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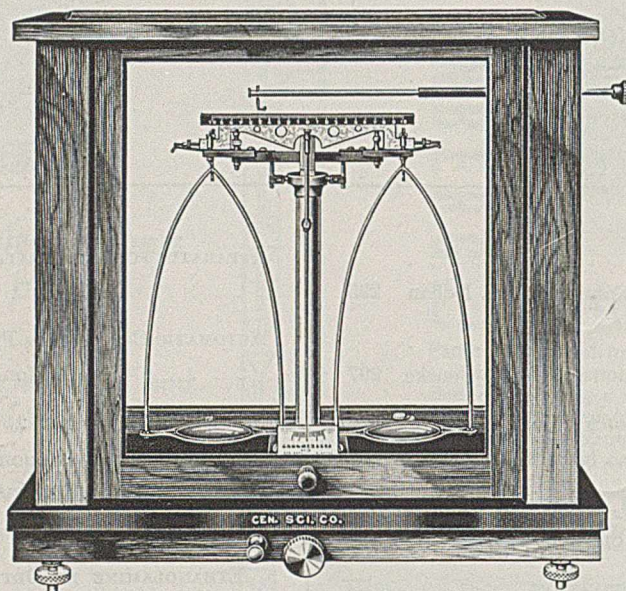
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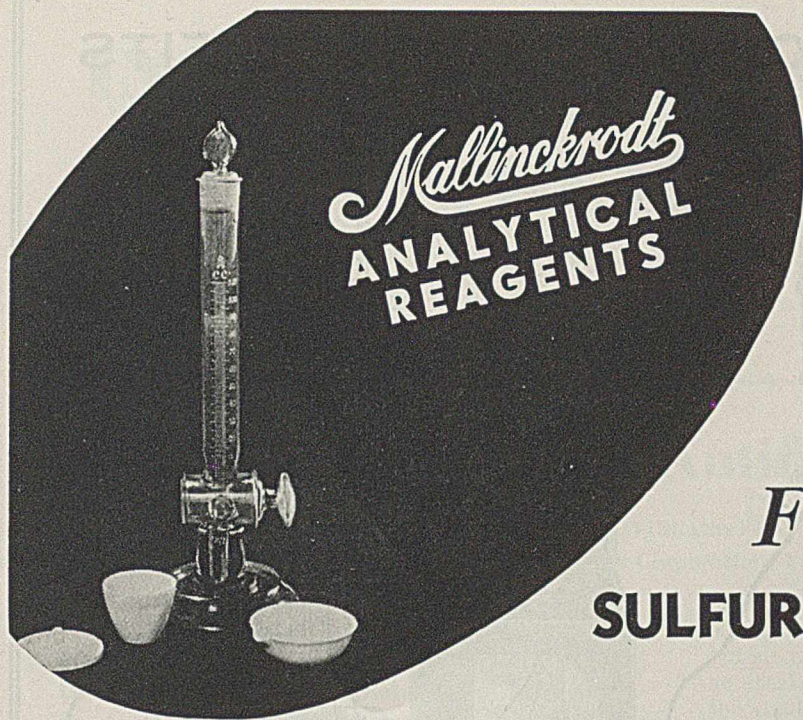
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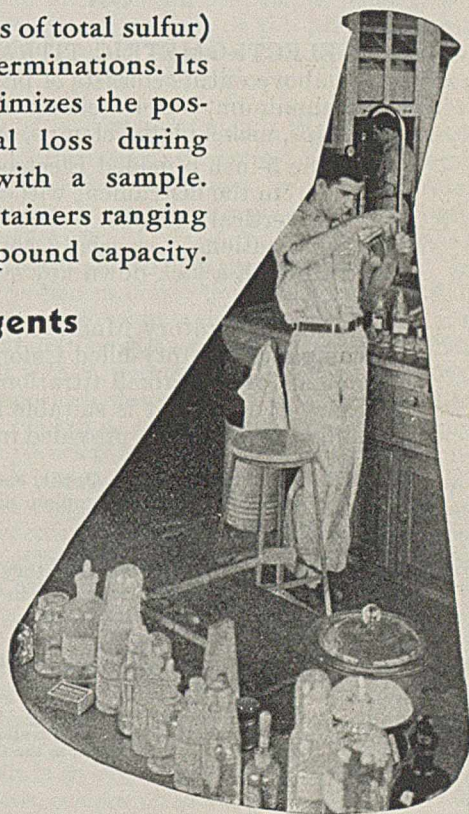
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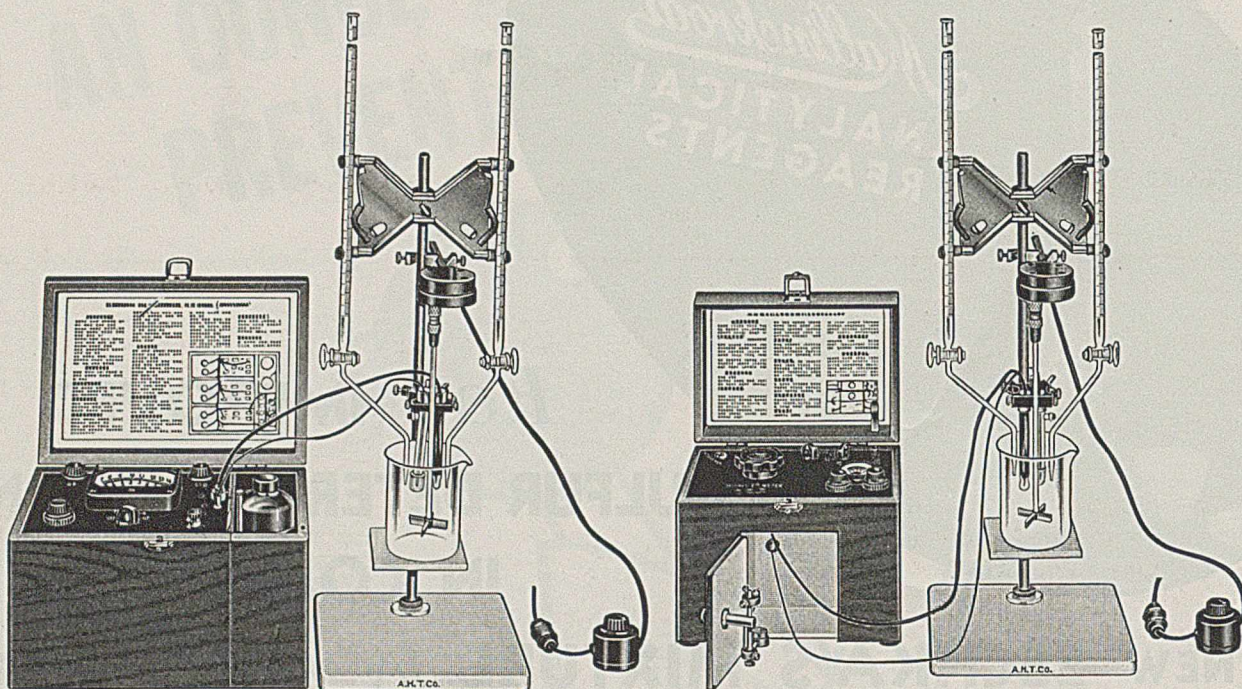
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INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

The Technic of Antifreeze Testing

KENNETH H. HOOVER AND FRANK E. DOLIAN
Commercial Solvents Corporation, Terre Haute, Ind.

The suitability of an antifreeze solution for use in a water-cooled internal-combustion engine is determined by the inherent properties—i. e., physical constants—of its principal component and by the properties imparted to it by the addition of certain modifying agents. The technic of testing the corrosive action on metals, storage properties, attack of rubber, and foaming tendency is discussed, and various apparatus are described. Particular emphasis is placed on methods of testing corrosive action which closely simulate actual conditions as found in automobile cooling systems. Field tests and their limitations are discussed.

THE commonly available antifreeze solutions for use in water-cooled internal-combustion engines are generally divided into two classes, known as volatile and nonvolatile or "permanent" types. All the preferred materials are alcohols, such as methanol, ethyl alcohol, ethylene glycol, and glycerol. Both trimethylene glycol and propylene glycol should also be satisfactory materials.

The suitability of an antifreeze is determined by the inherent properties of its principal component, and by the properties imparted to it by the addition of certain modifying agents. Inherent properties are physical constants and cannot be changed to any appreciable extent. Properties such as corrosive action on metals, attack of rubber, foaming tendency, etc., can be changed or modified, however, and, from a technical viewpoint, provide the only means of attaining competitive superiority. It is with these properties, therefore, that the evaluation of antifreeze solutions is chiefly concerned, and this paper will deal with the technic of testing these "imparted" properties of antifreeze solutions.

Corrosive Action on Metals

In the cooling system of an automobile engine, there are several different metals and alloys in contact with the cooling liquid. These metals or alloys are chiefly copper, brass, iron, solder, and sometimes aluminum (about one-fourth of the 1938 models are equipped with aluminum cylinder heads).

These metals are not only in contact with the cooling liquid, but are also in contact with each other in most cases, making an ideal situation for electrochemical corrosion. To make the conditions even more ideal for corrosion, nearly every cooling system is subject to a certain amount of aeration because of leaks in the cooling system on the low-pressure or intake side of the water pump. These leaks may not be of sufficient size to allow liquid to escape, but may be large enough to allow air to enter when the pump is running, and there is a positive external pressure on this part of the system. Aeration also occurs in the upper tank of the radiator.

The part played by oxygen in the mechanism of corrosion is well known. According to Speller (2), appreciable corrosion can take place only if the polarizing film of hydrogen atoms produced by the reaction of the metal with hydrogen ions in the solution is continuously removed by some means. This film of atomic hydrogen can be removed either by combining to form molecules of hydrogen which are released as gas, or by reaction with dissolved oxygen to form water. In either case, the continuous destruction of the hydrogen film allows the metal to go into solution and corrosion proceeds at a rapid rate. In neutral, or slightly alkaline, solutions, which are usually dealt with in working with antifreeze solutions, the amount of gaseous hydrogen is very small compared to the amount of hydrogen destroyed by oxidation. Not only dissolved oxygen plays a part in corrosion, but also mechanically entrained air is stated by certain investigators (1) to increase the rate of corrosion of brass. Therefore, in testing the corrosive properties of an antifreeze solution, there must be electrolytic couples and aeration if it is wished to simulate actual operating conditions. Much stress is placed here on these two factors because they are too often overlooked in testing.

The problem of corrosion by antifreeze solutions is considerably more complicated than most corrosion problems, both in the matter of testing and in the matter of protecting against corrosion. In the ordinary corrosion problem, only one metal is concerned, while in an automobile cooling system, there are at least four metals, comprising at least five elements, which must be protected simultaneously against corrosion by the addition of suitable inhibitors.

There are very few, if any, single inhibitors which protect all of the metals found in a cooling system. It is a comparatively simple matter, for instance, to find a material which will inhibit the corrosion of iron. Frequently, however, such an inhibitor for iron is harmful to one or more of the other metals. Hence, it becomes necessary to add an "inhibitor to inhibit an inhibitor" and the only way to get complete pro-

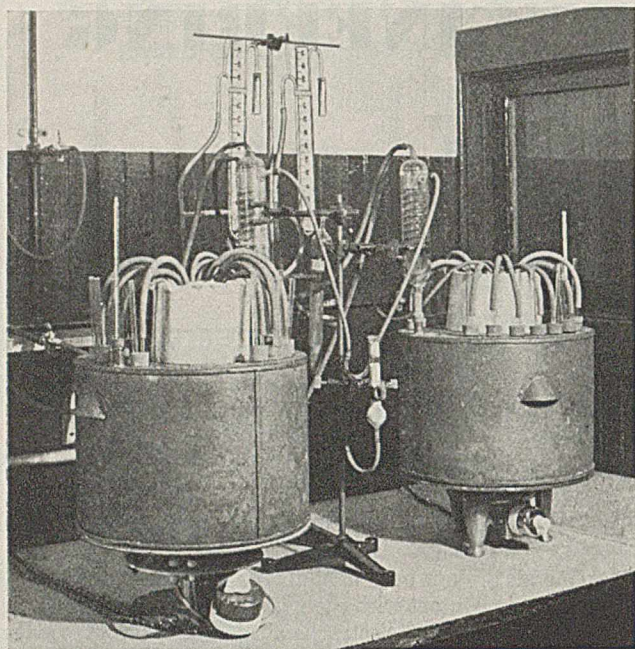


FIGURE 1. APPARATUS FOR PRELIMINARY CORROSION TESTS

tection of all metals is by the use of a combination of inhibitors.

In any case, the only way to obtain complete protection is by use of various combinations of inhibitors. In developing a satisfactory inhibiting combination, therefore, an enormous number of combinations must be tested, unless the experimenter is fortunate enough to find the right one early in his investigation. It is necessary for this reason to employ small scale testing equipment in which large numbers of preliminary tests can be made simultaneously, with consequent economies of time and money, thereby eliminating unsatisfactory combinations and singling out promising combinations for more extensive study in larger scale equipment.

The authors have found the equipment shown in Figure 1 very satisfactory for preliminary corrosion studies of antifreeze solutions.

A copper bath containing a suitable liquid refluxing at the temperature at which it is desired to make the tests serves as a constant-temperature bath. Each bath contains twenty-four wells, arranged around the edge in circular fashion, each of size to hold a 25 × 200 mm. test tube, and a large well in the center of size to accommodate a 0.946-liter (1-quart) wide-mouthed fruit jar. This jar serves both as an air distributor and as an air saturator. In testing antifreezes, provision must be made to minimize evaporation losses and consequent changes in concentration incurred by aeration in the test tubes containing the experimental antifreezes. The air is therefore passed through an antifreeze solution of the same concentration in the large center jar as is used in the corrosion tests, and is distributed through twenty-four holes in the specially constructed lid (Figure 2). A length of capillary tubing inserted in the rubber tubing running from each hole in the lid to each test tube meters the air, so that when twenty-four capillaries are used which deliver the same amount of air under the same pressure, the air flow to each tube is the same and can be controlled by varying the air pressure in the center jar. An air flow of approximately 5 cc. per minute to each tube is used. The air pressure in the jar is measured by a manometer and is kept constant by a suitable type of mercury regulator.

The tests are carried out in duplicate in 25 × 200 mm. test tubes, using in each tube 55 cc. of an antifreeze solution freezing at -20° F. This concentration was chosen merely because it happens to be a common degree of protection in actual midwinter use of antifreeze. Deep well water of fairly constant hardness (about 17 to 22 grains per gallon) is used in preparing the solutions. Test pieces of soft steel, brass, and solder, 11.43 × 1.27

× 0.08 cm. (4.5 × 0.5 × 0.031 inch) with a 0.48-cm. (0.188-inch) hole near one end, are ordinarily used, although other combinations, of course, may be employed. The three strips are fastened together at one end with a small brass bolt, using brass washers as spacers between the strips. In some cases, an aluminum test strip is also used, but this tends to make a crowded arrangement, and is not generally necessary in preliminary tests. Soft steel and brass have been found to behave very much like cast iron and copper, respectively, in regard to corrosion by antifreeze solutions. The extent of corrosion differs somewhat, but any solution which attacks soft steel will also attack cast iron (3), and most solutions which attack copper will also attack brass. Hence, soft steel is used in place of cast iron as a matter of convenience in making the test pieces.

In addition to the test pieces, 1 gram of steel wool is placed in each tube to provide a large iron surface such as is found in an automobile cooling system. The arrangement of the contents of each tube should be uniform, so as to preclude the possibility of errors creeping in due to changes in the relative positions of the test pieces, the steel wool, or the glass tube which discharges the air at the bottom of the test tube. Further reduction in evaporation losses is accomplished by fitting each tube with a 10-cm. (4-inch) air reflux condenser made of glass tubing (Figure 2, right).

In preparation for the tests, the metal specimens are first brightened on a steel brush buffer, then numbered with a metal stamping tool. They are washed with soap and water using a stiff brush, rinsed in clear water, and dried with a clean cloth. They are then immersed for a few minutes in a 50-50 mixture of toluene and ethyl acetate, carefully wiped dry with a clean soft cloth, and placed in a desiccator to await weighing.

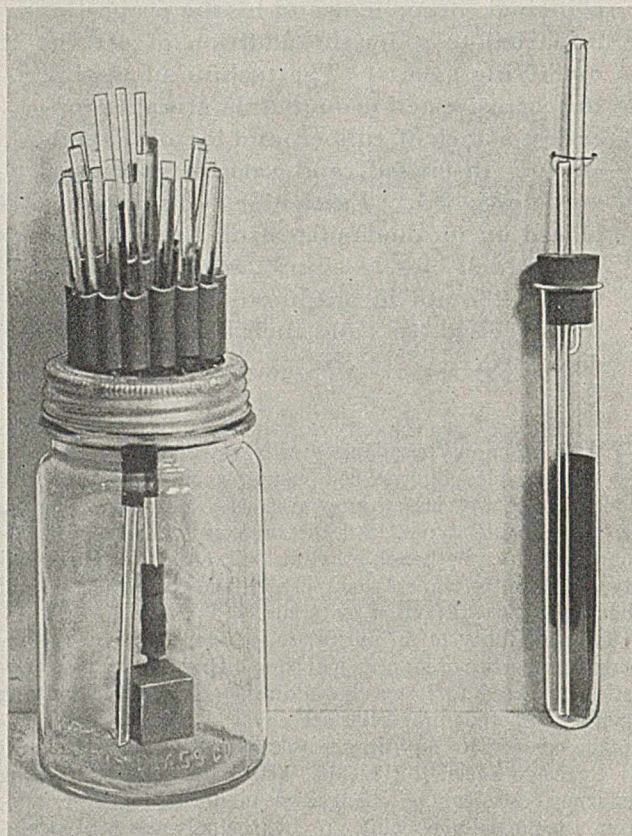


FIGURE 2. CLOSE-UP OF AIR DISTRIBUTOR AND OF TEST-TUBE ASSEMBLY USED IN PRELIMINARY CORROSION TESTS

At the end of the test, the metal strips are removed as quickly as possible and wiped dry. They are then washed with soap and water, followed by the toluene-ethyl acetate rinsing as described above. The strips are kept in a desiccator at all times while awaiting use or weighing. The extent of corrosion is expressed in terms of loss in weight, since all specimens have approximately the same surface area. The type of corrosion—e. g., pitting—is also always noted and recorded. Observations of the appearance of the solution and the metals are made periodically

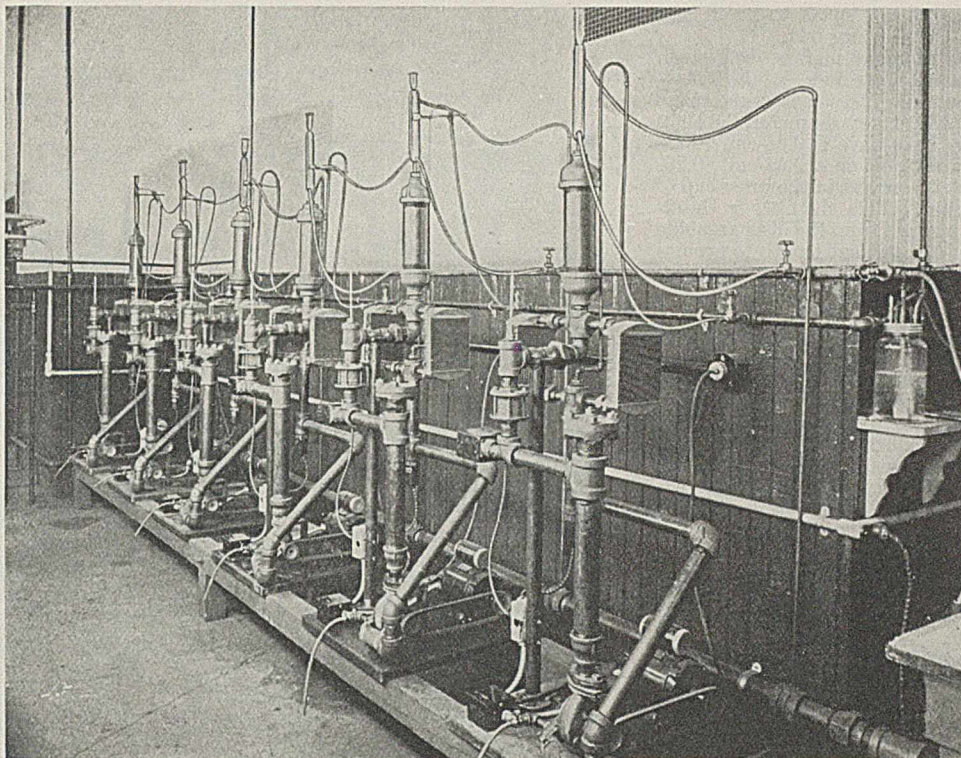


FIGURE 3. BATTERY OF CIRCULATING UNITS USED IN FINAL LABORATORY EVALUATION OF CORROSIVE PROPERTIES OF ANTIFREEZES

during the test and at the end of the test. The pH of the solution is also determined before and after the test.

Breakdown of an antifreeze solution is considered as the point where rusting begins. This is more or less arbitrary, since severe corrosion of some other metal may occur before rusting begins. Hence, these tubes are removed at the first appearance of rust and the strips are cleaned and weighed. If no rusting has occurred at the end of 6 weeks, the tests are stopped because it has been found that any solution, which will undergo the conditions imposed for 6 weeks without serious attack on steel, brass, and solder, is worthy of a larger scale test.

Preliminary tests such as the above, however, are not considered severe enough for final laboratory evaluation, nor do they approach the actual conditions of usage to which an antifreeze solution is subjected. It is necessary, therefore, to test an antifreeze under conditions as nearly duplicating those found in an automobile cooling system as is possible in the laboratory. For this purpose, the authors use the equipment shown in Figure 3. These testing units were designed to simulate the essential conditions of automotive usage, yet permit control of conditions within narrow limits, so that these can be duplicated in succeeding tests.

In these larger scale tests, the antifreeze solution is circulated continuously through a system having an operating capacity of about 6.43 liters (1.7 gallons) and made up for the most part of 1.25-inch iron pipe to represent the large amount of iron surface found in the automotive engine jacket. Special care was used in choosing the size of the pipe and all of the equipment through which the solution circulates so as to have no restricted flow. This is important because with restricted flow there would be a high-pressure differential between the intake and output sides of the pump, which would aggravate leakage.

Circulation is accomplished by means of a regular automobile water pump,¹ belt-driven by an electric motor at a speed of

¹ Nash Lafayette "400" (assembly No. 3728). This pump was chosen because it is one of the few independently mounted pumps now available.

