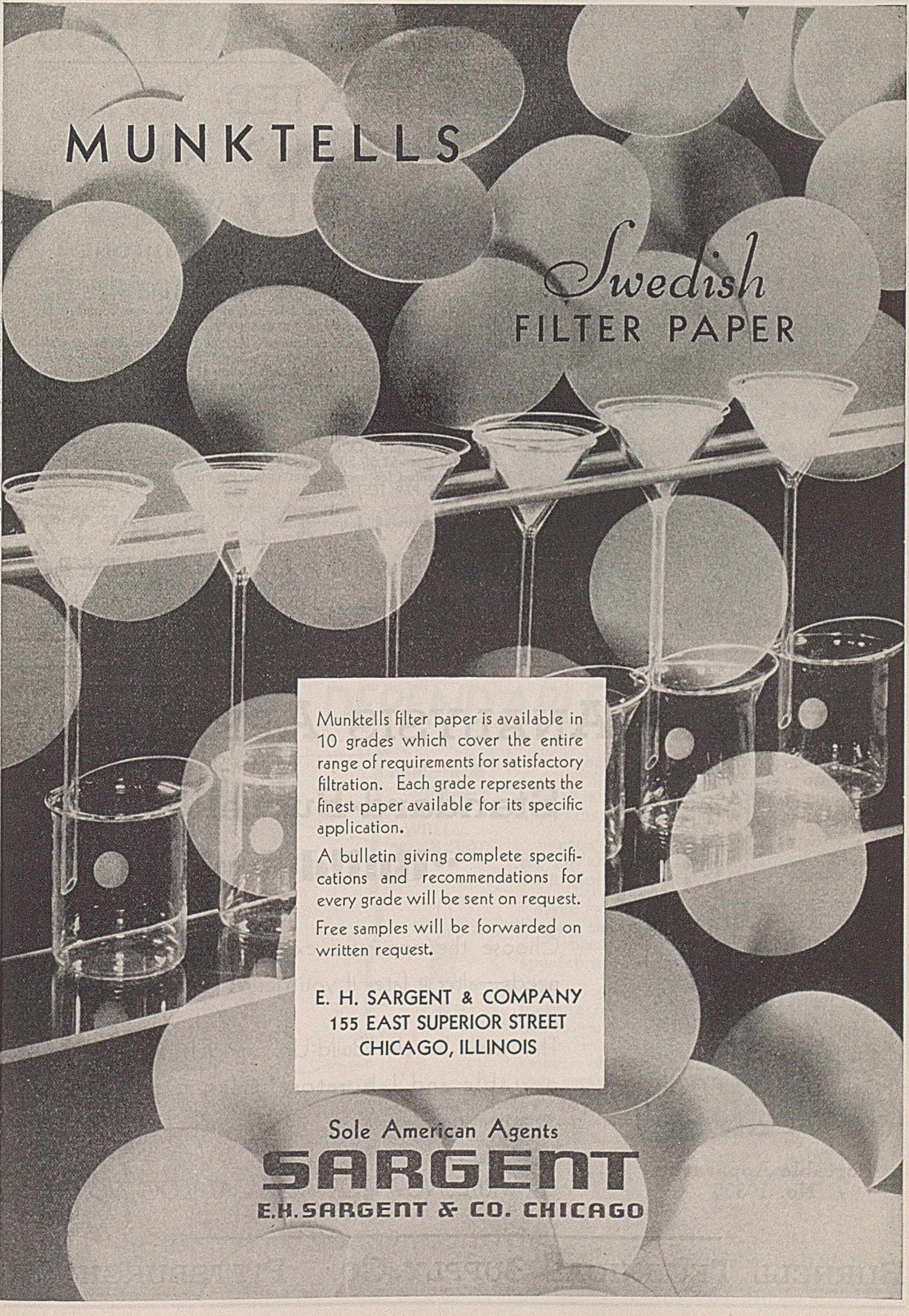

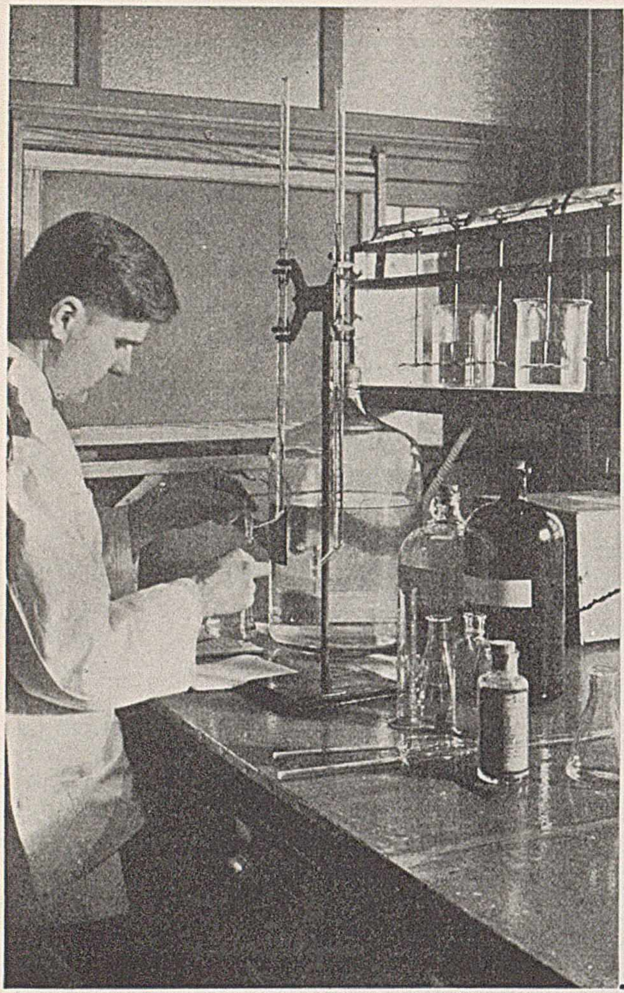

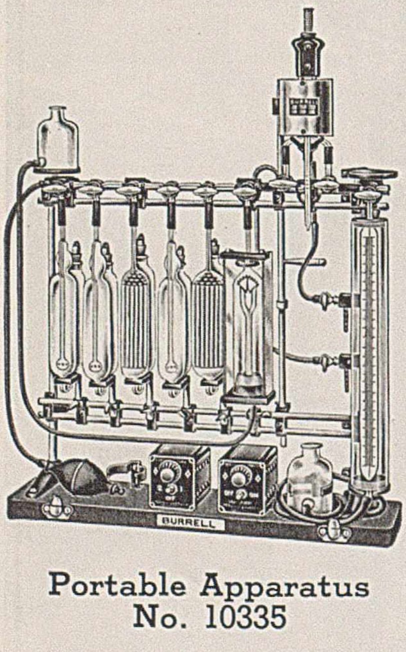
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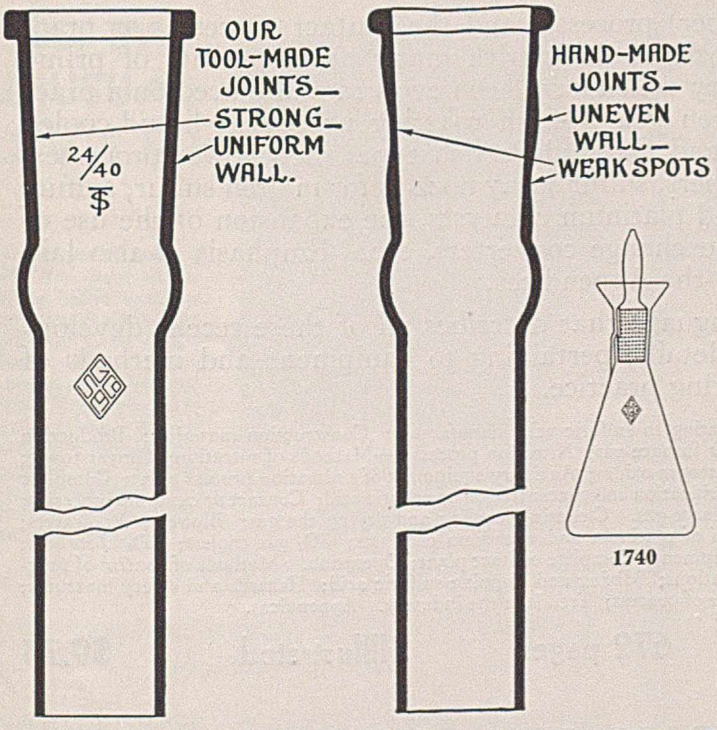
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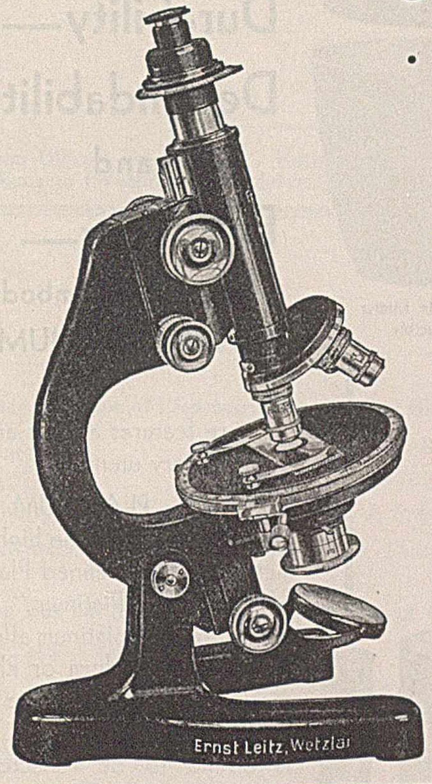
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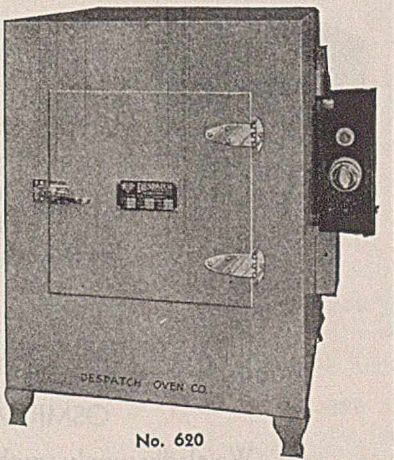
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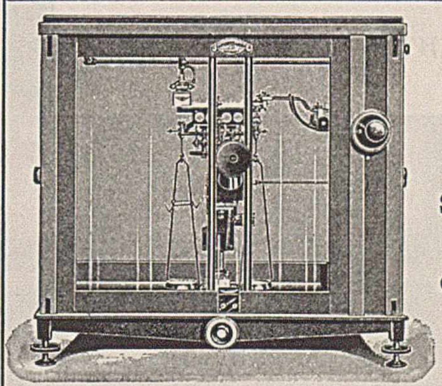