2200 r. p. m., which is roughly equivalent to an automobile speed of 30 miles per hour. Incorporated in the system are two copper radiator cores of the type used in automobile hot-water heaters. These represent the radiator of a cooling system. The solution is heated by an iron-jacketed electric immersion heater. The iron-jacketed type was chosen because in an automobile engine heat is transmitted through the iron of the cylinder walls to the cooling liquid; so also here the heat is transmitted from its source through iron to the solution. The temperature is automatically regulated by a Penn type LL thermostat which maintains the temperature within 2° C. of that desired. A length of regular automobile rubber radiator hose connects the intake of the pump with the remainder of the system. A sight glass is inserted in a convenient place so that the appearance of the solution can be observed. A loose 25-cm. (10-inch) length of 1-inch pipe, dropped in a vertical position into the top chamber, precludes the possibility of any static condition prevailing in this reservoir.

Throughout a test, the solution being circulated is aerated at a constant rate (25 cc. per minute), providing oxygen so that corrosion can proceed at a maximum rate. This amount of air was shown by experiment to contain oxygen in excess of that used during the most severe conditions of corrosion. The pump provides enough suction to take in this air, and the rate is controlled by insertion of a capillary of the necessary bore and length in a piece of rubber tubing connected to a small opening in the system on the suction side of the pump. As mentioned previously, in testing volatile-type antifreeze solutions, provisions must be made to prevent evaporation losses caused by aeration. The capillary, therefore, is connected with a source of air which is kept saturated with vapors of a solution of the same concentration as that being used in the test. A water condenser is used on the outlet of the top reservoir to condense vapors carried out by the air passing through the solution. In cutting the threads on the pipe used in constructing the units, some of the cutting oil usually gets down on the inside of the pipe. To prevent this cutting oil from affecting the corrosion results, each section of pipe is thoroughly cleaned internally with a mixture of equal volumes of toluene and ethyl acetate. Compound used on the threads to make a tight joint is placed only on the male end of the joint, so that it does not come in contact with the solution being tested.

After the completion of a test, the unit is dismantled and all of the iron pipe, joints, radiator, water pump, and hose connection are discarded and replaced by new parts when the unit is rebuilt. The few small brass parts used, the electric heater, and thermo-

stat are thoroughly cleaned, so as to avoid any contamination from the previous test.

Test disks of five different metals—soft steel, copper, brass, aluminum, and solder—of the following dimensions are ordinarily used in these tests: thickness, No. 16 B. & S. gage; diameter, 3.82 cm. (1.5 inches). These disks have a 0.64-cm. (0.25-inch) hole in the center to fit on a 0.64-cm. (0.25-inch) brass rod which is screwed in the brass cap of the test-piece chamber. This chamber is the 2-inch pipe extending upward from the discharge side of the pump, and is of sufficient length to accommodate eight sets of disks which are kept apart by 0.64-cm. (0.25-inch) brass spacers made from 0.125-inch brass pipe (Figure 4).

Before starting a test, the pump is repacked with a good grade of graphited asbestos packing. It is usually not necessary to repack the pump during a test. The unit is then filled with water, which is circulated at operating temperature for 24 hours. This 24-hour period is called the "prerust" period and serves several purposes, chief of which is to form a coating of rust on all the iron surfaces of the system. This is the condition found in the average automobile cooling system when an antifreeze is added. Less important functions of the prerust period are the opportunities it presents to check the unit for leaks and to regulate the thermostat to the temperature desired without interfering with the test. Two sets of test disks are placed in the test chamber during the prerust period. One set is removed and weighed after the prerust period, while the other set remains in the system along with the other seven sets which are put in. By comparing the losses in weight of these two sets of disks and the last set taken from the test during a run, a check can be made as to whether the antifreeze solution preferentially attacked freshly prepared and cleaned metal surfaces over previously corroded surfaces.

When the 24-hour prerust period is ended, the unit is drained and thoroughly flushed with water so as to remove all loose rust. Seven sets of weighed test disks are placed in the test chamber, 6300 cc. of the antifreeze solution of a concentration which freezes at -20° F. are added, and the unit is started. The air flow through the system is checked once each day with a eudiometer and is kept at 25 ± 2.5 cc. per minute. The pH of the solution is determined once each week, and even more often near the time that rusting begins. This is especially important in the testing of antifreeze solutions of the polyhydric alcohol type where the inception of rusting, or breakdown of the solution, may be accompanied by a marked drop in pH. The speed of the pump is also checked once each week and is maintained at 2200 ± 50 r. p. m. by adjustment of the driving belt.

One set of test disks is removed and weighed each week under ordinary circumstances. However, in cases where the antifreeze solution being tested is expected to have a life longer than 7 weeks, the first two or three sets may be removed at longer intervals, say, 2 weeks. As soon as rusting is indicated, a set of disks is removed and weighed. Any remaining sets are removed at 1- to 2-day intervals. Observations are made daily of the appearance of the solution as seen through the sight glass; it is not difficult to note the first appearance of rust. Test pieces are cleaned and handled in the same manner for these tests as described previously for the preliminary tests.

Storage Tests

Most present-day antifreezes are packaged in sealed cans, and this fact adds another to the long list of tests which an antifreeze must pass before it is pronounced satisfactory. Sometimes as much as a year or two elapses between the times of packaging and use. Therefore, an antifreeze must have good storage qualities. It must not corrode the package, and it must not lose its corrosion-inhibiting qualities on storage.

The authors make these tests in 0.473-liter (1-pint) friction-top cans. The cans are filled with the antifreezes under test and stored away at room temperature; every 3 months the cans are opened and observations are made as to any corrosion of the can which has taken place, or any change in appearance of the antifreeze, such as the appearance of a solid, or

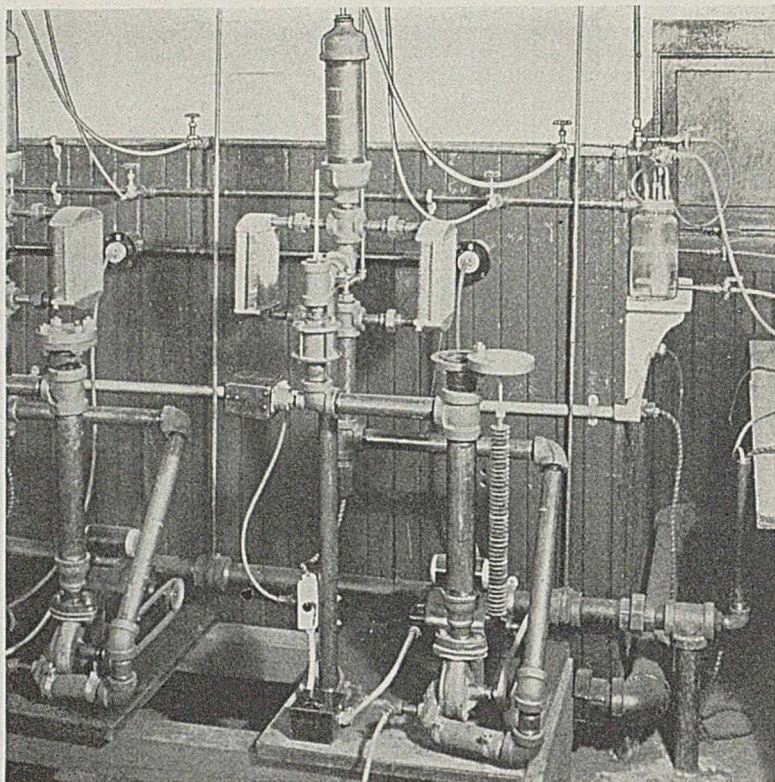


FIGURE 4. CIRCULATING UNIT, SHOWING TEST DISK ASSEMBLY REMOVED

another liquid phase. At the end of a year, a small-scale corrosion test of the antifreeze is made to determine whether it has retained its original corrosion-inhibiting properties.

Attack of Rubber

Attack of rubber by antifreeze solutions is important, because in an automobile cooling system the solution is constantly in contact with a large area of rubber surface in the form of rubber hose connections. While it is true that the basic material present in the antifreeze determines to a great extent the action of the antifreeze solution on rubber, materials added to the basic component to improve other qualities may also affect its behavior towards rubber. For this reason, an antifreeze should be tested for possible attack on rubber, by either of the two satisfactory methods described below.

In one method, a section of actual radiator hose is immersed in the antifreeze solution which is maintained at the normal operating range of temperature for 6 weeks. The section of hose is then removed, and the extent of swelling measured, and the appearance noted.

In the other method which the authors use, an examination is merely made at the end of the test of the hose connection used on the large-scale corrosion testing units previously described. If the hose connection survives a 5- to 6-week test on this unit without undue swelling or loss in mechanical strength, the antifreeze is considered satisfactory in this respect. This test is preferable because it closely approximates actual conditions of usage.

Foaming

Foaming of an antifreeze solution is highly undesirable for obvious reasons, the most important being the loss of solution from the cooling system via the overflow pipe. The chief aids to foaming are aeration and agitation, both of which ex-

ist in the corrosion tests in the circulation units previously described. Any tendency to foaming should, therefore, manifest itself during these tests. Observations are made periodically for evidence of foaming. A solution which foams to any serious extent will foam up into and out of the top of the reflux condenser which is located on the top reservoir of the unit.

Field Tests

Notwithstanding the care which is taken in making laboratory tests, and the effort which is made to duplicate actual conditions of use in an automobile, it is difficult to simulate all conditions. This could probably be accomplished if all automobile cooling systems were constructed exactly alike. Unfortunately, however, they all differ in some way, so that if the investigator simulates one particular cooling system in his laboratory tests, then his conditions of test and construction of equipment will not be wholly applicable to another.

Cooling systems of various makes of automobiles are likely to differ in one or more of the following characteristics: constructional design, materials of construction, metallic couples, rate of circulation, amount of aeration, and operating temperature.

It becomes necessary, therefore, in making the final evaluation of a new antifreeze, to employ field tests in a wide variety of automobiles under various conditions of use. Accurate comparative results cannot be obtained by road tests, it is true, because conditions cannot be controlled, but these tests do occasionally reveal a fault in an antifreeze which did not manifest itself in laboratory tests.

Acknowledgment

Earlier forms of the corrosion-testing equipment described herewith were originally developed by the senior author at The Miner Laboratories in connection with research fellowships of the Association of American Soap and Glycerine Producers, Inc.

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Viscosity Measurement

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Viscosity and viscosity temperature coefficients are valuable identifying properties of pure compounds and petroleum fractions. This paper discusses the operating characteristics of simple modified Ostwald viscometers that are suitable for covering a wide range of viscosity with accuracy. The important sources of error in capillary viscometers are analyzed briefly and equations for computing the necessary corrections are given. Comparisons are made with other types of capillary viscometers which show that the modified Ostwald is equal in accuracy to any now available.

FOR many years viscosity and viscosity-temperature coefficients of petroleum fractions have been regarded as important physical constants. The work of Mikeska (8) and Wiggins (13) on organic compounds shows these properties to be valuable identifying characteristics that will doubtless find greater application in future work. Since viscosity is intimately associated with structure, constitution, symmetry, polarity, saturation, and molecular size, it may be employed as a means of analysis. For example, the data of Wiggins (13) show the viscosity of diallyl, the diolefinic derivative of hexane, to be 15 per cent less than hexane at 0° C. and toluene differs from methylcyclohexane in viscosity by more than 20 per cent at 0° C. Many high-boiling petroleum fractions of

identical boiling points differ in viscosity by several hundred per cent.

It is the purpose of this paper to describe briefly suitable capillary-type viscometers for measuring viscosity in a simple but precise manner. In addition, the sources of error and their magnitude will be discussed, together with means of rendering these negligible.

Figure 1 is an illustration of an accurate routine viscometer, particularly designed for petroleum fractions, which is now in extensive use in the petroleum industry both in this country and abroad. A complete description and operating technic have been recently published by the American Society for Testing Materials (1).

The extra bulb on the capillary side of the instrument is for the purpose of incorporating an accurate loading device as an integral part of the viscometer. A glass bridge joins the two legs of the viscometer as shown; in addition heavy-walled glass is used throughout, so that the instrument is not fragile. Practically any size of working capillary can be used in the viscometer, so that very viscous fluids such as heavy lubricating oils can be tested quickly and accurately. For example, a series of four such instruments of different capillary bores will conveniently cover a viscosity range of 2 to 1000 centistokes: The instrument of smallest bore would be for a range of 2 to 10 centistokes, the next for 6 to 40 centistokes, the next for 30 to 200 centistokes, and the fourth for 150 to 1000 centistokes. Because of the low cost and ease of construction, it is possible to obtain viscometers with bores most convenient for the particular viscosity range in question. Six cubic centimeters of liquid are required for a test. The overall length of the instrument is approximately 25 cm. Six or more will readily fit into a small constant-temperature bath.

Operation of Modified Ostwald Viscometer

The viscometer is loaded at room temperature by holding it in an inverted vertical position with the capillary side submerged

in the liquid under test. Suction is then applied to the other arm of the instrument and both small bulbs on the capillary arm are filled with oil. The liquid is brought into the working capillary to the etched mark; hence, the total charging volume is that held by the two bulbs plus that held by the capillary extending to the open end of the instrument. After filling, the viscometer is revolved to its normal vertical position and placed in the constant-temperature bath. The liquid will drain into the lower reservoir during the time required for it to attain the bath temperature. When this temperature is reached, the efflux time is obtained by drawing the liquid up to the mark between the bulbs and measuring the time required for the meniscus to pass from the mark between the bulbs to the mark below the lower bulb on the capillary. The viscosity of the fluid is then obtained by multiplying the efflux time in seconds by the viscometer constant. The evaluation of the viscometer constant is discussed later. The only function of the upper bulb on the capillary arm is to serve as an accurate loading device in conjunction with the end capillary and efflux bulb. Laboratory experiments show that the instrument and liquid contents will reach a bath temperature of 37.78° C. (100° F.) in about 4 minutes and a temperature of 98.8° C. (210° F.) in approximately 10 minutes.

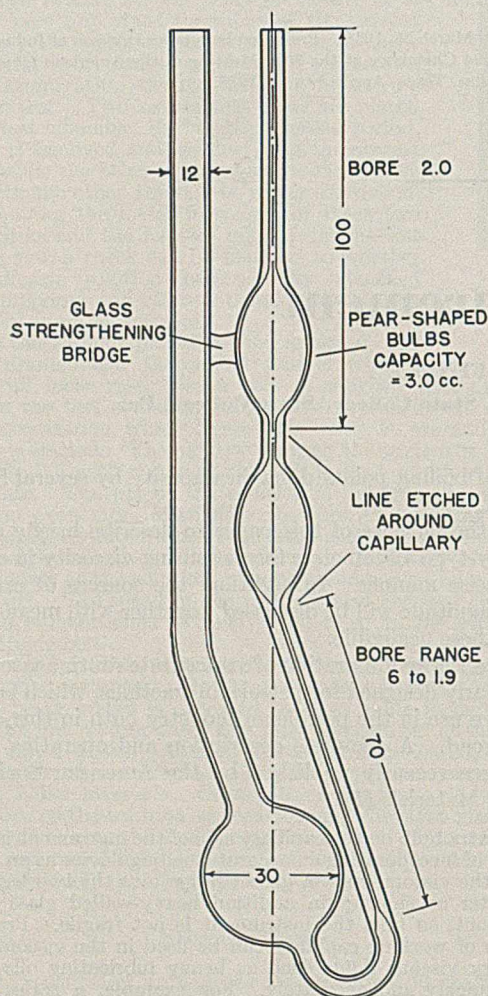


FIGURE 1. ROUTINE VISCOMETER FOR PETROLEUM PRODUCTS
Dimensions in mm.

A viscometer more suitable for nonviscous liquids is illustrated by Figure 2. This instrument differs from Figure 1 in several respects. The efflux volume and working capillary are considerably smaller and the diameters of the efflux bulb and the lower reservoir (actually part of the larger arm) are the same. These changes were made to reduce kinetic energy and surface tension corrections, but are not incorporated in the

routine type (Figure 1), first, because no kinetic energy corrections are encountered in products of 2 centistokes or more in these instruments if properly used, and secondly, because petroleum fractions do not differ sufficiently in surface tension to become an appreciable source of error. It will be shown later that a large difference in surface tension will necessitate only a small correction.

This second viscometer has an over-all length of approximately 30 cm. and requires a 2.5-cc. charge. The efflux bulb has a volume of 1.0 cc. It is recommended for viscosities ranging from 0.3 to 5 centistokes. It can be used for more viscous liquids, but the type shown as Figure 1 is more convenient for the higher viscosity range.

A semimicroviscometer (Figure 3) has an over-all length of approximately 30 cm. and requires a total charge of 0.25 cc. It can be made with practically any desired capillary bore to cover a range of 0.5 to 800 centistokes. The efflux volume is approximately 0.15 cc. and the efflux capillary and lower reservoir capillary are of the same diameter to eliminate surface tension corrections. Although the over-all length of these instruments is 30 cm., the length submerged in the bath is approximately 20 cm., so that a constant-temperature bath that is 20 cm. deep is suitable.

Magnitude and Source of Errors

Loading errors arise from the fact that the driving fluid head is dependent upon the amount of liquid in the instrument. Thus, if too much liquid is charged to the instrument, the level in the lower reservoir is too high and driving head is reduced by that amount. The expression for loading errors is:

$$\% \text{ error in loading} = \frac{100 \nu}{\pi r^2 H}$$

where ν is the loading error, r is the working radius of the lower reservoir, and H is the driving liquid head.

As a specific example of the magnitude of this error, consider a routine type of viscometer (Figure 1). In these instruments H is approximately 10 cm., r is 1.5 cm., and a working capillary of 0.1-cm. diameter will be considered. If, when loading, the operator misses the etched mark on the capillary by 0.1 cm., then ν will be 0.00079 cc. and the percentage error 0.001 per cent. To make an error of 0.1 per cent it would be necessary for the operator to miss the etched mark on the capillary by 12 cm. The viscometers shown as Figures 2 and 3 are more sensitive to loading errors, but the error is readily maintained below 0.1 per cent. The validity of this loading error equation was proved by weighing into several viscometers a known excess of test liquid and checking the results obtained with those predicted by the equation. Checks were also made by withdrawing known amounts, so that a deficient quantity of liquid was in the instrument. In all cases the experimental results agreed with those predicted by the equation.

Kinetic energy corrections are primarily due to contraction and expansion losses at the entrance and exit of the capillary. It is customary (2) to include the kinetic energy correction in Poiseuille's equation as follows:

$$KV = \frac{\omega}{\rho} = \frac{\pi g H r^4 t}{8 L V} - \frac{m V}{8 \pi L t}$$

where KV = kinematic viscosity in stokes

ω = viscosity in poises

ρ = density in grams per cc.

g = gravitational constant in cm. per sec. per sec.

H = fluid head in cm.

r = radius of capillary in cm.

t = efflux time in seconds

L = capillary length in cm.

V = efflux volume in cc.

m = kinetic energy coefficient

The second term on the right side of this equation is the kinetic energy correction. In a properly designed instrument this term should be very small compared with the first term on the same side of the equation. The percentage error or correction is more important than the absolute figure. The expression for the percentage correction can be obtained by dividing the kinetic energy term by the main term and multiplying by 100.

$$\text{Kinetic energy correction in per cent} = \frac{mU^2}{gH} 100$$

The velocity in the capillary is given by U . From this expression it is obvious that kinetic energy corrections will increase as the square of the velocity in the capillary.

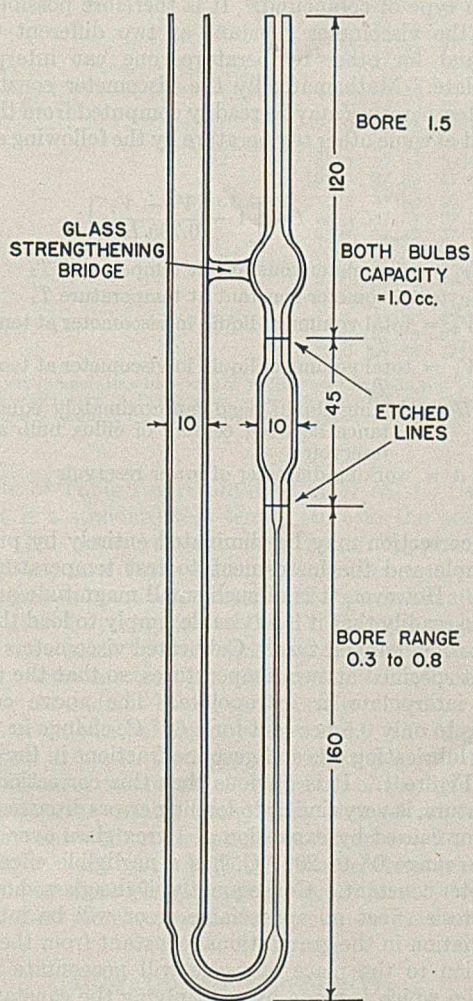


FIGURE 2. VISCOMETER FOR NONVISCIOUS FLUIDS
Dimensions in mm.

For most types of viscometers the correct value of m is not known, but it is probably intimately associated with the shape of the entrance and exit of the capillary. Values of $m = 0$ to $m = 1.12$ have been reported (2). In all the instruments discussed here the capillary openings are gradually tapered to give a trumpet-shaped opening. Bingham and Thompson (3) report a value of $m = 0.56$ for such openings. Granted that this value may not apply to other capillaries of similar construction, nevertheless it is probably of the proper magnitude and may be used to calculate the permissible velocity range in a

capillary so that kinetic energy corrections may be maintained below 0.2 per cent. This was verified by testing water at two different temperatures in each of two viscometers with capillaries of different size.

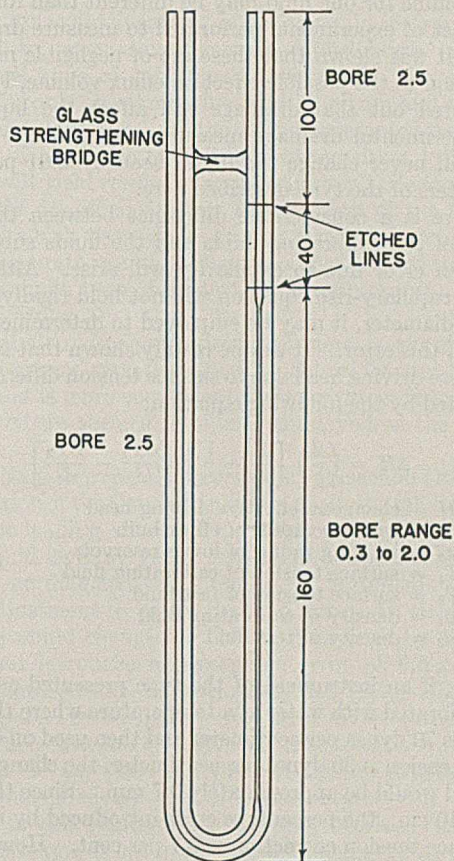


FIGURE 3. MICROVISCOMETER
Dimensions in mm.

The kinetic energy term needs special attention only when designing instruments for nonviscous liquids (2 centistokes or less). In viscometers designed for more viscous liquids the capillary is large enough to make this correction negligible. Since the value of m is not accurately known, it is not safe to allow the kinetic energy correction to become appreciable and attempt to apply this correction to the results. There is no assurance that m is a constant for a given instrument; it may vary with the velocity of the liquid in the capillary in addition to the shape of the capillary openings. It is a simple matter to construct a viscometer with dimensions such that the calculated kinetic energy correction is less than 0.2 per cent for liquids as low as 0.5 centistoke in viscosity. The viscometer shown as Figure 2 differs in its dimensions from that shown as Figure 1, mainly for the purpose of eliminating kinetic energy corrections. These corrections are not encountered in the first viscometer, since it is designed to cover a range of viscosity from 2 centistokes upward. The microviscometers are free from kinetic energy corrections if the dimensions are properly selected. It is obvious that the efflux volume and capillary diameter should be made small in order to reduce the kinetic energy correction. It is also reduced by increasing the driving fluid head—i. e., the distance between the efflux bulb and the lower reservoir.

As the fluid stream emerges from the capillary, it has a tendency to retain the shape of the capillary for a finite distance into the fluid medium. This apparent increase in capillary

length, known as the Couette correction, is a function of the capillary radius. It is included in the viscometer constant established by calibration.

Drainage errors arise from the fact that all liquids do not drain from a surface with equal ease; hence, the measured efflux volume for one fluid may be different than for another. In a series of experiments performed to measure drainage errors (4) it was shown that these are of negligible magnitude. In addition to the possible effect on efflux volume, Fitzsimons (6) pointed out that drainage will affect the liquid head. The experimental drainage measurements indicate that this effect will never change the liquid head by 0.01 per cent in viscometers of the type described here.

If there is a considerable difference between the surface tension of the calibrating fluids and the fluids subsequently tested, an error due to capillarity will arise. Although the familiar capillary-rise equation will not hold rigidly for tubes of large diameter, it may be employed to determine the magnitude of this error. It can be readily shown that the change in effective driving head due to surface tension difference is approximated by the following equation:

$$\Delta H = \left(\frac{2}{g}\right) \left[\frac{1}{r_1} - \frac{1}{r_2}\right] \left[\frac{ST_1}{d_1} - \frac{ST_2}{d_2}\right]$$

where ΔH = change in effective driving head
 r_1 = working radius of efflux bulb
 r_2 = working radius of lower reservoir
 ST_1 = surface tension of calibrating fluid
 ST_2 = surface tension of test fluid
 d_1 = density of calibrating fluid
 d_2 = density of test fluid

Hence, if an instrument of the type presented as Figure 1 were calibrated with water at a temperature where the surface tension is 70 dynes per centimeter and then used on oils whose surface tension is 30 dynes per centimeter, the change in effective head would be approximately 0.7 mm. Since the driving head is 10 cm., the percentage error introduced by neglecting the surface tension correction is 0.7 per cent. However, it is a simple matter to make this correction accurately or to calibrate the instruments by means of viscosity standards which have been standardized in master instruments especially constructed to maintain all errors negligible (5). It is evident that surface tension changes produce a very small effect, for in the case considered a change of over 200 per cent in surface tension necessitated a correction of only 0.7 per cent. The viscometers presented as Figures 2 and 3 are free from surface tension corrections because in the latter instrument the efflux and lower reservoir tubing are of the same diameter and in the instrument shown in Figure 2 practically all the efflux time is measured when the menisci of both the upper and lower levels are in tubes of equal diameter.

It is necessary to align the viscometer in the bath in an exact vertical position, so that the full available driving fluid head is utilized. If the center of the efflux bulb is joined to the center of the lower reservoir by an imaginary line which makes an angle of A degrees with the vertical, and if this should be moved dA degrees, then the resultant fractional change in the fluid head will be given by the expression:

$$1 - \frac{\cos(A + dA)}{\cos A}$$

For this to be a minimum, angle A should be zero. In other words, the upper efflux bulb and the lower reservoir should lie in the same vertical planes. With this type of construction the viscometer must be tilted 2.5° from the vertical to introduce an error of 0.1 per cent. A deviation of 2° is readily detected by visual inspection, but for safety the viscometer may be aligned vertically with the aid of a small plumb bob made from silk thread and a small piece of lead,

which is placed in the open arm of the viscometer. An experienced operator can load and align the viscometer in the bath in less than one minute. The viscometer of Figure 1 has the efflux bulb and lower reservoir directly in line for eliminating alignment errors. This modification has not been incorporated in the other two viscometers, because they are longer and readily adjusted to the vertical position. The vertical alignment of bulbs was originated by Gruneisen (2).

The viscometer constant will vary with the temperature, but the magnitude of the change is small and readily computed. This correction arises because of the change of specific volume with temperature. Thus, if the viscometer is loaded at 25°C . and then used at some higher temperature, say 100°C ., a correction should be applied. The thermal coefficients of cubical expansion of most hydrocarbons do not differ sufficiently to necessitate an individual correction for each type of compound. It is therefore possible to give simply the viscometer constant at two different temperatures, and for other temperatures one can interpolate or extrapolate. Mathematically the viscometer constant at a second temperature may be readily computed from the known constant at some other temperature by the following equation:

$$C_{T_2} = C_{T_1} \left[1 - \frac{V_2 - V_1}{0.785 Hd^2}\right]$$

where C_{T_2} = viscometer constant at temperature T_2
 C_{T_1} = viscometer constant at temperature T_1
 V_2 = total volume of liquid in viscometer at temperature T_2
 V_1 = total volume of liquid in viscometer at temperature T_1
 H = driving liquid head, approximately equal to distance between centers of efflux bulb and lower reservoir
 d = working diameter of lower reservoir

This correction may be eliminated entirely by preheating the sample and the instrument to test temperature before loading. However, it is of such small magnitude and determined so readily that it is advisable simply to load the instrument at room temperature. Calibrated viscometers have the constant specified at two temperatures, so that the user may readily interpolate or extrapolate. The above correction amounts to only 0.5 per cent for a 60°C . change in temperature for lubricating oils and gasoline fractions in the viscometers of Figure 1. It is obvious that this correction, due to temperature, is very similar to loading errors discussed earlier. The error caused by expansion of Pyrex glass over the temperature range 0° to 200°C . has a negligible effect on the viscometer constant. Consequently, if the glass should show a hysteresis effect no appreciable error will be introduced.

A variation in the gravitational constant from the place of calibration to the place of usage will necessitate a simple correction which is made by multiplying the constant of the viscometer by the ratio of g at the point in question to g at the point of calibration. As the value of g does not change by more than 0.1 per cent throughout the United States, this correction is of secondary importance.

Dark fluids will readily absorb radiant heat energy from solar or unshielded light sources. Consequently a dark fluid under test may be several tenths of a degree higher in temperature than the bath medium in which it is immersed. Since a slight change in temperature causes an appreciable change in viscosity of most fluids, it is important that lights employed in the immediate vicinity of the bath be shielded. Table I contains data which show the magnitude of this radiant energy effect. In most practical cases lights employed for good visibility in constant-temperature baths are not more than 25 watts and are placed in the rear, so that their distance from

the working area of the bath is greater than 10 cm. (4 inches). In most installations their effect will be small, but if proper care is not exercised the error so introduced may be of consequence.

TABLE I. MAGNITUDE OF TEMPERATURE INCREASE IN LIQUIDS CAUSED BY RADIANT ENERGY FROM UNSHIELDED LIGHT BULBS

Liquid	Color	Type of 110-Volt Light Bulb	Distance of Bulb Surface from Bath Surface		Temp. of Liquid ° C.	Temp. of Water Bath ° C.	Difference ° C.
			10.00	5.00			
Lube oil	A. S. T. M. No. 7	100-watt frosted	1.25	38.41	37.78	0.63	
			5.00	38.19	37.78	0.41	
		75-watt frosted	10.00	38.07	37.78	0.29	
			1.25	38.06	37.78	0.28	
		50-watt frosted	5.00	37.92	37.78	0.14	
			10.00	37.89	37.78	0.11	
Lube oil	A. S. T. M. No. 2.5	100-watt frosted	1.25	38.36	37.78	0.58	
			5.00	38.13	37.78	0.35	
		75-watt frosted	10.00	38.02	37.78	0.24	
			1.25	38.04	37.78	0.26	
		50-watt frosted	5.00	37.94	37.78	0.16	
			10.00	37.89	37.78	0.11	
Water	100-watt frosted	1.25	37.83	37.78	0.05	
			5.00	37.80	37.78	0.02	
		75-watt frosted	10.00	37.79	37.78	0.01	
			1.25	37.80	37.78	0.02	
		50-watt frosted	5.00	37.79	37.78	0.01	
			10.00	37.78	37.78	0.00	

The constant-temperature bath was of 36-liter capacity and was filled with water. The walls were of Pyrex glass approximately 0.6 cm. thick. The Pyrex test tube containing the sample was 5 cm. from the inner bath surface.

The data of Table I were obtained at 37.78° C. (100° F.) because it is a standard test temperature in the petroleum industry. The measurements were made by placing the fluid under test in a Pyrex test tube and then immersing it in a constant-temperature water bath automatically controlled at 100° F. to within $\pm 0.05^\circ$ F. Temperature measurements were made by very sensitive Bureau of Standards calibrated thermometers. In the experiments where water was tested, the radiant heat was probably picked up by the thermometer bulb rather than by the water. The magnitude of the actual errors in viscosity caused in this way depend upon the viscosity temperature coefficient of the fluid at the test temperature. Many heavy oils change in viscosity by 0.2 per cent with a temperature change of 0.1° F. in the vicinity of 100° F. At lower temperature levels the effect would be more pronounced because viscosity temperature coefficient increases with decreasing temperature level.

Calibration of Viscometers

A nearly ideal reference basis for viscosity work is pure water. Instruments which are designed to cover a viscosity range in the neighborhood of water can be calibrated directly against water. When an instrument is designed to cover a range far removed from water, such as that found in lubricating oils, direct calibration is not possible. However, water may be retained as the reference basis by standardizing a series of oils in suitable master instruments and then employing these oils as calibration standards. This procedure has been explained in detail elsewhere (5). As many oils are unstable and increase in viscosity with age as much as 2.0 per cent per year, it is advisable to check the viscosity of standardized oils from time to time. Solvent-treated or aluminum chloride-desludged oils of high viscosity index are the most stable and some vary only 0.2 per cent per year.

For accurate results it is necessary to employ sensitive and reliable auxiliary equipment. Descriptions of satisfactory units have been published (5).

Comparison with Other Viscometers

Various other modifications of the Ostwald instrument are advocated by some investigators. Ubbelohde's (12) suspended-level type of instrument differs from the type described here only in eliminating loading errors and reducing surface tension errors. In the design presented here such errors are of negligible magnitude; hence either type of instrument will yield results of equal accuracy. Zeitfuchs (14) has recently described another modification of the Ostwald instrument which also reduces loading errors and undoubtedly will yield accurate results. Slight modifications of the Ubbelohde type have been described by Fitzsimons (6) and by Payne and Miller (9).

The semimicroviscometer described here is simpler than the falling-sphere type described by Schneider and McConnell (11) and is more convenient than the type described by Levin (7) where surface tension is employed as the driving force.

The viscometer recently described by Raaschou (10) is also a modification of the Ostwald tube and again the main purpose is to reduce loading errors. This is accomplished by adjusting the liquid level by visual inspection of the meniscus in a tube of large diameter (17.5 mm.). It is difficult to make such an adjustment to better than 0.5 mm. An error of this magnitude would change the driving fluid head by the same amount and introduce a percentage error of 0.5 per cent (since the total head is approximately 100 mm.). For most practical purposes such an error is of little consequence. Raaschou uses a value of 1.0074 centistokes as the viscosity of water at 20° C., whereas a value of 1.0068 centistokes has been recommended by the American Society for Testing Materials as the standard for viscosity work. While this difference is slight, it has been included in this report to cover completely the many factors involved.

It appears, then, that there are available a number of capillary-type viscometers which will yield accurate results. The prospective user can be guided in his choice by such factors as cost, simplicity of design and operation, etc.

The reproducibility of results with the modified Ostwald viscometers described in this paper is ± 0.2 per cent. The accuracy of the results depends upon the accuracy with which the absolute viscosity of water is known at 20° C., since water is used as the ultimate reference basis. This error is probably in the neighborhood of ± 0.5 per cent. However, relative viscosities are very accurate and if the reference basis is clearly defined little confusion will exist and reported values of viscosities may be readily compared.

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Determination of Iron in Biological Material

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NUTRITION work being carried out in this laboratory required a method for the determination of total iron in a wide variety of biological materials, which would yield equally accurate results with all samples with only very minor modifications. Many methods for this determination have appeared in the literature, but they have all been for use on some particular material, and do not yield accurate results on other materials when only the quantities of reagents are varied. This observation led to a complete investigation of the sources of error inherent in this determination and of means by which they could be overcome. A method was developed that gave accurate results with whole rats, milk and milk products, and a large number of both fresh and dried foods.

Determination of Iron

The determination of total iron in any organic matter resolves itself into two main steps: the ashing of the sample, and the determination of the iron in this ash. A satisfactory procedure for accomplishing the second step with any type of ash was necessary before an investigation of the merits of various methods of ashing could be undertaken. The research was accordingly planned on this basis.

The iron-containing ashes were prepared by an adaptation of Klumpp's method (6), which he used in conjunction with his titanous sulfate titration. The material was dried with a small amount of concentrated sulfuric acid (about 2 ml. per gram dry weight of the sample) and ashed in a muffle at 500° to 550° C. The ash was then taken up in hydrochloric acid, filtered, and diluted to an appropriate volume.

For various reasons a colorimetric method of determination was preferred. The titanous sulfate titration procedure of King and Howard (5) and Klumpp (6) was inconvenient, because of the special precautions needed for the preservation and use of this reagent and the large samples required, particularly of materials containing small amounts of iron. These were not always readily procurable and introduced difficulties in ashing. Moreover, the end point of the titration, while sharp with standard iron solutions, was obscured by phosphates or a high salt concentration. Colorimetric methods require much smaller amounts of iron for the determination, and the use of an Evelyn photoelectric colorimeter (1, 2) for the estimation of the color removed the personal factor inherent in all visual colorimetric comparisons.

A comparison of the relative merits of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (known as ferron, 3) and of α, α' -dipyridyl as chromogenic agents led to the selection of the latter. Ferron, which is itself yellow, slowly develops an additional green color in the presence of ferric iron. This color did not obey Beer's law, the pH of the solution had to be accurately controlled, and no advantages, such as immunity to interfering substances, compensated for these defects.

The use of α, α' -dipyridyl for the determination of inorganic iron was introduced by Hill (4) and has since been used by Elvehjem (7) for the same purpose. It was found to have somewhat more than twice the sensitivity of ferron and was not affected by pH between the limits of 2.5 and 6.0. The color developed at once on addition of the reagent to standard iron solutions (buffered to about pH 4.0 and containing hydroquinone to reduce the iron to the ferrous state). It obeyed Beer's law almost exactly and was not affected by salt concentration or by orthophosphate. However, the

presence of pyrophosphate in amounts equivalent to those that could be expected in actual analyses delayed the production of the color and prevented its full development even after standing 24 hours, at which time the color had become constant.

The first determinations were made directly on the solution of ash. The excess acidity was neutralized by the addition of 25 per cent sodium hydroxide, an accurate aliquot of this solution was buffered to a pH of about 4.0 by the addition of an acetate buffer and hydroquinone, and the α, α' -dipyridyl was added. The presence of pyrophosphate was at once evidenced by the slow development of the color, which reached a maximum only after 24 to 48 hours. Heating the acid ash solution prior to neutralization for 18 hours at 80° C. completely hydrolyzed the pyrophosphate to orthophosphate. With the addition of this step the color of the iron— α, α' -dipyridyl complex developed to a maximum within a few minutes.

TABLE I. VARIATION OF TOTAL APPARENT IRON CONTENT WITH VOLUME OF ALIQUOT

Experiment	Ash Solution in Tube ML	Apparent Iron in Tube Mg.	Amount Expected from 1-Ml. Tube Mg.
After Hydrolysis of Pyrophosphate			
I	1	0.0020	0.0100
	5	0.0071	
II	1	0.0045	0.0135
	3	0.0108	
	5	0.0164	
III	2	0.0033	0.0082
	5	0.0060	
IV	2	0.0046	0.0115
	5	0.0085	
After Hydrolysis of Pyrophosphate and Fractionation of Iron by Ammonium Hydroxide and Hydrogen Sulfide			
V	1	0.0052	0.0156
	3	0.0158	
VI	1	0.0056	0.0168
	3	0.0170	
VII	1	0.0059	0.0177
	3	0.0172	
VIII	1	0.0099	0.0297
	3	0.0297	

By the use of this modified procedure close checks on successive aliquots of the same ash solution were obtained. However, if different aliquots were taken, the apparent iron recovered in them was not proportional to their volume. For example, if two colorimeter tubes were prepared using 1 and 3 ml., respectively, of the same ash solution (the difference in volume being made up by the addition of water), the apparent iron in the second tube was not three times the amount in the first, but somewhat less. This effect is illustrated by the first part of Table I. In every case the amount of iron found in the tubes containing the larger aliquots was considerably less than expected.

This observation led to the conclusion that an additional interfering substance or substances were present in these ash solutions. The interfering substances were not common to all materials. There was little or none to be found in cereals or in whole rats, but dried tomatoes and spinach were particularly bad offenders in this respect. Thus, while the modified procedure was satisfactory for some materials, it could not be trusted to give truthful results when applied indiscriminately to biological products in general.

It was thought that this interference might be due to some product formed during the ashing and that the difficulty might be overcome by judicious selection of a procedure for this step in the analysis. However, it was present after all

procedures that were tried, which included both wet- and dry-ashing methods. Experiments III and IV (Table I) were done on an ash solution obtained by wet-ashing dried tomatoes with nitric, sulfuric, and perchloric acids.

It was found that by precipitation with hydrogen sulfide in ammoniacal solution, following the procedure described below, the iron could be completely separated from the interfering substances, which remained in the filtrate. The iron was recovered from the precipitate by dissolving it in hydrochloric acid. The filtrate, after boiling off the excess ammonium hydroxide and hydrogen sulfide and concentrating it about four times, gave no color with α, α' -dipyridyl. Iron was recovered quantitatively when added to the ash solution, or when the iron standard solution alone was treated by this procedure, whether in the presence or absence of calcium phosphate. Experiments V to VIII (Table I) show that interfering substances were removed. The only difference between these two sets of experiments was the introduction of the hydrogen sulfide-ammonium hydroxide precipitation. The same sample of dried tomato was used in both cases. In each case the amount of iron found in the aliquot is closely proportional to the volume of the aliquot.

Ashing Methods

The method as thus modified could be depended on to give accurate results when applied to any type of ash. The next step in the investigation became an inquiry into the merits of the various recognized ashing procedures. The greatest difficulty to be overcome was the possibility of loss of iron as the chloride, particularly in materials containing large amounts of sodium or potassium chlorides relative to the iron content. Methods of ashing have been designed to minimize this loss as much as possible, an object which is only approximated by many.

Four methods of ashing were tried: dry-ashing with addition of sodium carbonate, dry-ashing with addition of a small amount of sulfuric acid (6), dry-ashing after covering the sample with a layer of iron-free calcium carbonate (3), and wet-ashing using nitric, sulfuric, and perchloric acids. Dry-ashing with sodium carbonate was soon discarded because of the poor checks obtained. Klumpp's and Farrar's methods gave fairly consistent checks and recoveries of added iron with an occasional erratic result. Wet-ashing gave consistently good checks and iron recoveries. As a final test of the efficiency of these three methods, an organic solution containing a known amount of iron was prepared and ashed. This solution consisted of 7.5 per cent of glucose, 2.5 per cent of urea, 100 mg. per cent of calcium phosphate, 100 mg. per cent of sodium chloride, and 1.00 mg. per cent of iron added as a standard iron solution dissolved in hydrochloric acid. When 10-ml. aliquots of this solution were dried down and ashed, with Klumpp's method the best recovery was 54 per cent of the known iron content, while most of the recoveries were about 40 per cent. The recoveries with Farrar's calcium carbonate method were 80 to 87 per cent, much better than Klumpp's, but still not good enough. When the glucose-urea solution was wet-ashed, the recoveries were 100 per cent, with an error of ± 1 per cent. Wet-ashing was thus demonstrated to be the only acceptable method of those tested. The following method of analysis was finally adopted for general application.

Method

A convenient sized sample of material, containing at least 0.02 mg. of iron, was accurately measured and placed in a 300-cc. Kjeldahl flask. If the sample was a dry powder, a few milliliters of water were added. Five milliliters of nitric acid (distilled to remove iron impurities) and 1 cc. of concentrated sulfuric acid were added, and the flask was gently heated so that

the solution was just boiling. Further 5-ml. additions of nitric acid were made as the solution began to char, until the oxidation had practically ceased. One milliliter of perchloric acid was then added and the flask was heated slightly more vigorously until white fumes began to form. Heating was stopped at this stage if the solution was colorless; otherwise, it was continued until this point was reached. After cooling, the solution was diluted to about 25 ml. Usually the solution was clear, but if a precipitate of calcium sulfate was present, as with milk samples where there is a large proportion of calcium to iron, this was filtered off and the filter paper washed.

A drop of bromophenol blue was added to the acid ash solution and concentrated ammonium hydroxide added until the acid was neutralized. About 3 ml. excess ammonium hydroxide was then run in, a total of 8 ml. usually being required, and hydrogen sulfide was passed in until the solution became saturated. It was allowed to stand a few minutes and filtered by suction on a fine Jena glass filter, the filtrate being discarded. This type of filter would pick up a precipitate so finely dispersed as to appear only as a faint green coloration, if visible at all. Care was taken not to suck the precipitate dry, as this might result in some loss of iron due to oxidation to the soluble sulfate. Without washing, the precipitate was dissolved in 1.0 ml. of 1 to 1 hydrochloric acid. The Kjeldahl flask was rinsed into the filter once with 1 ml. of 1 to 1 hydrochloric acid and several times with small amounts of water, and the whole was sucked through the filter, which was washed several times with water. The combined filtrate and washings were boiled to remove excess hydrogen sulfide, and effect solution of any colloidal sulfur. After cooling, the solution was quantitatively transferred to an appropriate volumetric flask and the excess acidity neutralized with 25 per cent sodium hydroxide. The solution was left sufficiently acid to remain perfectly clear. It was then diluted to the mark.