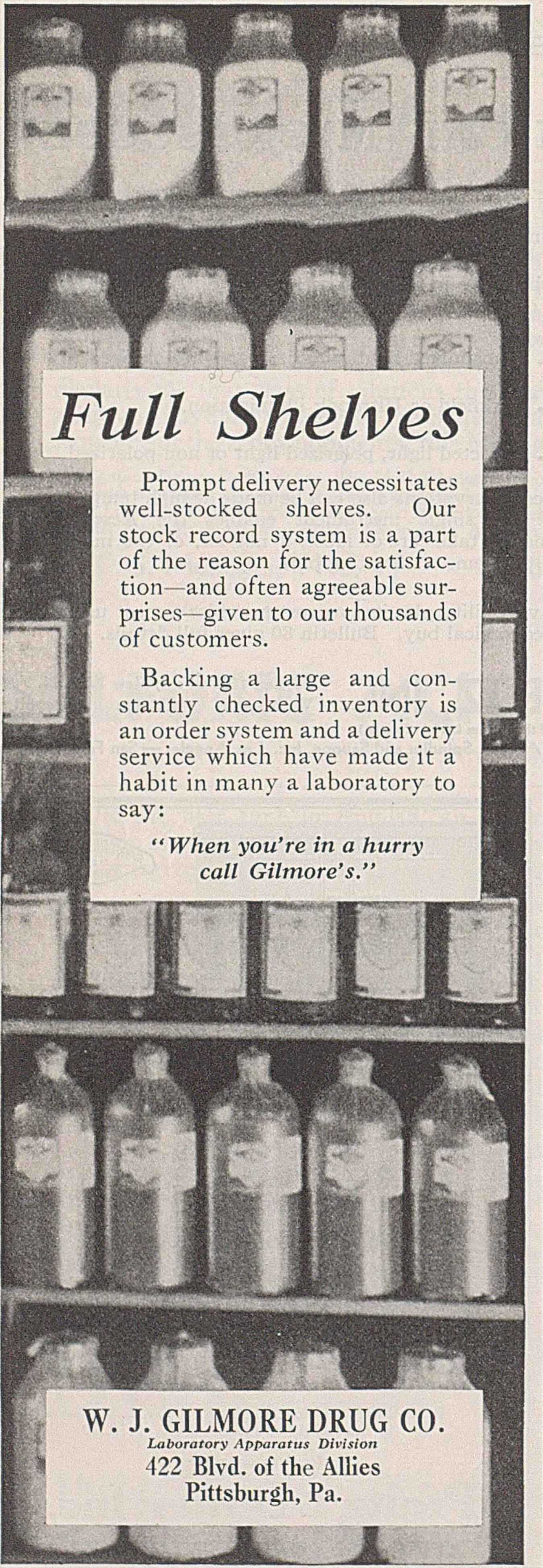

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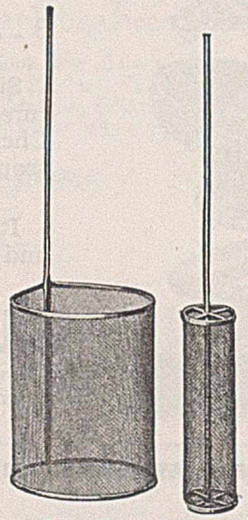

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