The Evelyn photoelectric colorimeter (1, 2) was used for the actual determination of the iron.

An accurately measured aliquot of the iron solution containing about 0.01 mg. of iron was placed in a colorimeter tube and 3 ml. of an acetate buffer containing 83 grams per liter of sodium acetate and 120 ml. per liter of glacial acetic acid were added, with sufficient water to bring the total volume to 12 ml. About 50 mg. of hydroquinone, gaged roughly on the tip of a spatula, was dissolved in the solution. On the addition of 1 ml. of 0.1 per cent α, α' -dipyridyl solution, the characteristic pink color developed immediately. A blank was carried through the entire procedure at the same time. The color was estimated with the colorimeter, using Evelyn's filter 520 and setting the galvanometer to read 100 with the blank in place in the tube holder. By so doing, the effect of any iron contamination in the reagents was automatically eliminated. The use of a wet-ashing procedure largely prevented the formation of pyrophosphates. However, if there was any delay in the maximum color development, the iron solution was acidified and heated, and the iron estimation repeated.

TABLE II. IRON CONTENT DETERMINED BY FINAL METHOD
(Duplicates carried through entire procedure)

Material	Galvanometer Reading	Iron in Tube Mg.	Iron Found Mg./100 g.
Dried spinach and corn-starch	68.5	0.0079	3.95
	69	0.0077	3.85
Pabulum	71.5	0.0069	27.6
	71.25	0.0070	28.0
Dried spinach	58.5	0.0112	44.8
	59	0.0110	44.0
Cornstarch	70.75	0.0072	1.80
	70.75	0.0072	1.80
Farina	83	0.0038	0.95
	83.75	0.0036	0.90
Milk powder	67.5	0.0082	1.37
	68	0.0080	1.33
Whole rat (aliquots of same ash solution)	37	0.0210	7.0
	37	0.0210	7.0 (mg. in total rat)

The amount of iron in the volume of unknown added to the colorimeter tube for the corresponding galvanometer reading was read directly off a previously determined calibration curve.

Alternatively, the value could be calculated from the

formula $M = \frac{2 - \log G}{K}$, where M = mg. of iron in the aliquot added to the tube, G = corrected galvanometer reading, and K = a constant. For this determination K varied slightly from 20.6 in the range of $M = 0.005$ mg. to 21.9 in the range $M = 0.020$ mg. Table II shows some results on widely varying materials.

Summary

A general method for the determination of total iron in biological materials with α, α' -dipyridyl is described in detail.

Evidence is given for the interference of pyrophosphate and of a second unidentified substance or substances with

the development of the color. Steps are included in the procedure which successfully circumvent these difficulties.

Various ashing procedures have been investigated.

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Cerate Oxidimetry

Evaluation of Solutions Using Sodium Oxalate, Arsenious Acid, and Iron as Standards of Reference, and Ferroin and Nitro-Ferroin as Indicators

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CERATE oxidimetry involves the use of the anions $(\text{CeCl}_6)^{--}$, $\text{Ce}(\text{SO}_4)_3^{--}$, $\text{Ce}(\text{NO}_3)_6^{--}$, and $\text{Ce}(\text{ClO}_4)_6^{--}$ in the form of the free acids or their ammonium or potassium salts. The first paper of this series (2) has shown that the single-electrode potentials at standard state for these cerate anion species in equilibrium with the cerous ion in hydrochloric, sulfuric, nitric, and perchloric acid solution increase in the order given by 200, 150, and 100 millivolts, starting with the value 1.28 volts in the case of the hexachlorocate ion and ending in the value 1.7 volts in the case of the hexaperchlorato cerate ion. With conditions defined for the attainment of potentials in the range 1.6 to 1.86 volts using cerate solutions in nitric and perchloric acid of various strengths, favorable effects in the oxidation of various reductants might be expected.

It is the purpose of the present paper to point out the increased facility with which the oxalate ion can be determined using the higher potentials provided by cerate oxidimetry. The accuracy obtained has been tested, using as additional standards of reference arsenious oxide and ferrous sulfate solutions that were standardized by comparison with the sulfato cerate ion in sulfuric acid solution through the medium of sodium oxalate. A further objective in the present paper is the description of the advantages attained by the use of nitro-ferroin (nitro-*o*-phenanthroline ferrous ion) as compared to ferroin (*o*-phenanthroline ferrous ion) as a reversible oxidation-reduction indicator in cerate oxidimetry.

The determination of the oxalate ion using the sulfato

cerate ion in sulfuric acid solution requires that the reaction be carried out at or near the boiling point of such solutions. Even under these conditions the reaction is sluggish and the end point is best determined potentiometrically. In this respect the determination is similar to the permanganate oxidation of the oxalate ion, except that in the latter case a potentiometric end point determination is not required. The oxidation of the oxalate ion has been carried out using the chlorocate ion in hydrochloric acid solution as described by Willard and Young (4). In this case the reaction is not satisfactorily rapid at room temperature, but by employing iodine monochloride at a temperature of 50° C., the use of ferroin as indicator avoids the necessity for a potentiometric end point. This reaction is undesirably slow even at 50° C., which cannot be exceeded without destroying the ferroin indicator. The determination of the arsenite ion in sulfuric acid solution using the sulfato cerate ion has been described by Gleu (1). The reaction at ordinary temperatures is negligible unless osmic acid is present as catalyst. Ferroin is used as indicator and the reaction is inconveniently slow in the region of the equivalence point.

Ferroin and Nitro-Ferroin as Indicators

Ferroin and nitro-ferroin as high-potential oxidation-reduction indicators, introduced by Walden, Hammett, and Chapman (3), have transition potentials of 1.14 and 1.25 volts, respectively. Nitro-ferroin cannot be used successfully in sulfato cerate oxidimetry, since potentials of at least 1.55 to

1.6 volts are required, and for this reason it has not heretofore been employed in any practical quantitative application. For the same reason its use in nitrate and perchlorate cerate oxidimetry is very desirable. Fortunately, however, ferroin may be used with entirely satisfactory results, since nitro-ferroin is more expensive than ferroin from which it is prepared. Nitro-*o*-phenanthro-

TABLE I. COMPOSITION OF SOLUTIONS OF $\text{Ce}(\text{ClO}_4)_6^{--}$ AND $\text{Ce}(\text{NO}_3)_6^{--}$ STANDARDIZED

Solution No.	Cerate Ion Present	Acid Used	Method of Preparation	Cerate-Ion Concentration <i>N</i>	Remarks
1	$\text{Ce}(\text{ClO}_4)_6^{--}$	<i>N</i> HClO ₄	Electrolytic	0.05624	Cerous-ion concentration practically nil Solution contained small amounts of other cerium group metals Solution contained some free $\text{H}_2\text{Ce}(\text{NO}_3)_6$, K^+ , NH_4^+ , and a small amount of other earths Solution prepared from 96 per cent pure stock
2	$\text{Ce}(\text{ClO}_4)_6^{--}$	3 <i>N</i> HClO ₄	Electrolytic	0.05651	
3	$\text{Ce}(\text{ClO}_4)_6^{--}$	8 <i>N</i> HClO ₄	Electrolytic	0.05440	
4	$\text{Ce}(\text{ClO}_4)_6^{--}$	4 <i>N</i> HClO ₄	Electrolytic	0.09702	
5	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> HNO ₃	Electrolytic	0.05333	
6	$\text{Ce}(\text{NO}_3)_6^{--}$	3 <i>N</i> HNO ₃	Electrolytic	0.05146	
7	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> HClO ₄	$\text{K}_2\text{Ce}(\text{NO}_3)_6$ + $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	0.04269	
8	$\text{Ce}(\text{NO}_3)_6^{--}$	<i>N</i> HClO ₄	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	0.08320	

line was found to have a melting point of 201.5° C. as contrasted with *o*-phenanthroline monohydrate, 99–100° C. The former dye base is light yellow in color and the latter pure white.

Determination of Oxalate and Arsenite

The preparation of perchlorato and nitrate cerate solutions has been described (2). The oxidation of sodium oxalate and sodium arsenite using the perchlorato cerate ions was carried out potentiometrically, using *N* perchloric acid solutions of the $C_2O_4^{--}$ and AsO_3^{--} ions at room temperature. The same potentiometric assembly of apparatus was employed as that previously described (2). Nitro-ferroin was added as indicator to compare the visual and potentiometric end-point phenomena. The results are shown graphically in Figure 1.

The equivalence-point "break" in potential is 650 mv. in the case of the oxalate titration and 600 mv. in the case of the arsenite oxidation. Nitro-ferroin as indicator has its transition interval at an average potential of 1.25 volts, which corresponds to a value 0.11 volt higher than would be the case if ferroin were used. There is a noticeable advantage in the use of the former, since with ferroin a momentary preferential oxidation of the indicator occurs and a second or two is required for the pink color to return.

Standardization

Eight solutions of perchlorato and nitrate cerate in various concentrations of perchloric and nitric acids were prepared. The details of their preparation and composition are given in Table I.

SULFATO CERATE AND FERROUS SULFATE SOLUTIONS. An approximately 0.05 *N* solution of sulfato cerate ion was prepared by dissolving ceric sulfate in *N* sulfuric acid. A 10-liter solution of an approximately 0.05 *N* solution of ferrous sulfate in dilute sulfuric acid was prepared and stored under hydrogen to prevent change of titer. The sulfato cerate solution was compared with the ferrous sulfate solution and the ratio found to be 1.0248, the latter being somewhat stronger.

The sulfato cerate solution was then standardized by use of Bureau of Standards sodium oxalate which had been dried at 105° C. for 1 hour. An excess of the sulfato cerate solution was added to the sulfuric acid solution of weighed portions of the oxalate. The solutions were then heated to 50° C. for 5 minutes and after cooling were back-titrated, using the ferrous sulfate solution with ferroin as indicator. The results are shown in Table II.

TABLE II. STANDARDIZATION OF SULFATO CERATE SOLUTION USING SODIUM OXALATE

$Na_2C_2O_4$ Gram	$H_2Ce(SO_4)_3$ Taken Ml.	$FeSO_4$ Taken Ml.	$H_2Ce(SO_4)_3$ Required Ml.	Calculated Normality	Deviation from Average %
0.1132	50	14.82	34.81	0.04856	0.04
0.1092	50	15.97	33.63	0.04849	0.10
0.0883	50	22.29	27.16	0.04855	0.02
0.0958	50	20.04	29.46	0.04856	0.02
			Av. 0.04854		0.045

From the results of Table II and the standard factor for the sulfato cerate solution, the ferrous sulfate solution is found to be 0.04974 *N*.

COMPARISON STANDARDIZATIONS. The eight cerate solutions described in Table I were now standardized, using weighed portions of U. S. Bureau of Standards sodium

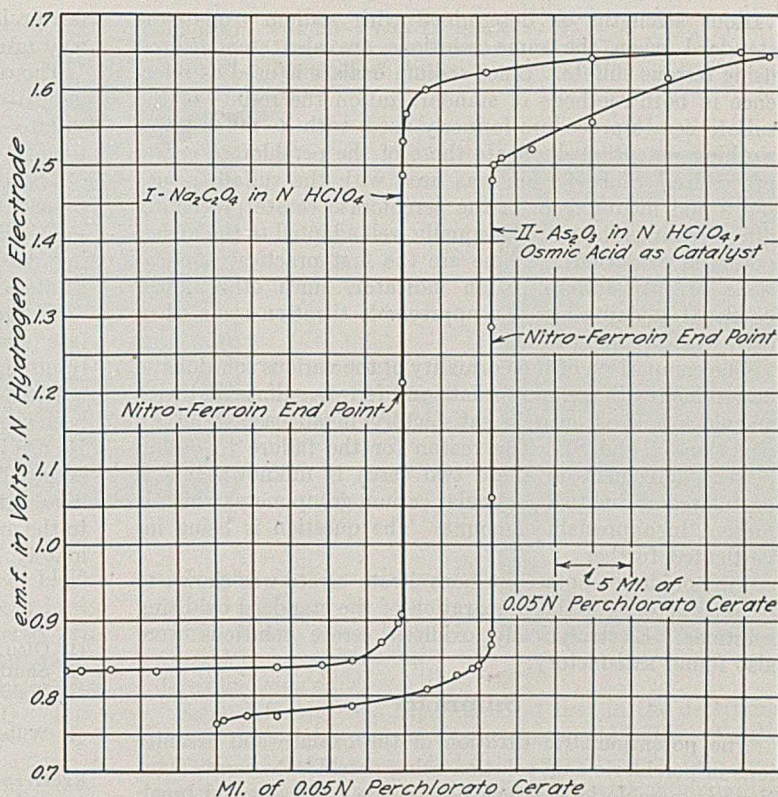


FIGURE 1

oxalate and arsenious oxide and measured volumes of standard ferrous sulfate.

TABLE III. STANDARDIZATION OF NITRATO AND SULFATO CERATE SOLUTIONS USING $Na_2C_2O_4$, As_2O_3 , and $FeSO_4$

Solution No.	$Na_2C_2O_4$		$FeSO_4$		As_2O_3		Average Result <i>N</i>
	Factor <i>N</i>	No. of determinations	Factor <i>N</i>	No. of determinations	Factor <i>N</i>	No. of determinations	
1	0.05624	5	0.05624	3	0.05627	4	0.05625
2	0.05642	6	0.05649	3	0.05663	5	0.05651
3	0.05439	7	0.05438	4	0.05442	4	0.05440
4	0.09700	7	0.09704	3	0.09746 ^a	6	0.09702
5	0.05333	4	0.05332	3	0.05344	4	0.05336
6	0.05147	6	0.05146	4	0.05147	5	0.05147
7	0.04274	5	0.04265	4	0.04267	5	0.04269
8	0.08313	4	0.08227	3	0.08220

^a Omitted from average value for this solution.

All standardizations of a given cerate solution were carried out on the same day to eliminate the factor of possible instability of the various cerate solutions. In the case of sodium oxalate and arsenious acid the weighed portions were dissolved in 2 *N* perchloric acid before titration, and nitro-ferroin was used as indicator. The arsenious oxide was first dissolved in 1 gram sodium hydroxide, then acidified, and one drop of osmic acid as catalyst was added in the form of 0.01 *N* solution in 0.1 *N* sulfuric acid. In the case of the ferrous sulfate solutions, dilute sulfuric acid was added to give 1.5 *N* concentration at the time of titration and ferroin was used as indicator. In the case of the nitrate cerate solutions in nitric acid, the nitro-ferroin indicator reaction in the neighborhood of the equivalence point of the oxidation was not as satisfactory as in the absence of nitric acid but was still applicable. The results of the comparative standardizations are shown in Table III.

Discussion of Results

Table III shows a very satisfactory agreement between the values for the normality of perchlorato cerate and nitrate cerate solutions dissolved in nitric and perchloric acids of

various strengths as determined with sodium oxalate as standard when the same solutions are also standardized using ferrous sulfate. Since sodium oxalate is used as reference in both methods of standardization the results of the sulfato cerate procedure formerly used, with its much lower working potential, duplicate those of the perchlorato cerate procedure. Since ferroin was used with the sulfato cerate series and nitro-ferroin in the perchlorato cerate procedure, nitro-ferroin is shown to be equally well adapted to the higher potential oxidations. These are the first practical applications of nitro-ferroin as an indicator, since other lower potential oxidants have an appreciable titration error when used with this indicator.

The comparison of the normality of the various solutions as determined with sodium oxalate and ferrous sulfate and with arsenious acid is entirely satisfactory in all cases but two (solutions 4 and 8). The reason for the failure to obtain perfect agreement in these two cases is unknown but is postulated as due to a particular cerium group metal which is present in appreciable amount. The question is being investigated further.

Ammonium or potassium hexanitrate cerate was shown to be satisfactory for the preparation of the standard oxidizing solutions. Electrolytically oxidized cerate solutions were also found satisfactory.

Summary

The potentiometric titration of the oxalate and arsenite ions in perchloric acid solution using perchlorato cerate solutions in perchloric acid has been made. A potential break of 650 and 600 mv., respectively, was obtained and nitro-

ferroin is shown to have a color transition point at the half-way interval of both potentiometric inflections.

The determination of the oxalate ion under the conditions indicated above has the advantage over permanganate and sulfato cerate that the reaction can be carried out at room temperature.

The determination of the arsenite ion in perchloric acid solution with osmic acid as catalyst and perchlorato cerate solutions as oxidant is more satisfactory than the corresponding determination in sulfuric acid solutions using sulfato cerate as oxidant.

Sodium oxalate, arsenious acid, and standard ferrous sulfate (standardized indirectly against oxalate) give concordant results in evaluating perchlorato or nitrate cerate solutions.

Nitro-ferroin (nitro-*o*-phenanthroline ferrous complex) has been used for the first time as an oxidation-reduction indicator. Its use in the case of perchlorate and nitrate cerate oxidations is practicable because of the high potential relationships involved in these cases. The transition from the reduced to the oxidized form of nitro-ferroin was found to be approximately 1.25 volts.

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Chemical Studies of Wood Preservation

The Wood-Block Method of Toxicity Assay

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Actual decay resistance of treated wood is used as the basis for a simple laboratory technic in the assay of materials advocated for the protection of wood. In its present stage of development the test is a valuable tool in wood preservation studies.

EXTENSIVE use of the more vulnerable species of timber for industrial purposes has focused attention on the development of technics for evaluating various preservatives advocated for the protection of this timber from the ravages of its natural enemies—fungi and termites. Using the substrate as a basis of classification, these technics fall roughly into two categories, nutrient agar tests exemplified by the Petri dish method as developed by the workers at the Forest Products Laboratory (4), and the wood-block test typified by the Kolle flask method (5), which has been widely used in Europe. The accumulation of toxicity data resulting from the use of both methods has received considerable study and the conclusions drawn by the various investigators have for the most part served only as a stimulus to controversies.

Discussion of the limitations of both methods in a previous paper (6) indicated the need for either modifying or supplanting these procedures. Both have at times been found to give misleading results which were detected only on actual exposure trials of corresponding materials. The principal shortcoming of the Petri dish method seems to be the artificial character of the dispersion of preservative in agar; that of the Kolle flask method the liability to inhibition of decay by excessive supply of water to the test block. The method described herein, slowly evolving during the course of the last 5 years, is an attempt to fulfill the requirements demanded of a laboratory technic for evaluating wood preservatives. It is felt that this test in its present stage of development combines the best features of the Petri dish and Kolle flask. The results to date show a much better correlation than those of either of the older methods with results of the more expensive and prolonged outdoor exposure tests.

While primarily intended for appraisal of preservatives, the method also lends itself to studies of rot-resistance of various woods, etc. Test blocks made from the heartwood and sapwood of many different species, from old poles which have been in service, from test posts (3), and from treated saplings (7) have yielded interesting information. Com-

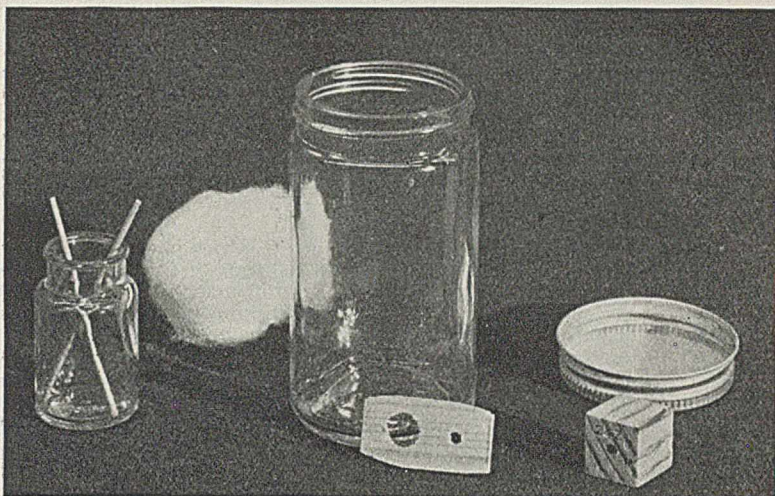


FIGURE 1 (Left). APPARATUS REQUIRED FOR MODIFIED WOOD-BLOCK METHOD OF ASSAY

mercially treated wood may be tested by the use of blocks cut from it, but in the majority of cases will not decay in the test unless the wood has been previously weathered artificially or naturally. However, most of the laboratory studies have been made on southern pine sapwood blocks impregnated with the preservative under test.

Apparatus

Simplicity and low cost are obtained by using easily available apparatus.

Two sizes of bottles (\$0.12 per pair in gross lots), shown separately in Figure 1, are assembled as in Figure 2. The larger, screw-topped bottle (12 cm. high and 6 cm. in diameter) serves as a chamber in which moisture conditions optimal for decay are maintained. The smaller bottle (6 cm. high and 3 cm. in diameter) supports a thin slab of untreated sapwood ($4.5 \times 2.5 \times 0.3$ cm., bored with two holes 0.5 and 0.2 cm. in diameter and approximately 1 cm. apart). The slab of sapwood acts as a substrate for growth of the fungus in a manner analogous to the artificial nutrient agar of the classical methods. The impregnated block under test is anchored upon the thin slab of sapwood by half-lengths of standard wooden applicators (16.5 cm. long) passed through holes bored in the slab and block.

After assembling the apparatus, water is added to the outer bottle to a depth of a few centimeters but not to the inner bottle. (Addition of the water to the small inner bottle is effected after sterilization to prevent the wood-cell vacuum formed during cooling from drawing up this water, thus saturating the piece to such an extent as to inhibit decay.) Sterilization is then effected by placing the complete setup in the autoclave for 30 minutes at 15 pounds' pressure. When the bottles have cooled sufficiently, sterile water is added to the inner bottle by means of a siphon arrangement. The additional moisture over that of fiber saturation which seems necessary for maximum decay is supplied to the fungus by conduction through the applicators. By means of a platinum spatula, previously flamed and cooled, a small inoculum is cut from a pure culture on agar of a wood-destroying fungus and is placed on the untreated slab at the end opposite the test block. The inoculation now completed, the bottles are recapped and placed in an incubation room at 26° to 28° C. for a period, customarily 24 weeks.

Preparation of the Test Blocks

Care must be exercised in selecting wood for the test blocks. The wood, usually southern pine of the short-leaf type, must be of uniform growth rate, density, and ratio of springwood to summerwood. The presence of any heartwood, or of sapstain or other indication of incipient invasion by organisms, is sufficient reason for rejection. Blocks usually $2 \times 2 \times 2$ cm. cut from such wood, bored with a hole 0.2 cm. in diameter

and numbered, are placed on racks (Figure 3) made from 1.25-cm. angle brass to which have been soldered finishing nails.

Some difficulty was experienced at first in the determination of the weights and volumes of the wood blocks. Weights taken at ordinary room conditions varied widely because of the moisture pickup of wood at different relative humidities. To avoid this, all blocks are brought to a constant relative humidity of 76 per cent at 30° C., which is obtained by fitting a bacteriological incubator with slow-moving fans and pans of saturated sodium chloride solution (Figure 4). Weighing the blocks is expedited by making initial weights at room conditions and properly arranging the blocks in order of either ascending or descending weight on the racks. The length of time required to reach equilibrium weights varies according to the amount of dry wood in the chamber and external atmospheric humidity, but the average period is from 3 to 4 days.

Volume determinations were first made by direct measurement with a micrometer, but this method was very slow and corrections for the hole could be only an approximation. A mercury-displacement method was devised which is far more precise and facile.

A 100-cc. beaker of mercury is placed on one pan of a rough balance and is counterpoised by weights on the other pan. The block is impaled on a dissection needle and forced beneath the surface of the mercury, care being taken that the block does not come into contact with the sides of the vessel holding the mercury. The force of the hand necessary to keep the block beneath the surface of the liquid is counterbalanced by additional weights on the opposite pan. (Experiments are now under way to devise a simple piece of apparatus to supplant the use of the hand in forcing the blocks beneath the mercury.) These weights, representing the weight of the mercury displaced, are then transposed into the volume of the block, correcting for the effect of temperature on the specific volume of mercury. Finally the blocks are brushed free of any mercury which might be retained on the

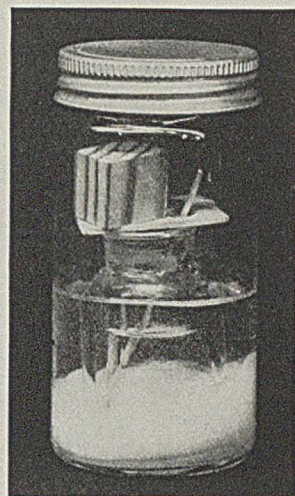


FIGURE 2 (Right). ASSEMBLY OF APPARATUS

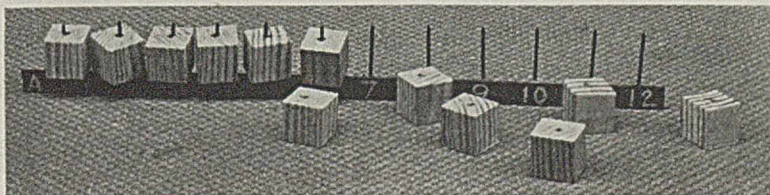


FIGURE 3. TEST BLOCKS AND RACK



FIGURE 4. CONSTANT-HUMIDITY CHAMBER FILLED WITH TEST BLOCKS

surface of the blocks; a final equilibrium weighing serves to detect such an occurrence.

Treatment of the Test Blocks

The blocks are now ready for impregnation with the preservative to be tested. A considerable range of retents can be obtained by the use of the empty-cell process with the straight preservative, and while it is difficult to secure a predetermined range of concentration in this manner, the empty-cell process has been used to some extent in preparing test specimens. Since lower concentrations than those obtained with the undiluted preservative are often desirable, the proper amount of the compound to be tested is usually dissolved in an appropriate solvent. Usually a graded series of dilutions is desirable in order to approximate minimal effective concentration in at least one case.

The necessary number of blocks, weighted to ensure immersion, are placed in a container of convenient size under a bell jar fitted with a separatory funnel (Figure 5). After evacuation of the bell

jar to a pressure not greater than 2 cm. as measured by a mercury manometer, the vacuum is held for 5 minutes. The stopcock in the pump line is then closed and sufficient solution is admitted from the separatory funnel to submerge the blocks completely when the air is admitted. After remaining in the solution for a short time, the blocks are wiped superficially and weighed. This treated weight is used for calculation of the theoretical retent according to the following formula:

$$R = \frac{GC (62.5)}{100 V}$$

in which R = pounds per cubic foot, G = gain in weight in grams, C = grams of the preservative in 100 grams of solution, and V = volume of the test piece in cubic centimeters. When the solvent has evaporated from the blocks they are placed on the racks (Figure 3), returned to the humidity chamber, and again brought to constant weight. The difference between the humidity weights before and after treatment serves as the basis for calculating the actual retent and the final equilibrium weight is used also as the initial weight of the treated block before exposure to the fungus.

Selection of Fungi

In each test at least four organisms from the following list are used in duplicate. The choice of each is based on their relative economic importance, the vigor of growth, amount of decay as measured by loss in weight of untreated specimens, and their known idiosyncracies for certain types of compounds. Another vital factor in the original selection of most of these fungi was their repeated isolation from de-

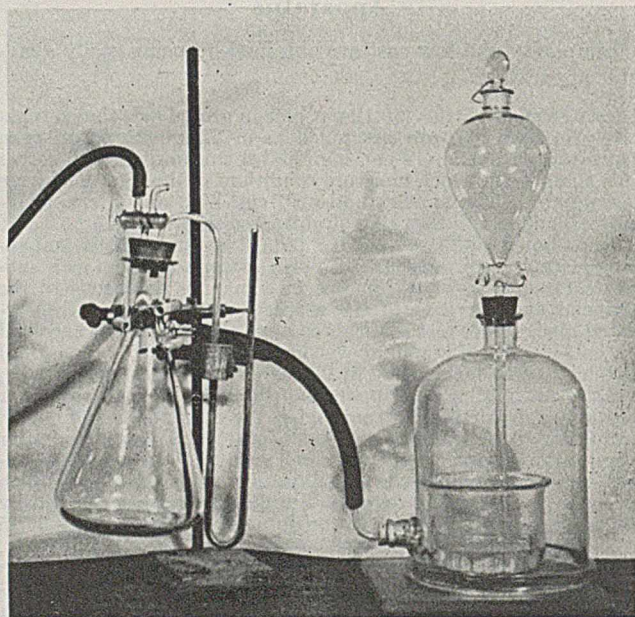


FIGURE 5. APPARATUS FOR FULL-CELL SOLUTION TREATMENTS OF TEST BLOCKS



FIGURE 6. ASSAY OF WORTHLESS PRESERVATIVE AT MAXIMUM CONCENTRATION
Fungi in duplicate, left to right, *Lenzites trabea*, U-10, *Fomes roseus*, and *Lentinus lepideus*

cayed pine poles sent in from widely separated areas.

Included in the list of fungi is *Lentinus lepideus*, which is used for the most part in the assay of organic preservatives but seldom for testing metallic salts, to which it is particularly sensitive. Similarly, the fungus *Lenzites trabea* exhibits a parallel resistance and sensitivity but the type

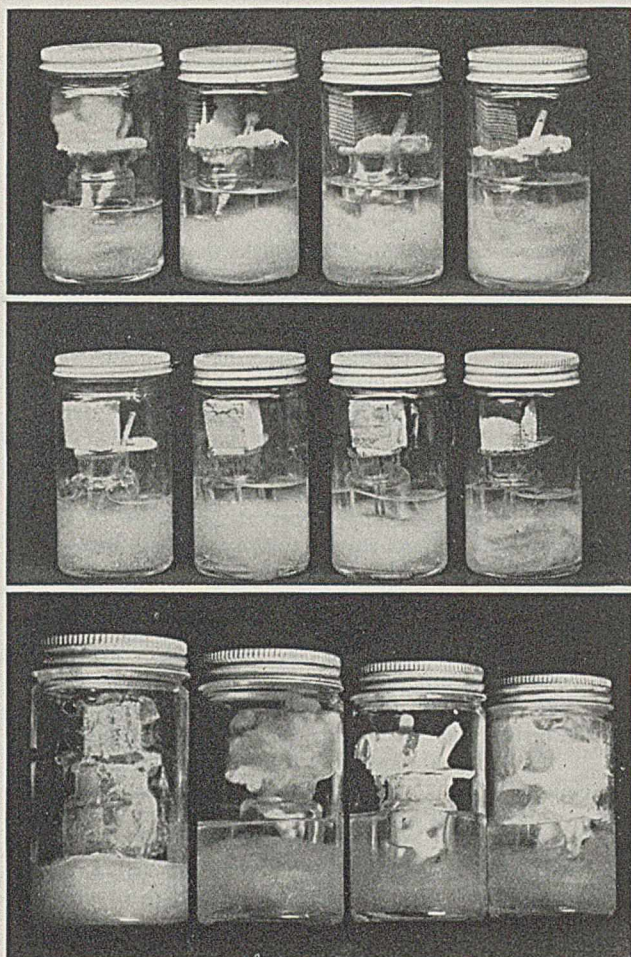


FIGURE 7. TOXICITY ASSAYS

Upper. Polychlorophenol, showing effect of increasing concentration. Test organism, *Lenzites trabea*. Growth ratings, left to right, 4-4, 3-4, 1-3, and N. G. 4.

Center. Same range of concentration as in upper figure. Test organism, *Fomes roseus*. Growth ratings, left to right, 4-4, 4-4, 4-3, and 3-3.

Lower. Growth on untreated Baltic pine (*Pinus sylvestris*). Test organisms, *Lenzites trabea*, *Lenzites trabea*, *Fomes roseus*, and U-10.

of rot differs greatly, producing a marked surface erosion of the blocks. The common "dry rot" fungi, specifically *Poria incrustata*, *Coniophora cerebella*, and *Polyporus vaporarius*, are most frequently used in the assay of inorganic compounds, since years of experimentation have demonstrated the relative resistance of these fungi to most such materials. *Fomes roseus*, another fungus of wide distribution, is able to withstand certain classes of compounds to a remarkable degree and hence is included in assays of all new compounds. One other organism (U-10) is used in all assays. Unfortunately, it has yet to be identified. Isolated several years ago from a decayed pine pole, U-10 is especially valuable when a quick indication of the merits of a new preservative is needed, as a very appreciable weight loss results from its attack in about 3 months. From time to time other organisms, such as *Trametes serialis*, *Lenzites sepiaria*, *Polystictus versicolor*, *Polyporus sulphureus*, *Fomes pinicola*, and other isolations from decayed poles and test posts (6) have supplemented the fungi regularly in use. Practically all of the above-mentioned have

been cited by investigators as of considerable economic importance in the decay of structural timbers.

Expression of Results

The interpretation of results is greatly facilitated by proper controls, which include untreated blocks exposed to each of the test fungi and impregnated blocks put through the entire cycle without fungal inoculation. The untreated controls indicate the marked differences in the rapidity of growth and the amount of decay peculiar to various fungi on the species of wood being used. The impregnated controls serve as a check on the loss in weight due to leaching and evaporation occurring during the entire course of the test and are of further importance when the exposed blocks are dissected and rated on a strength basis. Using such controls three criteria are available:

1. The growth rating made every 4 weeks with reference to the inoculated untreated norm. The designation of growth is a pair of numbers, the first of which gives the extent of the block covered and the second the intensity and vigor. Based on "4-4" as the maximum, "2-4" would mean that the block is partly covered with normal growth of the fungal mycelium and "4-2" wholly covered with sparse mycelial growth. Additional designations to describe the absence of growth on the test specimens are used and include the "√" mark when the inoculum is dead or totally inhibited and "N. G." for no growth on the test piece. A number following the latter designation indicates the extent of the growth on the untreated slab of supporting wood. The notation "N. G. 2" would mean that growth of the fungus has only partially covered the untreated wood used as the secondary substrate but is not yet in contact with the treated specimen. Such a notation is typical when there is some leaching of the preservative and attendant diffusion into the untreated slab.

2. The weight loss computed from the equilibrium weights before and after exposure to the fungus. Appreciable weight losses on the uninoculated, impregnated controls indicate that the preservative may be water-soluble, volatile, or reactive with the wood. Particularly when this latter condition prevails it is often difficult to distinguish the disintegration due to the chemical from the decay caused by the fungus, but the two effects can be separated by subtracting the per cent loss in weight calculated for the controls from the per cent loss in weight of the exposed specimens.

3. The third basis for judging the merits of a preservative is determined by dissecting and breaking the blocks into small pieces. The residual strength of the exposed blocks can thus be compared with the strength of the uninoculated, impregnated controls treated in the same manner. Dissection of the control also offers an indication of any chemical effect of the preservative on the wood. An empirical rating of 10 denotes no detectable loss in strength as compared to the control, and 0 denotes complete disintegration.

Modifications and Special Features

While the assay method per se was not planned to include a test of permanency, correlative information in this regard



FIGURE 8. ASSAY OF FULL-CELL SOLUTION TREATMENT OF A CREOSOTE

Test organism, *Lenzites trabea*. Concentrations are, roughly, 1, 2, 3, and 6 pounds per cubic foot of creosote. Growth ratings, 4-4, 4-2, 3-1, and N. G. 1. For purposes of better reproduction inner bottles were removed from larger outer bottles.

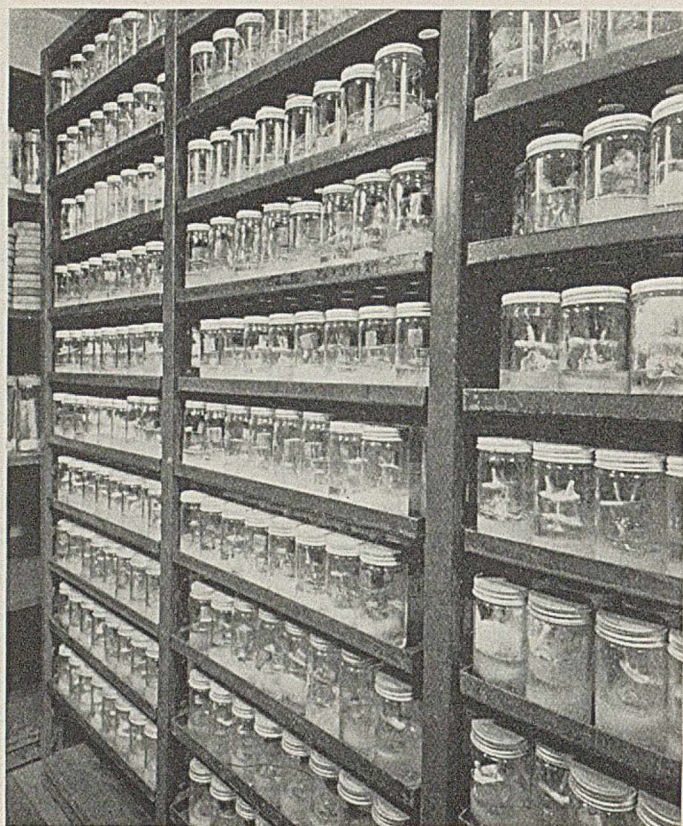


FIGURE 9. INCUBATOR WITH TEST IN PROGRESS

on the more volatile preservatives may be obtained following the normal technic. Most of the solvents used in obtaining concentration ranges of oily preservatives are very toxic and considerable evaporation of high vapor pressure fractions is unavoidable not only during the evaporation of the solvent but also during the period while the test pieces are coming to constant weight in the humidity chamber and finally in connection with the sterilization. For instance, pieces treated with moderate amounts of a volatile material of known preservative value, such as naphthalene, when put through the regular routine showed no rot-resisting properties. Accordingly, whenever highly volatile compounds are under consideration, a generous quantity of the material is injected into the blocks to allow for partial evaporation. Actual retent can be calculated from the difference between the humidity weights of the untreated blocks and the weights of the impregnated blocks just prior to fungal exposure. Instead of subjecting blocks treated with volatile materials to sterilization, the technic is modified in a manner somewhat similar to the Kolle flask method. The fungus is first allowed to cover the untreated slab of sapwood for a period of 3 to 4 weeks before the specimens are treated. When the fungus is growing vigorously and no contaminations are apparent, the treated block, immediately after the final weighing, is placed in direct contact with the mycelial mats. A sterile applicator passed through the hole in the block is an aid in placing the block in position. When allowed to remain it ensures a sufficient supply of moisture to the test block.

The danger of foreign contaminations is heightened by omission of the sterilization, but in spite of this the results have been reasonably acceptable although somewhat irregular. This modification is far more satisfactory in the assays of single compounds than in assays of volatile mix-

tures. In both cases total evaporation is easily ascertained, but computation of the loss of each individual constituent of a mixture is practically impossible. Another method of avoiding the loss of volatile compounds is to place each weighed block in a small, tightly stoppered container during sterilization. Such a method is being more fully studied at this time.

When materials are known or suspected to be water-soluble, the injected blocks may be run through a standard leaching cycle before being subjected to the toxicity test. Or, in cases where the compounds are soluble and volatile, the specimens can first be exposed on artificial weathering machines such as were used by Rhodes *et al.* (1). If the preservative is likely to prove volatile but is inappreciably soluble, a standard heating cycle may be used. Such cycles give definite indication of the comparative values of preservatives from the standpoint of permanence. Indeed, many preservatives are so toxic that significant differences in toxicity among them often cannot be detected unless the blocks are first subjected to a depletion process imitative of the weather. As an alternate the blocks may be injected with very low concentrations as compared with those of commercial practice.

A standard leaching cycle which is dependent on diffusion and is to some extent a simulation of the action of ground waters on soluble materials injected into the wood is described below. Since the duplication of varied environmental factors in service is impossible, an arbitrary schedule was chosen which is adapted to usual working hours and is consistent with a minimum amount of supervision.

The individual impregnated blocks are numbered and then placed in the constant-humidity chamber (Figure 4) until an equilibrium weight is reached. All the blocks impregnated with the same preservative in equal concentration are then placed in a

TABLE I. AVERAGE WEIGHT LOSS BY KOLLE FLASK AND BELL TELEPHONE LABORATORIES METHOD

(Comparison of results on untreated *Pinus sylvestris* exposed to different fungi)

Organism	Strain	European Research Workers Using Kolle Flask				B. T. L. Method ^a No. of specimens	Results %
		Baven- damm %	Liese %	Peters %	Ra- dam banus %		
<i>Polyporus vapor- arius</i>	Eberswalde	15	26	12	19	2	25.3
	Baarn	2	7	5	11
<i>Lentinus lepideus</i>	Princes Risborough	..	8	6	10
	Eberswalde	4	12	42	19	6	19.1
	Eberswalde	..	13
	Princes Risborough	3	12	21	14
<i>Lenzites sepiaria</i>	Princes Risborough	..	15
	Eberswalde	7	24	..	21	6	47.0
	Princes Risborough	5	19	..	14
<i>Lenzites trabea</i>	Madison	3	14	..	21
	U-10	6	35.2
<i>Fomes roseus</i>	U-10	6	43.2
	U-10	4	22.2

^a Strains of fungi, with the exception of U-10, used at Bell Telephone Laboratories were supplied by Forest Products Laboratory, Madison, Wis.

container of convenient size, weighted to ensure immersion during the early stages of the cycle, and covered with distilled water, allowing 50 cc. for each block (7 to 8 cc.). The containers are covered with a watchglass and set aside in a constant-temperature room at 26° to 28° C. The water is drained from the blocks and an equal amount of fresh water is again added at the end of

TABLE II. WEIGHT LOSSES AND DISSECTION RATINGS
(Untreated southern pine blocks exposed to most common test fungi for 24 weeks)

Organism	Initial Weight		Final Weight		Empirical Loss, Rating		Description of Decay
	relative humidity	Oven-dry	relative humidity	Oven-dry	on Dry Weights	on Dissection	
	76% Grams	76% Grams	76% Grams	76% Grams	%	%	
<i>Lentinus lepideus</i>	2.34	2.05	1.87	1.64	20.0	4	Rather advanced decay throughout
	2.35	2.06	1.87	1.64	20.4	4	Rather advanced decay throughout
	2.25	1.97	1.85	1.62	17.8	5	Moderately advanced decay throughout
	2.26	1.98	1.77	1.55	21.7	4	Rather advanced decay throughout
<i>Fomes roseus</i>	2.25	1.97	1.84	1.61	18.3	4	Rather advanced decay throughout
	2.27	1.99	1.84	1.61	19.1	4	Rather advanced decay throughout
	2.22	1.95	1.78	1.56	20.0	4	Rather advanced decay throughout
	2.21	1.94	1.56	1.37	29.4	1	Thoroughly rotted
U-10	2.33	2.04	1.13	0.99	51.5	0	Complete disintegration
	2.33	2.04	1.37	1.20	41.2	0	Complete disintegration
	2.20	1.93	1.08	0.95	50.8	0	Complete disintegration
	2.18	1.91	1.19	1.04	45.5	0	Complete disintegration
<i>Lenzites trabea</i>	2.32	2.03	1.73	1.52	25.1	2	Deep surface disintegration, advanced decay elsewhere
	2.33	2.04	1.76	1.54	24.5	3	Deep surface disintegration, rather advanced decay elsewhere
	2.07	1.81	1.51	1.32	27.1	2	Advanced decay
<i>Polyporus vaporarius</i>	2.09	1.83	1.29	1.13	38.3	1	Thoroughly rotted
	2.12	1.86	1.69	1.48	20.4	4	Rather advanced decay throughout
	2.01	1.76	1.74	1.53	13.1	6	Mild decay throughout
	2.18	1.91	1.78	1.56	18.3	4	Rather advanced decay throughout
	2.26	1.98	1.82	1.60	19.2	4	Rather advanced decay throughout

Growth rating in all cases was 4-4, signifying that test blocks were covered with heavy normal growth.

the following periods: after a total of 7, 24, 48, 79, 168, and 336 hours. At the end of this 2-week period, the blocks are removed from the beakers; the water is allowed to evaporate after the blocks are placed on racks (Figure 3). The blocks are finally brought to a constant weight in the humidity chamber and run through the regular assay cycle. The weight before and after leaching is an indication of the amount of material lost through leaching. A further check is often made by analyzing the leach waters for the active constituents.

Results

Table I gives results by the new method on untreated *Pinus sylvestris* (Baltic or Scots pine) exposed to various fungi, compared with those of several other research workers (2) using the Kolle flask technic on the same species of wood. The agreement in general is very satisfactory. In the case of the fungus *Lenzites sepiaria*, the weight losses are about

double those of any other investigator, indicating that these test conditions are highly favorable for it. The results on this organism are the average of six individual blocks; the maximum weight loss was 50.6 per cent and the minimum 44.1 per cent. This is rather close agreement for biological test methods and is a good example of results obtained by this method. Although strictly comparable results are not available for the sapwood of the various species of southern yellow pine (*Pinus taeda*, *Pinus echinata*, *Pinus palustris*, and *Pinus caribaea*), the weight losses in Table II are in a general way typical of untreated wood of these species when assayed by the method described in this paper.

The gradual evolution of this laboratory assay to its present stage of development has been accompanied by the accumulation of a considerable mass of data on materials advocated for the preservation of wood. Since many of these compounds are of recent acquisition, data for them which are comparable to those obtained by other investigators using the Kolle flask technic are as yet lacking. Some typical results are discussed below.

From a large number of creosotes tested, toxicity assays and chemical analysis of a random choice are given in Tables III, IV, and V. Results are for duplicate blocks at each concentration of the creosote in both full- and empty-cell treatment, together with duplicate blocks put through the standard leaching cycle referred to above. The resultant good agreement for duplicate blocks exposed to the same fungus is rather surprising, in view of the fact that evaporation losses are unavoidable when handling blocks impregnated with relatively volatile materials such as creosotes. When discrepancies arise, indications of the probable result may be obtained by comparison with the next higher or lower concentration, but the best policy is to make a duplicate test.

TABLE III. ASSAY OF CREOSOTE
(Full-cell benzene solution treatment)

Concentration Lb./cu. ft. ^a	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
6.6 Original	1-1	3.7	10	√	3.8	10	√	3.6	10	N. G. 2	3.9	10	3.7	10
	√	3.8	10	√	3.2	10	√	3.1	10	N. G. 2	3.7	10	3.3	10
Leached	N. G. 4	2.5	10	1-1	1.8	10	2-1	1.4	10	N. G. 4 ^b	2.4	10	1.8	10
	1-1	2.0	10	1-1	1.6	10	3-3	0.9	10	N. G. 4 ^b	2.1	10	1.0	10
3.5 Original	4-1	2.7	10?	1-1	1.4	10	1-1	1.6	10	N. G. 1	1.1	10	1.2	10
	4-1	2.1	10?	1-1	1.0	10	1-1	1.0	10	N. G. 1	0.9	10	1.0	10
Leached	4-2	1.4	10?	3-4	6.3	8	4-4	13.0	6	3-2 ^b	7.9	8	0.8	10
	4-2	0.9	10?	4-2	1.4	9	4-4	3.0	9	2-2 ^b	3.1	9	0.5	10
1.7 Original	4-4	17.9	4	4-2	6.9	8	4-4	15.1	5	4-4	14.7	6	0.9	10
	4-2	2.1	9	2-2	6.3	8	4-4	8.9	7	4-3	10.4	7	0.5	10
Leached	4-4	10.0	7	4-4	9.8	7	4-4	7.4	7	4-3 ^b	10.7	7	0.3	10
	4-4	8.9	7	4-4	9.4	7	4-3	4.5	8	4-3 ^b	10.0	7	0.0	10
0.8 Original	4-4	16.9	4	4-4	7.9	7	4-4	11.5	6	4-4	16.3	5	0.9	10
	4-4	16.0	4	4-4	6.0	7	4-4	11.1	6	4-4	15.8	5	0.5	10
Leached	4-4	12.2	6	4-4	12.9	6	4-4	37.2	0	4-4 ^b	23.7	2	0.6	10
	4-4	11.2	6	4-4	9.7	7	4-4	22.0	2	4-4 ^b	21.2	2	0.0	10
0.4 Original	4-4	33.0	1	4-4	14.2	6	4-4	44.1	0	4-4	25.4	2	0.5	10
	4-4	29.7	1	4-4	3.8	8	4-4	39.7	0	4-4	22.2	2	0.0	10
Leached	4-4	16.1	5	4-4	22.3	3	4-4	47.7	0	4-4 ^b	16.6	4	0.7	10
	4-4	13.3	5	4-4	16.8	5	4-4	45.8	0	4-4 ^b	16.1	4	0.3	10

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.
^b *Lenzites sepiaria* used in these cases.

TABLE IV. ASSAY OF CREOSOTE
(Empty-cell treatment)

Concentration Lb./cu. ft. ^a	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	% loss	Dissec- tion rating
8.1 Original	2-1	1.8	10	1-1	0.9	10	1-1	1.8	10	1-1	3.2	10	2.8	10
	1-1	1.6	10	1-1	0.4	10	1-2	0.5	10	2-1	3.2	10	2.2	10
Leached	1-1	3.6	10	N. G. 2	2.3	10	N. G. 1	2.3	10	N. G. 1	2.9	10	2.3	10
	1-1	2.7	10	N. G. 1	1.8	10	√	3.1	10	N. G. 2	2.2	10	2.0	10
4.0 Original	3-1	1.3	10	2-1	0.9	10	1-1	0.5	10	2-2	5.1	9	0.8	10
	1-1	0.5	10	1-1	0.4	10	1-1	0.0	10	3-2	3.8	9	0.0	10
Leached	2-1	0.0	10	2-1	0.4	10	2-1	0.0	10	1-1	0.0	10	0.2	10
	2-1	0.0	10	2-1	0.0	10	2-1	0.0	10	N. G. 3	0.8	10	0.0	10
3.4 ^b Original	4-1	1.0	10	2-1	1.4	9	4-3	9.1	6	3-2	5.2	7	0.9	10
	4-1	0.4	10	2-1	0.0	10	4-2	6.1	7	2-1	4.9	8	0.3	10

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.^b Not enough of specimen available for leaching.TABLE V. ANALYSIS OF CREOSOTE REFERRED TO IN TABLES III
AND IV

(Analysis according to Bell Telephone Laboratories specification 6591)		
Specific gravity at 38°/15.5° C.	1.063	
Water	Trace	
Distillation	%	
To 210° C.	0.00	
210-235° C.	10.30	white crystals
235-245° C.	12.75	pale yellow crystals
245-270° C.	22.83	yellow liquid + crystals 1 to 1
270-300° C.	15.79	brown liquid + yellow crystals
300-315° C.	7.63	lemon solid
315-355° C.	20.94	lemon solid
Residue	9.51	
	Total	99.75
Sulfonation residue (210-355° C., composite)		0.4 cc./100 grams
Tar acids (210-355° C., composite)		5.4 cc./100 grams
Benzene-insoluble	0.12%	
Coke test	0.44%	

Both here and in other laboratories considerable attention has been given to tetrachlorophenol in petroleum oil mixtures as possible wood preservatives, and the assay of a full-cell solution treatment of a 10 per cent mixture is illustrated in Table VI. The effect of leaching blocks treated with such a mixture is more noticeable than in the case of the creosote-treated blocks. Also of particular interest is the specificity of the fungus *Fomes roseus* towards this compound, which is typical of its reaction with related chlorophenols. Results of an empty-cell treatment of a 5 per cent solution of this compound are given in Table VII. As further depletion by leaching seems unnecessary, such a test was not made.

TABLE VI. ASSAY OF 10 PER CENT SOLUTION OF TETRACHLOROPHENOL IN PETROLEUM
(Full-cell benzene solution treatment)

Concentration Lb./cu. ft. ^a	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	% loss	Dissec- tion rating
6.9 Original	√	4.4	10	N. G. 1	5.9	10	√	4.1	10	√	5.0	10	5.0	10
	√	3.6	10	N. G. 3	5.9	10	√	3.5	10	√	4.5	10	5.8	10
Leached	N. G. 1	3.6	10	1-2	4.7	9	N. G. 2	3.2	10	1-1	3.8	10	3.8	10
	N. G. 1	2.7	10	1-1	4.0	9	√	2.7	10	1-1	3.6	10	3.2	10
3.3 Original	N. G. 2	4.0	10	2-1	6.7	9	√	2.6	10	√	3.4	10	4.0	10
	N. G. 1	5.2	10	1-1	4.7	10	√	2.5	10	√	3.3	10	3.5	10
Leached	N. G. 3	2.4	10	3-4	14.7	5	N. G. 2	1.5	10	1-3	3.8	9	2.2	10
	N. G. 1	1.9	10	1-2	1.9	9	N. G. 1	1.7	10	1-3	3.6	9	2.0	10
1.6 Original	N. G. 4	3.3	10	4-4	14.2	6	N. G. 2	3.0	10	√	2.2	10	3.0	10
	N. G. 3	3.1	10	4-4	12.1	7	1-1	2.7	10	√	2.2	10	2.5	10
Leached	1-2	1.5	9	4-4	13.8	6	1-4	3.4	9	4-4	14.3	6	0.7	10
	N. G. 2	0.5	10	4-3	12.7	6	√	0.4	10	2-3	8.1	7	0.5	10
0.8 Original	2-2	6.9	7	4-4	21.0	3	4-4	9.5	7	3-2	12.7	7	2.2	10
	1-2	2.7	9	4-4	18.5	3	4-4	5.5	8	N. G. 1	3.2	10	1.8	10
Leached	3-4	10.2	6	4-4	18.6	3	4-4	29.0	1	4-4	16.6	4	0.9	10
	3-4	8.3	7	4-4	15.3	4	4-3	2.3	9	4-4	15.5	4	0.5	10
0.4 Original	4-4	15.2	4	4-4	17.1	3	4-4	37.4	0	4-4	21.6	3	0.2	10
	4-3	9.6	6	4-4	15.9	3	4-4	25.8	1	4-4	19.4	3	0.0	10
Leached	4-4	16.0	4	4-4	15.0	3	4-4	44.9	0	4-4	25.7	1	0.0	10
	4-4	12.6	6	4-4	6.1	7	4-4	40.6	0	4-4	22.0	2	0.0	10

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.TABLE VII. ASSAY OF 5 PER CENT SOLUTION OF TETRACHLOROPHENOL IN PETROLEUM
(Empty-cell treatment)

Concentration Lb./cu. ft. ^a	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Lenzites trabea</i>			Uninoculated Control	
	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	Growth rating	% loss	Dissec- tion rating	% loss	Dissec- tion rating
5.1 Original	N. G. 3	5.0	10	4-3	9.6	7	√	5.0	10	3-3	7.9	8	3.9	10
	1-1	4.7	10	4-3	9.3	7	√	4.2	10	4-3	7.6	8	3.8	10
3.9 Original	1-1	2.7	10	4-4	21.5	3	N. G. 2	2.7	10	4-3	11.1	6	2.8	10
	1-1	2.7	10	4-4	14.6	5	√	2.9	10	4-2	8.9	7	2.6	10
2.5 Original	1-2	2.8	9	4-4	17.2	5	√	3.2	10	4-3	11.4	8	3.2	10
	1-1	3.3	10	4-4	8.2	8	√	2.9	10	4-4	10.2	7	2.8	10

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.

TABLE VIII. ASSAY OF A MIXTURE OF POTASSIUM DICHROMATE, SODIUM FLUORIDE, SODIUM ARSENITE, AND DINITROPHENOL (Full-cell water solution treatment. Assay made early in development of method. Duplicates and controls were not used.)

Concentration Lb./cu. ft. ^{a,b}	<i>Lentinus lepideus</i>			<i>Fomes roseus</i>			U-10			<i>Polyporus vaporarius</i>		
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating
1.2 Original	N. G. 1	1.3	10	N. G. 3	1.0	10	N. G. 1	1.6	10	N. G. 1	1.2	10
Leached	1-4	0.3	10	4-4	0.3	10	1-4	3.0	9	4-4	6.4	7
0.6 Original	N. G. 3	0.9	10	N. G. 4	0.7	10	N. G. 4	0.5	10	✓	0.3	10
Leached	2-4	0.0	10	3-3	1.1	10	4-3	2.4	10	4-4	23.0	2
0.3 Original	N. G. 1	0.5	10	N. G. 4	0.7	10	N. G. 2	0.3	10	N. G. 3	0.4	10
Leached	1-4	0.5	10	4-3	+0.5	10	4-4	13.4	6	4-4	59.5	0
0.1 Original	N. G. 2	0.5	10	N. G. 4	0.0	10	N. G. 4	0.4	10	N. G. 4	0.2	10
Leached	4-4	5.3	7	4-4	4.9	7	4-4	39.1	0	4-4	8.0 ^c	7

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.
^b Expressed in terms of dry salts.
^c Specimen saturated with water.

TABLE IX. ASSAY OF A MIXTURE OF ZINC CHLORIDE AND SODIUM DICHROMATE (Full-cell water solution treatment)

Concentration Lb./cu. ft. ^{a,b}	<i>Poria incrassata</i>			<i>Coniophora cerebella</i>			U-10			<i>Polyporus vaporarius</i>			Uninoculated Control	
	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	Growth rating	% loss	Dissection rating	% loss	Dissection rating
2.2 Original	N. G. 2	2.6	10	1-1	2.9	10	N. G. 3	2.8	10	1-1	2.3	10	2.0	10
N. G. 2	1.4	10	1-1	1.6	10	N. G. 2	2.8	10	N. G. 3	1.5	10	2.3	10	
Leached	4-4	10.5	6	4-3	6.4	7	4-4	19.7	3	4-4	14.1	6	0.8	10
	2-4	3.3	8	4-3	5.0	7	4-4	19.6	3	4-4	11.3	6	0.4	10
1.2 Original	2-2	1.6	10	1-1	2.3	10	N. G. 3	0.0	10	3-3	4.2	9	0.9	10
N. G. 3	1.1	10	1-1	3.0	10	1-3	0.7	10	1-1	2.6	10	1.1	10	
Leached	4-4	9.7	6	4-3	10.8	6	4-4	34.4	0	4-4	32.2	1	0.5	10
	4-4	6.7	6	4-3	6.9	7	4-4	31.6	0	4-4	8.7	5	0.8	10
0.7 Original	N. G. 3	0.9	10	2-2	2.7	9	1-2	1.4	10	4-4	8.1	7	0.3	10
	2-1	0.7	10	4-1	1.9	10	N. G. 4	0.5	10	4-2	3.4	9	0.0	10
Leached	4-4	19.7	3	4-4	11.4	6	4-4	25.5	2	4-4	25.4	2	0.6	10
	4-4	15.2	4	4-4	10.9	6	4-4	12.0	6	4-4	17.4	4	0.2	10
0.3 Original	4-4	22.5	3	4-3	11.4	6	4-4	14.8	5	4-4	10.8	6	0.0	10
	4-2	11.5 ^c	6	4-3	7.4	7	4-4	10.9	6	4-4	8.9	6	0.0	10
Leached	4-4	11.4	6	4-3	14.0	5	4-4	24.7	2	4-4	16.5	4	0.0	10
	4-4	10.5	6	4-4	11.9	6	4-4	16.1	4	4-4	10.1	6	0.3	10
0.2 Original	4-4	28.6	1	4-2	12.0	6	4-4	31.9	0	4-4	8.6	6	0.2	10
	4-4	24.6	2	3-2	11.3	6	4-4	12.9	6	4-4	8.2	6	0.0	10
Leached	4-4	16.8	4	4-3	9.8	7	4-4	30.2	0	4-4	12.5	5	0.1	10
	4-4	14.1	5	4-3	9.6	7	4-4	23.8	2	4-4	8.9	6	0.0	10

^a 1 gram per 100 cc. equals 0.625 pound per cubic foot.
^b Expressed in terms of dry salts.
^c Contamination present.

Two compounds of an inorganic nature are also included, a mixture of potassium dichromate, sodium fluoride, sodium arsenite, and dinitrophenol (Table VIII) and a mixture of zinc chloride and sodium dichromate (Table IX). Both products, especially the former, are reasonably effective before leaching but, from the appreciable decay found in several specimens subjected to the water cycle previously mentioned, it is obvious that in neither is there complete fixation of the toxic principles. Further indications that large amounts of the materials were extracted from the wood when in contact with water were obtained by analyzing the leach waters. However, both products represent a real advance in the search for a truly permanent water-borne preservative.

The assay in Table VIII was made during the evolutionary period of the method, as is evidenced by the use of single blocks and the lack of uninoculated controls. Two of the test organisms used at that time, *Lentinus lepideus* and *Fomes roseus*, were innocuous except at the very lowest concentration of the leached specimens. By the time the assay in Table IX was carried out it had been realized that these organisms were unsuitable for the evaluation of the inorganic type of preservatives and *Coniophora cerebella* and *Poria incrassata* had been substituted in such studies. That this was a happy choice is indicated by the extensive decay brought about by these fungi.

Discussion and Summary

An attempt at the reproduction of natural conditions in the laboratory is always attended by many difficulties, particularly when endeavoring to imitate biological phenomena in a state of dynamic equilibria. The laboratory method described in this paper, however, does have many features to recommend it:

1. The medium is the natural one.
2. The organisms are selected on the basis of their virulence in attacking the specific medium used and their resistance to the class of compounds under consideration.
3. Because of limiting factors inherent in organic systems, it is difficult to establish environmental optima for all the fungi, but for the most part the conditions of the test meet these criteria.
4. Each block has a specific identity, treatment, and case history.
5. The test furnishes important indications of the degree of permanence and other chemical properties of the preservatives as well as its toxicity.
6. Low-cost apparatus and a simple technic result in an inexpensive assay method, especially when compared with the more expensive outdoor exposure tests which can often be entirely eliminated in the case of unpromising materials.
7. Evidence is accumulating from correlated field-exposure tests which indicates a high degree of specificity for the method.

8. While results on quadruplicate untreated blocks (Table II) and duplicate treated blocks show good agreement, data on reproducibility of this technic in other hands are not available at the present time, and definite claims for the true reproducibility of the method must await trial by other workers.

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Thermal Conductivity of Liquids

Binary Mixtures of Water-Methyl Alcohol and Water-Ethyl Alcohol

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The paper presents improvements in the operation of the apparatus previously reported (1, 2), and the results of the determinations of the thermal conductivity and temperature coefficients of thermal conductivity for water-methyl alcohol and water-ethyl alcohol binary mixtures.

BATES reported in detail the method of determining the thermal conductivity of liquids, a description of the apparatus, and the calculation of the coefficients in previous papers (1, 2). Figure 1 gives a general view of the present setup. However, two changes have been made in the operation of the apparatus from that previously reported.

To minimize conduction from the room to the calorimeters, the calorimeter water must be kept at room temperature, besides insulating heavily with rock wool and magnesia insulation. During the winter months electrical heating of the calorimeter cooling water from 5° to 20° C. requires the continuous use of about 2 kilowatts. To reduce the power consumption and eliminate the necessity for thermostatic controls, the authors recirculated the cooling water, taking special care to keep the temperature constant.

A small centrifugal pump (B, Figure 2) delivered the cooling water from the calorimeters back to the constant-head tank, located some 2 meters (6 feet) above the apparatus. To prevent vibration from reaching the apparatus, the pump was cushioned by several inches of sponge rubber, and all piping insulated from the walls by sponge rubber. Cold water from the secondary constant-head tank (C, Figure 2) was added to the circulating water at an open tank at the inlet to the pump, to balance the heat picked up in passing through the calorimeters. A specially constructed needle valve in the outlet of the secondary constant-head tank accurately controlled the amount of water added. In this manner, the temperature of the test calorimeter was maintained very steadily. Since the work requires equilibrium temperature conditions, this method of controlling the temperature of the water flowing through the calorimeters seemed superior to electrical heating and thermostatic control.

The line voltage must be controlled very closely to eliminate fluctuations of the heater temperature. A 250-watt Raytheon voltage

regulator (A, Figure 2) provided a completely constant voltage and, with the recirculating water system described above, virtually eliminated temperature fluctuations of the apparatus.

Procedure

A previous paper (1) explained in detail the experimental procedure and method of calculation of the various coefficients. The values of the several coefficients were calculated from the temperature gradient curves drawn for each series of runs. In this case, a series of tests was made for liquid mixtures of the following compositions (in per cent by weight):

Methanol-Water

Distilled water	
9.0 per cent methanol-91.0 per cent water	
18.4 per cent methanol-81.6 per cent water	
35.8 per cent methanol-64.2 per cent water	
58.0 per cent methanol-42.0 per cent water	
77.1 per cent methanol-22.9 per cent water	
89.2 per cent methanol-10.8 per cent water	
99.4 per cent methanol- 0.6 per cent water	

The methanol was received from E. I. du Pont de Nemours & Co., Inc. The composition was reported as 99.85 per cent or better, and the specific gravity given as 0.79620 at

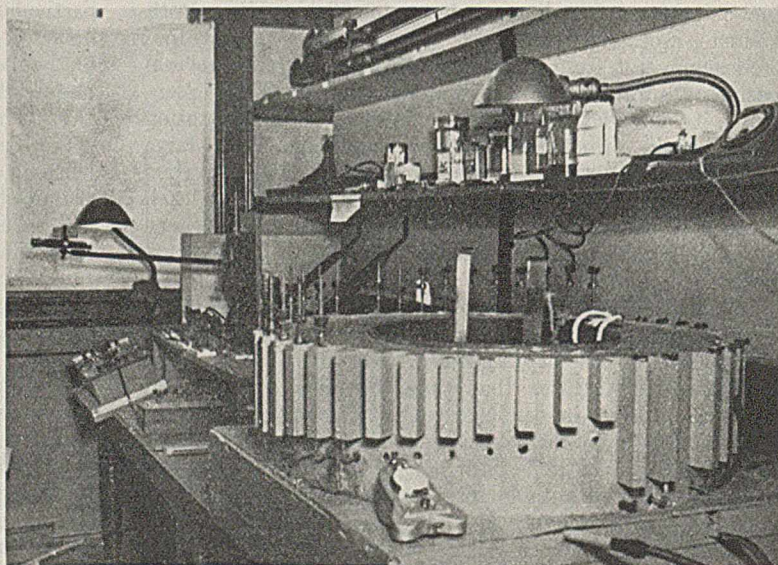


FIGURE 1. GENERAL LAYOUT OF APPARATUS

TABLE I. TRUE COEFFICIENT OF THERMAL CONDUCTIVITY (K_t)

Water % by weight	Methanol % by weight	Values of K_t Gram calories, second ⁻¹ , cm. ⁻² , ° C. ⁻¹ , cm.-a							α_{20}^b %, ° C. ⁻¹	Equations for True Coefficient of Thermal Conductivity
		10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.		
100	(Pure water)	0.00138	0.00141	0.00145	0.00149	0.00152	0.00156	0.00160	0.27	$K_t = 0.00134 + 0.00000365 (t)$
95	5	0.00132	0.00135	0.00139	0.00142	0.00146	0.00149	0.00151	0.26	$K_t = 0.00128 + 0.00000350 (t)$
90	10	0.00126	0.00129	0.00132	0.00135	0.00139	0.00142	0.00145	0.25	$K_t = 0.00123 + 0.00000315 (t)$
85	15	0.00120	0.00123	0.00126	0.00129	0.00132	0.00134	0.00137	0.22	$K_t = 0.00118 + 0.00000275 (t)$
80	20	0.00115	0.00117	0.00120	0.00122	0.00125	0.00127	0.00129	0.21	$K_t = 0.00113 + 0.00000225 (t)$
75	25	0.00110	0.00112	0.00114	0.00116	0.00118	0.00120	0.00122	0.18	$K_t = 0.00108 + 0.00000200 (t)$
70	30	0.00105	0.00107	0.00108	0.00110	0.00112	0.00113	0.00115	0.14	$K_t = 0.00103 + 0.00000175 (t)$
65	35	0.00100	0.00101	0.00103	0.00104	0.00105	0.00106	...	0.12	$K_t = 0.00099 + 0.00000125 (t)$
60	40	0.00096	0.00096	0.00097	0.00098	0.00099	0.00100	...	0.10	$K_t = 0.00095 + 0.00000075 (t)$
55	45	0.00091	0.00092	0.00092	0.00093	0.00093	0.00094	...	0.06	$K_t = 0.00091 + 0.00000050 (t)$
50	50	0.00088	0.00088	0.00088	0.00088	0.00088	0.00088	...	0.00	$K_t = 0.00088$
45	55	0.00083	0.00083	0.00083	0.00082	0.00082	0.00082	...	-0.03	$K_t = 0.00083 - 0.00000025 (t)$
40	60	0.00079	0.00079	0.00078	0.00078	0.00077	0.00077	...	-0.06	$K_t = 0.00080 - 0.00000050 (t)$
35	65	0.00076	0.00075	0.00074	0.00073	0.00072	0.00072	...	-0.10	$K_t = 0.00076 - 0.00000075 (t)$
30	70	0.00072	0.00071	0.00070	0.00069	0.00068	0.00067	...	-0.11	$K_t = 0.00073 - 0.00000100 (t)$
25	75	0.00069	0.00067	0.00066	0.00065	0.00064	-0.11	$K_t = 0.00070 - 0.00000125 (t)$
20	80	0.00065	0.00064	0.00062	0.00061	0.00060	-0.16	$K_t = 0.00066 - 0.00000125 (t)$
15	85	0.00062	0.00060	0.00059	0.00058	0.00056	-0.17	$K_t = 0.00063 - 0.00000125 (t)$
10	90	0.00059	0.00057	0.00056	0.00054	0.00053	-0.18	$K_t = 0.00060 - 0.00000150 (t)$
5	95	0.00055	0.00054	0.00052	0.00051	0.00050	-0.19	$K_t = 0.00057 - 0.00000150 (t)$
(Pure methanol)	100	0.00053	0.00051	0.00050	0.00048	0.00047	-0.20	$K_t = 0.00054 - 0.00000150 (t)$

^a K_t (cal., sec.⁻¹, cm.⁻², ° C.⁻¹, cm.) 2900 = K_t (B. t. u., hr.⁻¹, ft.⁻², ° F.⁻¹, inch).
C. g. s. system English system

^b α_{20} as defined by $K_t = K_{20}[1 + \alpha_{20}(t - 20)]$.

TABLE II. TRUE COEFFICIENT OF THERMAL CONDUCTIVITY (K_t)

Water % by weight	Ethyl Alcohol % by weight	Values of K_t Gram calories, second ⁻¹ , cm. ⁻² , ° C. ⁻¹ , cm.-a					α_{20}^b %, ° C. ⁻¹	Equations for True Coefficient of Thermal Conductivity	
		10° C.	20° C.	30° C.	40° C.	50° C.			60° C.
100	(Pure water)	0.00138	0.00141	0.00145	0.00149	0.00152	0.00156	0.27	$K_t = 0.00134 + 0.00000365 (t)$
95	5	0.00131	0.00135	0.00139	0.00142	0.00145	0.00149	0.25	$K_t = 0.00128 + 0.00000335 (t)$
90	10	0.00125	0.00128	0.00132	0.00135	0.00138	0.00141	0.23	$K_t = 0.00122 + 0.00000300 (t)$
85	15	0.00119	0.00122	0.00125	0.00128	0.00130	0.00133	0.22	$K_t = 0.00116 + 0.00000270 (t)$
80	20	0.00113	0.00116	0.00119	0.00121	0.00123	0.00126	0.21	$K_t = 0.00111 + 0.00000245 (t)$
75	25	0.00108	0.00110	0.00112	0.00114	0.00116	0.00118	0.18	$K_t = 0.00106 + 0.00000200 (t)$
70	30	0.00102	0.00104	0.00106	0.00107	0.00109	0.00110	0.16	$K_t = 0.00101 + 0.00000165 (t)$
65	35	0.00097	0.00098	0.00099	0.00101	0.00102	0.00103	0.14	$K_t = 0.00095 + 0.00000130 (t)$
60	40	0.00092	0.00093	0.00093	0.00094	0.00095	0.00096	0.11	$K_t = 0.00091 + 0.00000100 (t)$
55	45	0.00087	0.00087	0.00088	0.00088	0.00089	0.00089	0.08	$K_t = 0.00086 + 0.00000070 (t)$
50	50	0.00082	0.00082	0.00083	0.00083	0.00083	0.00083	0.04	$K_t = 0.00082 + 0.00000030 (t)$
45	55	0.00078	0.00077	0.00077	0.00077	0.00077	0.00077	0.00	$K_t = 0.00078$
40	60	0.00073	0.00073	0.00072	0.00072	0.00072	0.00071	-0.05	$K_t = 0.00074 - 0.00000035 (t)$
35	65	0.00069	0.00068	0.00068	0.00067	0.00066	0.00066	-0.10	$K_t = 0.00070 - 0.00000070 (t)$
30	70	0.00065	0.00064	0.00063	0.00062	0.00061	0.00060	-0.16	$K_t = 0.00067 - 0.00000115 (t)$
25	75	0.00062	0.00061	0.00059	0.00058	0.00057	0.00056	-0.22	$K_t = 0.00063 - 0.00000130 (t)$
20	80	0.00058	0.00057	0.00055	0.00054	0.00052	0.00051	-0.25	$K_t = 0.00059 - 0.00000140 (t)$
15	85	0.00055	0.00053	0.00051	0.00050	0.00048	0.00046	-0.32	$K_t = 0.00056 - 0.00000170 (t)$
10	90	0.00052	0.00050	0.00048	0.00046	0.00044	0.00042	-0.40	$K_t = 0.00054 - 0.00000200 (t)$
5	95	0.00049	0.00047	0.00044	0.00042	0.00040	0.00038	-0.48	$K_t = 0.00052 - 0.00000235 (t)$
(Pure ethyl)	100	0.00046	0.00043	0.00041	0.00038	0.00036	0.00033	-0.54	$K_t = 0.00048 - 0.00000250 (t)$

^a K_t (cal., sec.⁻¹, cm.⁻², ° C.⁻¹, cm.) 2900 = K_t (B. t. u., hr.⁻¹, ft.⁻², ° F.⁻¹, inch).
C. g. s. system English system

^b α_{20} as defined by $K_t = K_{20}[1 + \alpha_{20}(t - 20)]$.

15° C./4° C. The distillation range did not exceed 1° C. from first drop to dry on an Engler distillation unit.

vs. true thermal conductivity curves were drawn for every 10° C. interval.

Ethyl Alcohol-Water

- Distilled water
- 11.0 per cent ethyl alcohol-89.0 per cent water
- 20.2 per cent ethyl alcohol-79.8 per cent water
- 37.4 per cent ethyl alcohol-62.6 per cent water
- 64.9 per cent ethyl alcohol-35.1 per cent water
- 79.2 per cent ethyl alcohol-20.8 per cent water
- 91.7 per cent ethyl alcohol- 8.3 per cent water

The ethyl alcohol used was 190 proof industrial alcohol U. S. P., manufactured by the U. S. Industrial Alcohol Co.

From the calorimetric determinations and the temperature gradient curves, the true thermal conductivities were determined for the binary liquid mixtures listed above over the range of temperature covered for the particular runs. In every case, within the accuracy of the tests, the true thermal conductivity was a linear function of the temperature—that is, a straight-line relation. From these curves, composition

True Thermal Conductivity, K_t

The final data given in Tables I and II and graphically in Figures 3, 4, 5, and 6 were obtained from the conductivity-composition curves. By means of either the tables or the graphs it is possible to determine the true thermal conductivity of binary liquid mixtures of both methanol-water and ethyl alcohol-water for any temperature from 10° to 70° C. and for any composition from distilled water to pure alcohol.

Average or Mean Thermal Conductivity

The average thermal conductivity, K_t^a between any two temperatures, t_2 and t_1 , covered by the experiments and for any composition, can also be readily determined by using the average or mean temperature from Tables I and II and Figures 3, 4, 5, and 6. Since the true thermal conductivity is a linear

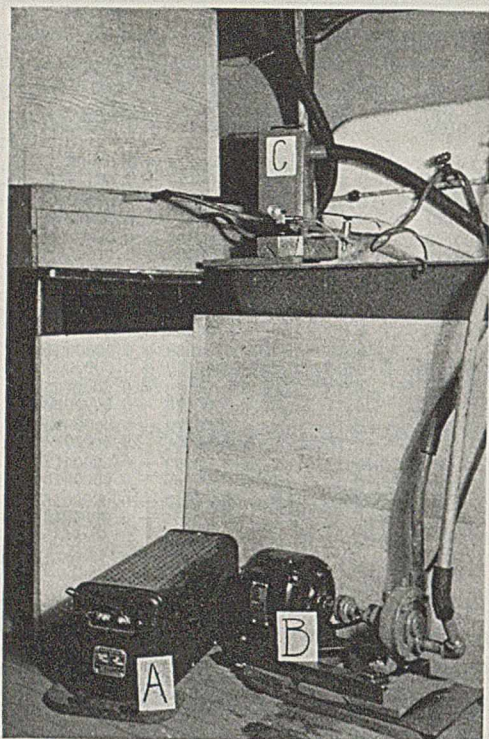


FIGURE 2. VOLTAGE REGULATOR, A, CENTRIFUGAL PUMP, B, AND SECONDARY CONSTANT-HEAD TANK, C

function of the temperature, the average thermal conductivity between temperatures t_2 and t_1 must be the same as the true coefficient at $\frac{t_2 + t_1}{2}$ or the average of the two temperatures.

Discussion of Results

The thermal conductivity values calculated from new tests run on redistilled water checked with the results given by Bates in 1936 (2). His investigation was carried on with the same apparatus, but at the Massachusetts Institute of Technology, with electrically heated, thermostatically controlled calorimeter water.

Results for both binary mixtures (methanol-water and ethyl alcohol-water) show a temperature coefficient which reduces to zero at approximately a 50 per cent solution, going negative for alcohol concentrations higher than 50 per cent. In other words, the temperature coefficient of thermal conductivity is positive for distilled water ($\alpha_{20} = +0.26\%$, $^{\circ}\text{C}^{-1}$), approaches zero at 50 per cent methanol-50 per cent water, and is negative for pure methanol ($\alpha_{20} = -0.20\%$, $^{\circ}\text{C}^{-1}$). For ethyl alcohol-water mixtures the zero coefficient occurs around 52 per cent ethyl alcohol-48 per cent water, and is negative for pure ethyl alcohol ($\alpha_{20} = -0.54\%$, $^{\circ}\text{C}^{-1}$).

Table III gives a comparison of the thermal conductivity values for water, methanol, and ethyl alcohol with those found by other observers.

Barratt and Nettleton in the International Critical Tables proposed an equation for cal-

culating the true thermal conductivity of binary liquid mixtures when the conductivities of the two liquids are known. The equation is

$$K \sinh(100\mu) = K_1 \sinh(p_1\mu) + K_2 \sinh(p_2\mu)$$

"where p_1 and p_2 are the percentages by weight of the two constituents and μ is a constant depending upon the constituents and the temperature." The following is a sample calculation using the above equation:

Calculation of the thermal conductivity of a 40 per cent ethyl alcohol-60 per cent water binary mixture at 20°C .

$$\begin{aligned} p_1 &= 40, p_2 = 60 \\ K_1 &= 0.00043, K_2 = 0.00141 \text{ (Table II)} \\ 100\mu &= 0.94 \end{aligned}$$

TABLE III. COMPARISON OF VALUES FOR TRUE THERMAL CONDUCTIVITY OF WATER, METHYL ALCOHOL, AND ETHYL ALCOHOL

Liquid	Observer	Year	K_1^a (True)	Temperature, $^{\circ}\text{C}$.	α_{20}^b ($\%$, $^{\circ}\text{C}^{-1}$)
Water	I. C. T. (3)	1929	0.00138	20	0.28
	Bates (2)	1936	0.00141	20	0.26
	Bates, Hazzard, Palmer	1938	0.00141	20	0.26
Methyl alcohol	I. C. T.	1929	0.00050	20	-0.053
	Bates, Hazzard, Palmer	1938	0.00051	20	-0.20
Ethyl alcohol	I. C. T.	1929	0.000435	20	-0.071
	Bates, Hazzard, Palmer	1938	0.00043	20	-0.54
	Schack (5)	1933	0.00041	40
	Saha and Srivastava (4)	1931	0.00043	25

^a Units of K_1 = gram cal., sec.⁻¹, cm.⁻², $^{\circ}\text{C}^{-1}$, cm.
^b α_{20} as defined by $K_t = K_{20} [1 + \alpha_{20}(t - 20)]$.

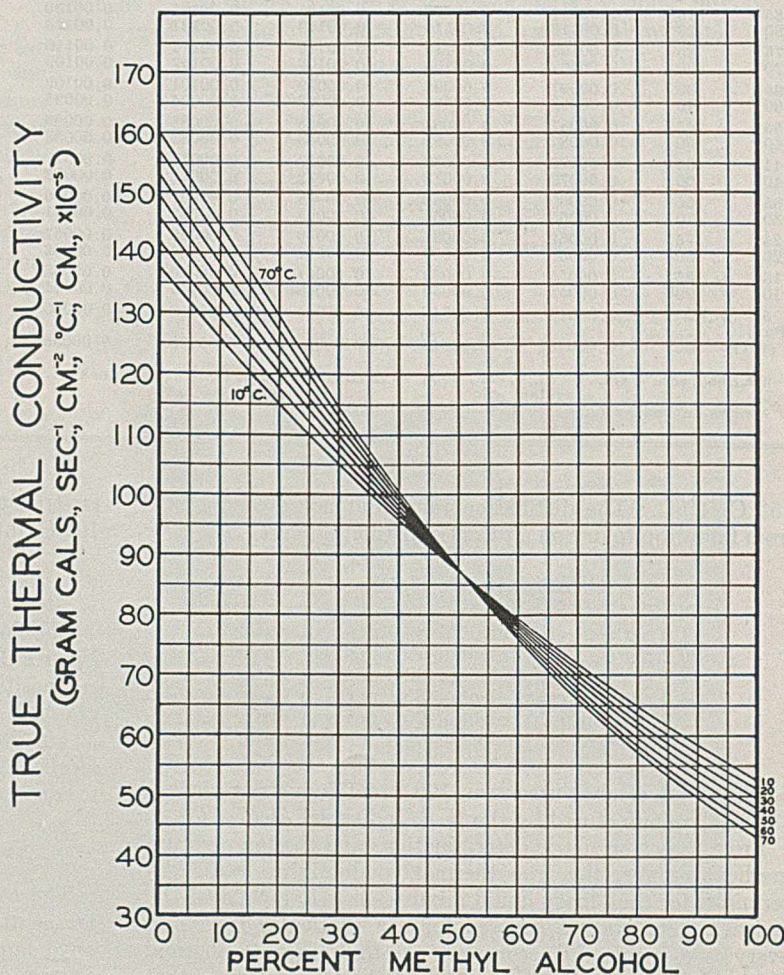


FIGURE 3. THERMAL CONDUCTIVITY-COMPOSITION CURVES FOR METHYL ALCOHOL-WATER SOLUTIONS

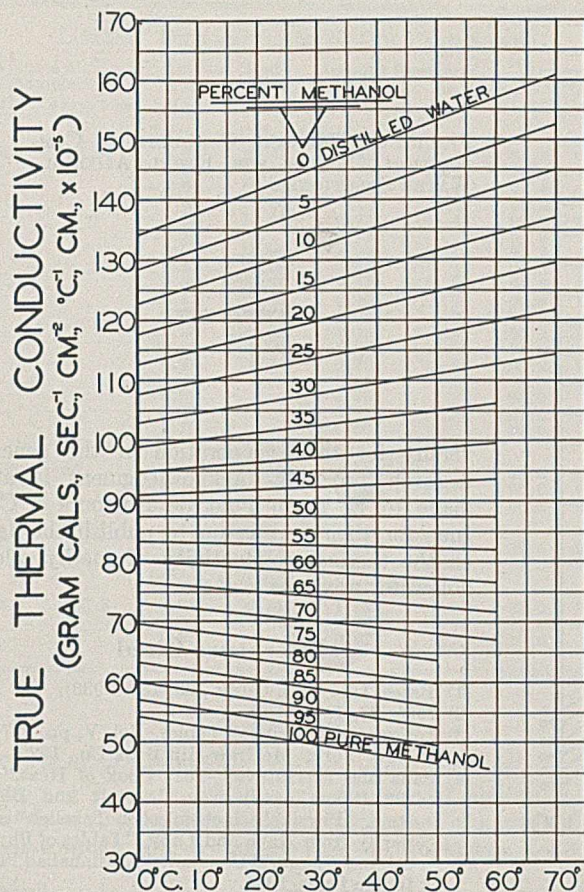


FIGURE 4. THERMAL CONDUCTIVITY-TEMPERATURE CURVES FOR METHYL ALCOHOL-WATER SOLUTIONS

Therefore,

$$K = \frac{0.00043 \sinh(40 \times 0.0094) + 0.00141 \sinh(60 \times 0.0094)}{\sinh(0.94)}$$

From a table of hyperbolic sines, we get:

$$\sinh 0.94 = 1.085, \sinh 0.376 = 0.385, \sinh 0.564 = 0.594$$

Substituting these values and solving,

$$K = 0.000925$$

Using the authors' values of K_1 and values of μ given in the International Critical Tables (3), they found variations of .5

TABLE IV. COMPARISON OF OBSERVED THERMAL CONDUCTIVITIES WITH CONDUCTIVITIES COMPUTED FROM EQUATION $K \sinh(100\mu) = K_1 \sinh(p_1\mu) + K_2 \sinh(p_2\mu)$

Water Solutions of	Composition % by weight	$K_{obs.}$ at 20° C.	$K_{calc.}$ at 20° C. ^a	$\Delta \times 10^{-5}$	$K_{calc.}$ at 20° C. ^b	$\Delta \times 10^{-5}$
Ethyl alcohol	20	0.00116	0.00109	7	0.00115	1.0
	40	0.00093	0.00084	9	0.000925	0.5
	60	0.00073	0.00066	7	0.000735	-0.5
	80	0.00057	0.00053	4	0.00057	0
Methyl alcohol	20	0.00117	0.00111	6	0.001175	-0.5
	40	0.00096	0.00088	8	0.00096	0
	60	0.00079	0.00071	8	0.00079	0
	80	0.00064	0.00059	5	0.00064	0
Glycerol ^c	20	0.00124	0.00125	-1	0.001215	2.5
	40	0.00107	0.00111	-4	0.001065	0.5
	60	0.00091	0.00095	-4	0.00092	-1.0
	80	0.00078	0.00081	-3	0.000795	-1.5

^a $K_{calc.}$ is obtained from the above equation using values of $100\mu_{20}$ for ethyl alcohol = 1.34, for methyl alcohol = 1.30, and for glycerol = 0.40 as given in International Critical Tables.

^b $K_{calc.}$ is obtained from the above equation using values of $100\mu_{20}$ for ethyl alcohol = 0.94, for methyl alcohol = 0.90, and for glycerol = 0.65 as determined by the authors.

^c Values for K_1 of glycerol were obtained from (2).
 $\Delta = K_{obs.} - K_{calc.}$

to 10 per cent of the calculated K_t from the observed K_t (Table IV). However, since the residuals (Δ) were all of the same sign, it seemed necessary to change only μ to make the equation fit. When μ is changed to make the sum of the residuals (Δ) as small as possible, the equation fits the data very well. On the basis of the above calculations, the authors suggest the following values of 100μ at 20° C.: ethyl alcohol = 0.94, methyl alcohol = 0.90, glycerol = 0.65.

The International Critical Tables suggest that μ is a function of the temperature but give only the value at 20° C. Values of K_t calculated for higher temperatures, the authors' values for $100 \mu_{20}$ suggested above being used, showed fairly good agreement with observed conductivities at those temperatures. Since the agreement up to 80° C. is good (Table V), it would seem useless to change μ at higher temperatures,

TABLE V. COMPARISON OF OBSERVED AND COMPUTED VALUES OF K_t

(Showing the degree of independence of μ with temperature)

Water Solutions of	Composition % by weight	Temperature ° C.	$K_{obs.}$	$K_{calc.}$	$\Delta \times 10^{-5}$
Ethyl alcohol	20	60	0.00126	0.00124	2
	40		0.00096	0.00097	-1
	60		0.00071	0.000735	-2.5
	80		0.00051	0.00052	-1
Methyl alcohol	20	50	0.00125	0.00124	1
	40		0.00099	0.00101	-2
	60		0.00077	0.000805	-3.5
	80		0.00060	0.00063	-3
Glycerol	20	80	0.00141	0.00140	1
	40		0.00118	0.00119	-1
	60		0.00096	0.00101	-5
	80		0.00079	0.00085	-6

$$\Delta = K_{obs.} - K_{calc.}$$

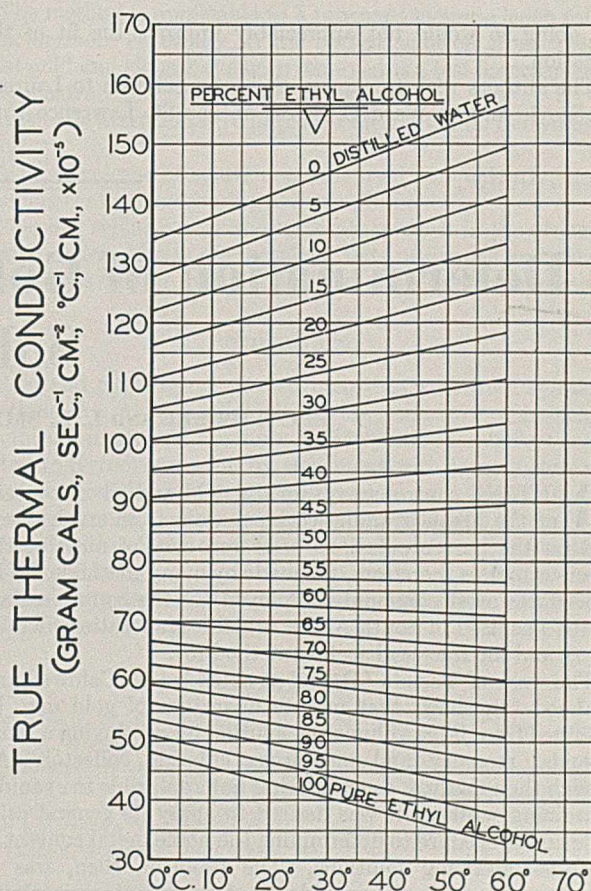


FIGURE 5. THERMAL CONDUCTIVITY-TEMPERATURE CURVES FOR ETHYL ALCOHOL-WATER SOLUTIONS

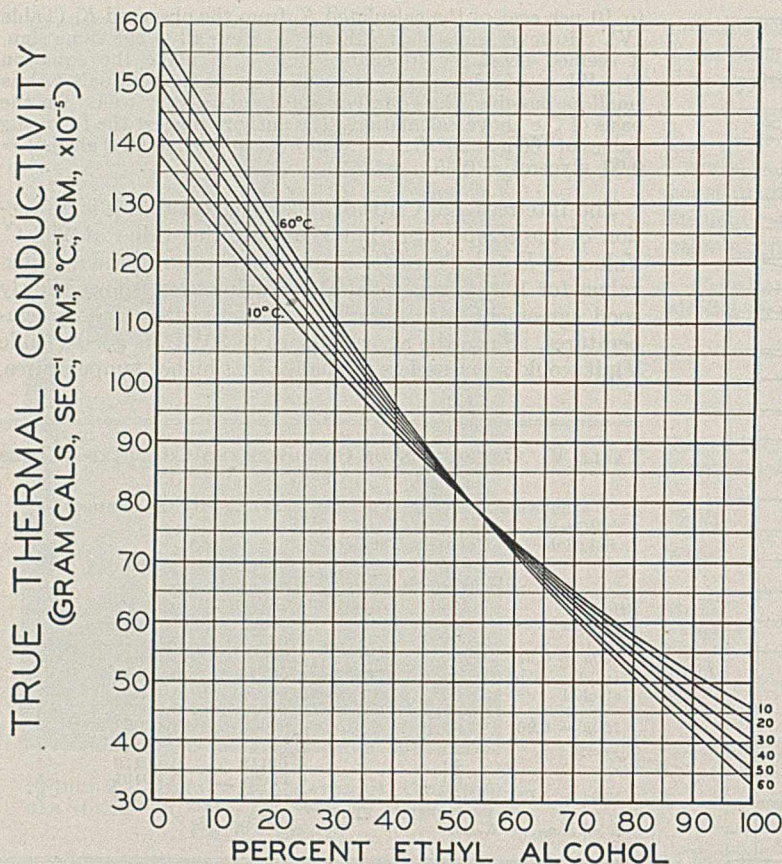


FIGURE 6. THERMAL CONDUCTIVITY-COMPOSITION CURVES FOR ETHYL ALCOHOL-WATER SOLUTIONS

for doing so would not appreciably improve the fit of the equation.

The authors wish to express their appreciation to Laurens H. Seeyle and to Ward C. Priest of The St. Lawrence Uni-

versity for their coöperation in the general research program. Acknowledgment is also made to E. I. du Pont de Nemours & Co., Inc., for their permission to publish the data on the thermal conductivity of methyl alcohol-water mixtures.

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Determination of Gold and Silver in Cyanide Solutions

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ROUTINE control assays for the gold and silver content of the alkali cyanide leach solutions from crushed ore, and on the barren solutions after recovery of most of the precious metals therefrom, are made by many methods. The procedures most commonly employed are the copper sulfate method as used in South Africa (2), the evaporation method (2, 3), and the zinc-lead acetate method (3).

The work of Yasuda (4), and as extended by Caldwell and McLeod (1), shows that minute quantities of gold may be obtained from large volumes of solution by employing a semicolloidal mercury and mercurous chloride collector. Although their method, as reported, is not applicable to cyanide-containing solution, it was desired to apply its general principle and procedure to determining the noble metal content of cyanide-containing solutions. The problem, then, was to destroy or eliminate the cyanide ion of the samples containing noble metal so that it would not interfere with collection of gold from solution by mercurous precipitate.

A well-known inorganic reaction is the formation of potassium ferrocyanide by the reaction of ferrous sulfate and potassium cyanide. It seemed feasible with the use of ferrous sulfate to eliminate the cyanide ions from the solution that the colloidal mercury fall method should yield good results as a collector of gold and silver from solution.

To test the applicability of the semicolloidal mercury fall method in collecting and recovering gold and silver from cyanide-containing solution, if the cyanide ion is converted to ferrocyanide by use of ferrous sulfate, numerous experimental runs were made. Simulated cyanide leach solutions as from gold ores were prepared. Particles of pure gold, weighed to within 0.01 mg., were dissolved in the minimum quantity of aqua regia and transferred to water in 2-liter bottles. A measured volume of standard silver nitrate was introduced. Potassium cyanide was added to yield solutions of various percentages of cyanide, but in general of about 0.025 per cent, which is representative of economic leach solutions.

TABLE I. DETERMINATION OF GOLD AND SILVER

Volume of Sample Ml.	Assay tons	Amount Used		Amount Recovered		Recovery	
		Au Mg.	Ag Mg.	Au Mg.	Ag Mg.	Au %	Ag %
Ferrous Sulfate-Mercurial Method							
2000	66.67	4.56	10.48	4.38	10.37	96.2	98.8
		6.80	31.44	6.39	29.21	93.9	93.0
		0.65	10.48	0.62	9.96	95.4	95.0
		1.87	20.96	1.80	20.69	96.2	98.8
		1.84	31.44	1.77	31.40	96.2	99.6
		13.85	...	1.13	...	94.8	...
		2.08	20.96	1.99	18.49	95.5	84.0
		0.52	10.48	0.49	8.17	94.3	78.0
		0.80	20.96	0.77	16.88	96.3	77.0
		0.11	11.84	0.10	9.70	90.9	82.0
		0.05	8.78	0.047	6.77	94.0	77.0
		22.93	123.00	21.36	115.00	93.2	93.5
		60.22	262.00	57.04	251.00	94.8	96.0
		0.76	22.7	0.70	18.5	92.2	81.0
291	2.80	96.2	..		
6.65	6.39	96.0	..		
0.37	0.36	97.0	..		
1.70	1.60	94.0	..		
Copper Sulfate Method							
600	20	0.90	11.52	0.86	10.99	95.6	95.4
		3.12	15.75	3.00	14.7	96.0	93.4
		12.54	62.9	12.17	59.88	96.8	95.2
Chiddey Method							
600	20	0.12	5.24	0.115	4.68	89.5	95.6
		4.96	20.96	4.79	19.46	93.0	96.5
Ferrous Sulfate-Mercurial Method							
10,000	333.3	2.08	22.21	1.95	19.68	93.0	90.0
		1.98	19.87	1.80	17.51	91.0	88.0
		0.30	...	0.27	90.0	..

Method

The method for analyzing for gold and silver from cyanide-containing solution, which has been proved applicable by analysis of simulated cyanide leach solutions of known noble metal content, and by check runs on unknowns, follows:

To 2-liter samples (about 66.67 assay tons) of cyanide-containing noble metal solution add a solution containing ferrous sulfate approximately ten times the weight of the cyanide in the sample. Add 50 cc. of a saturated mercuric chloride solution, 5 grams of magnesium powder, and 60 cc. of concentrated hydrochloric acid. Pour the acid in by portions to prevent bubbling over. If the volume of sample taken is much greater than the 66.67 assay tons (about 10 liters, 333.3 assay tons), double the amount of mercuric chloride, magnesium, and acid used. Allow to stand 6 to 8 hours, or overnight. Siphon off the clear liquid and transfer the residue from the bottle into a beaker, rinsing out any residue remaining in the bottle with small portions of water. Let it settle for a few minutes and then filter, using a rough quantitative filter paper. As the bulk of the residue is being washed onto the filter paper, sprinkle in about 20 grams of granular test lead so that the two will become intimately mixed. Allow to drain and dry.

On a bone-ash cupel weighing about 60 grams spread a layer of test lead, following the general concave shape of the cupel. Remove as much of the dried residue from the filter paper as is convenient, mash the lumps, and place in the center of the cupel. With a little lead cover the residue remaining on the filter paper, wad it up, and place on top of the cupel. Cover the residue with more test lead. The total weight of lead used should not greatly exceed 45 grams.

Introduce the cupel slowly into the muffle, so that the filter paper will be burned and mercury and its salts volatilized. This last-mentioned step must be executed cautiously and requires the close attention of the analyst; otherwise, a too rapid volatilization of the mercurial residue will cause spitting and serious losses of value, or perhaps salting of an adjacent cupellation. When a cupel has been placed in the hottest part of the muffle, increase the temperature to nearly 1000° C. and create a reducing atmosphere by putting near the cupel bits of wood, cork, or like material. When the lead has "uncovered," as shown by its bright red appearance, cool the muffle to normal cupellation temperatures. Upon completing the cupellation, weigh for gold and silver as usual in analyzing. Table I lists results of analysis.

Still more accurate results may be obtained by scorification of the mercurial noble metal collection residue prior to cupellation. It is recommended that the filter paper with residue be scorified in a 6.25-cm. (2.5-inch) scorifier. Place in the bottom of the scorifier a 10-gram sheet of lead molded to the form of the scorifier. This prevents absorption of water and subsequent splattering during scorification. Add appropriate amounts of test lead and a little silica-borax glass. The scorification can be carried on so as to

yield an 18- to 30-gram button, in which case smaller sized cupels may be used.

Discussion of Results

A few results of analyses for gold and silver from cyanide solution by the copper sulfate method (2), and by the Chiddey or zinc-lead acetate method (3) are recorded in Table I. The percentage recovery is practically the same in the three methods. The chief advantage of the mercurial method is, then, simplicity of procedure and application to larger volumes of solution. The major loss in the various processes is probably gold and silver cupellation loss.

Analyses for gold and silver in 10 liters of cyanide-containing sample show slightly decreased noble metal recovery.

In examining the results of numerous runs it was noticed that the gold recovery was between 94 and 96 per cent. If 95 per cent is considered the average of recovery, and a correction factor is applied to the weight of gold obtained, in most cases the corrected value of gold was within 0.01 mg. of the theoretical yield.

Application of the Method

The mercurial method is applicable to the assay of a cyanide leach solution when accuracy is desired. The corrected recovery of 0.01 mg. of gold from 66.67 assay tons of solution is estimation of the gold value to \$0.0053 per ton at the present price of gold (about \$35.00 per ounce).

The recovery of silver is subject to errors due to cupellation procedure. If, however, silver is determined within 2 mg. from 66.67 assay tons, the estimation of its value is made to within 1.5 cents per ton at the present variable market quotation of 50 cents per ounce.

The method is applicable to a pregnant cyanide leach solution, or more especially to the barren solution from which most gold and silver have been removed as a test for completeness of extraction. Merits of the method are:

But little attention is required for an individual determination.

A large volume of solution can be used conveniently, thus reducing errors in measuring and sampling.

Mercury replaces only those metals below it in the electro-motive series—the noble metals. Salts of copper and other base metals in the cyanide leach solution are not reduced.

Summary

Gold and silver are recovered quantitatively from cyanide solutions by a semicolloidal mercury-mercurous chloride precipitate in an acid medium, if the cyanide ion is first converted to ferrocyanide ion by treatment with ferrous sulfate.

A determinative method for gold and silver in cyanide solutions is presented. An accuracy within 0.01 to 0.02 mg. for gold and within 2 mg. for silver is obtained from 66.67 assay tons of solution.

But slightly decreased gold and silver recovery is attainable from 333.3 assay tons of sample.

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Photometric Determination of Vanillin in Vanilla Extracts

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ALTHOUGH the method of Folin and Denis (2) as outlined by the Association of Official Agricultural Chemists for the colorimetric determination of vanillin by means of phosphotungstic-phosphomolybdic acid reagent is in general satisfactory, it was observed that *o*-iodoxy ammonium benzoate develops a color with solutions of vanillin, suitable for photometric analysis. Because of the comparative ease of duplication of results with photometric methods, it appeared desirable to make a more detailed study of the method.

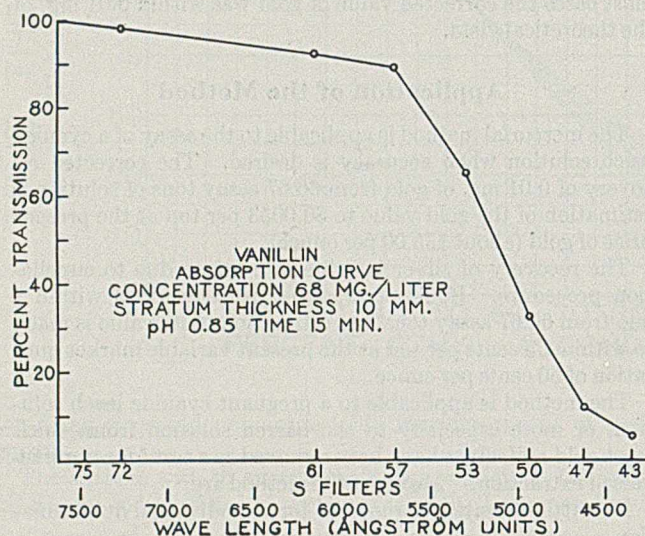


FIGURE 1

Leake (5) and his associates (Emerson, 1, and Moody, 6) have reported the use of *o*-iodoxy ammonium benzoate for the colorimetric determination of morphine and epinephrine. It was suggested by the above workers that this reagent was specific for "free phenolic hydroxyls." The authors have found that it forms color complexes with a relatively large number of types of compounds, a more detailed study of which will be reported at a later date.

Greenbaum (4) has developed a satisfactory method for the preparation of *o*-iodoxy benzoic acid and certain of its salts. The ammonium salt may be obtained under the trade name of "Amidoxyl benzoate" from the Abbott Laboratories, North Chicago, Ill.

In developing the present method it was observed that the color complex was influenced markedly by such variables as concentration of the solvent and time allowed for the development of color. A detailed study was made of the following factors in order to determine the extent of the variation: degree of absorption of the color for various segments of the spectrum, influence of hydrogen-ion concentration on the formation of the color, influence of concentration of reagent, and influence of time.

Experimental

Figure 1 gives the light transmission of the color complex for various segments of the spectrum when the spectrum (S) filters are used. The maximum absorption occurs at the

lowest portion of the visible spectrum. Filter S43 was found to be most satisfactory for use.

By keeping the time and concentrations of vanillin and reagent constant, a study was made of the light transmission with change in hydrogen-ion concentration. It had been previously determined that a strongly acidic solution is necessary for the reaction (curve II, Figure 2). At a pH of 0.85 to 0.94, the absorption is greatest and the color is most stable.

Working at a pH of 0.87 and keeping the concentrations of vanillin and reagent constant, a study was made of the effect of time on transmission.

TABLE I. ANALYSIS OF VANILLIN SOLUTIONS

Sample	Vanillin Present G./100 cc.	Vanillin Found	
		By official colorimetric method G./100 cc.	By photometric method G./100 cc.
1	0.100	0.107	0.098
2	0.150	0.149	0.145
3	0.200	0.188	0.205
4	0.250	0.239	0.247
5	0.300	0.279	0.298

The results are shown in Figure 2 (curve I). It will be observed that it requires 15 minutes for the full development of color, following which it remains constant for several minutes. Repeated determinations show that best results are obtained by starting the readings exactly 15 minutes after the addition of the reagent, and by completing the readings during the next 5-minute interval.

REAGENTS. *o*-Iodoxy Ammonium Benzoate. Dissolve 1 gram of *o*-iodoxy ammonium benzoate in 200 cc. of distilled water.

Hydrochloric Acid. Employing constant-boiling acid, make 1 liter of 0.167 N hydrochloric acid. (See Foulk and Hollingsworth, 3, for table of concentrations of constant-boiling hydrochloric acid.)

PROCEDURE. Pipet 10 cc. of the vanilla extract into a 50-cc. volumetric flask, add 25 cc. of water and 5 cc. of 8 per cent lead

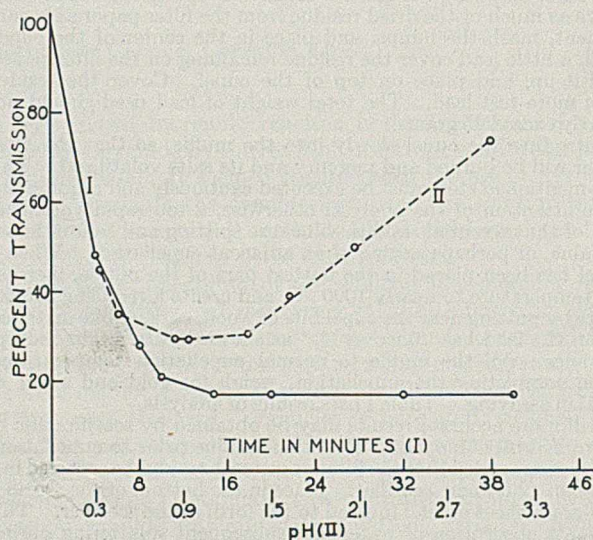


FIGURE 2

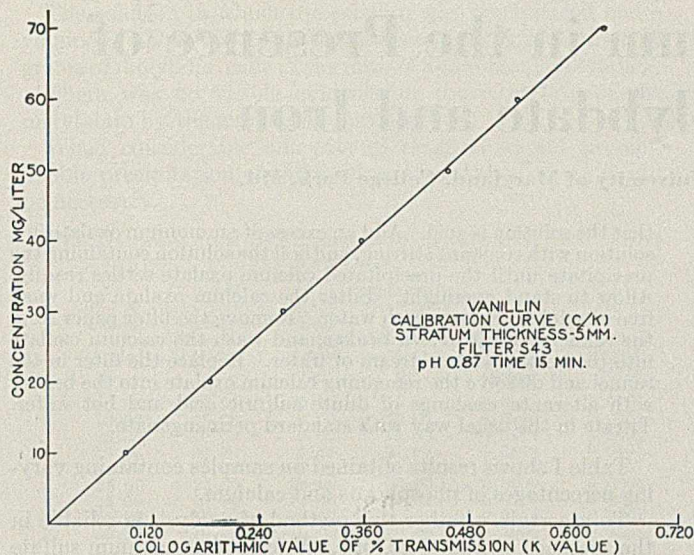


FIGURE 3

acetate solution, and make up to 50 cc. with water. Filter through a dry filter. (If a complete analysis is being conducted, 2 cc. of the clear lead filtrate as prepared for the official gravimetric determination of vanillin and coumarin may be employed.)

Pipet 5 cc. of the clear lead filtrate into a 50-cc. volumetric flask and add 25 cc. of 0.167 *N* hydrochloric acid. Shake, add 3 cc. of a 0.5 per cent solution (2 cc. are sufficient for lower concentrations) of *o*-iodoxy ammonium benzoate, and fill the flask to the mark with 0.167 *N* hydrochloric acid. Shake thoroughly and allow the mixture to stand for exactly 15 minutes. In the meantime prepare in the same manner a reference solution, omitting the reagent. Transfer to 5-mm. photometer cells and read the per cent of transmission on spectrum filter S43. Filtration of the color complex is not necessary.

By referring to the concentration curve (Figure 3), the concentration of vanillin may be read off directly from the *K* value (cologarithm of per cent transmission) in milligrams per liter. This value must be multiplied by 5.0 to convert it to milligrams in 100 cc. of the original extract. The straight-line graph shows that Beer's law holds within these limits. The concentration curve was prepared from known concentrations of vanillin (Monsanto).

Table I shows the results of analysis of vanillin solutions of known strength by both the official colorimetric method and the above photometric method.

Determinations were made on two samples of commercial vanilla extracts in order to compare the method with the standard gravimetric procedure. The extractions were made in triplicate and the average of the three determinations was taken (Table II).

TABLE II. ANALYSIS OF VANILLA EXTRACTS

Sample	Gravimetric Method G./100 cc.	Photometric Method G./100 cc.
1	0.360	0.365
2	0.086	0.082

Sample 1 was an imitation vanilla extract, colored artificially. Upon extraction and evaporation of the solvent it gave residues that were almost free from color. Sample 2 was a commercial tincture of vanilla, N. F. V. The residues obtained on extraction contained an appreciable amount of color and probably should have been further purified.

Use of the Cenco-Sanford-Sheard Photometer

The Cenco-Sanford-Sheard photometer may also be employed for the above method by using a 10-mm. cell and a

Corning filter (H. R. lantern blue 554, 5.10-mm. thickness). A satisfactory concentration curve (Figure 4) is obtained by employing 5 cc. of the lead filtrate from the vanilla extract and only 2 cc. of the *o*-iodoxy ammonium benzoate solution. By plotting transmission against concentration on semilogarithmic paper *w/v* per cent of vanillin may be read directly from the graph. Because of the filter characteristics it is essential, in using this method, to make the readings exactly 15 minutes after the addition of the reagent. Concentrations from 0.05 to 0.25 per cent give most satisfactory results. Suitable quantities of the lead filtrate from the vanilla extract should be employed to give vanillin concentrations in this range.

Summary

o-Iodoxy ammonium benzoate has been used in the quantitative determination of vanillin in vanilla extracts. The method is suitable for use with the Pulfrich photometer and with the Cenco-Sanford-Sheard photometer. In concentrations of 10 to 70 mg. per liter, the color complex gives a concentration curve with the Pulfrich photometer that closely approximates Beer's law. In this range determinations may be made with an accuracy of 2 to 3 per cent. Coumarin and other constituents normally remaining in the lead filtrate from vanilla extracts do not interfere. The method has been used for the past 2 years in a student laboratory and is more accurate and convenient than the accepted colorimetric procedure.

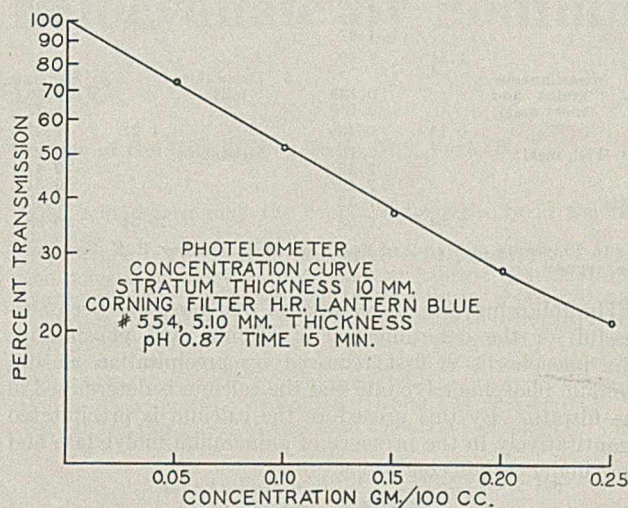


FIGURE 4

The authors wish to acknowledge with thanks the coöperation of C. D. Leake for the loan and use of the Cenco-Sanford-Sheard photometer and C. B. Gentle of the Redman Scientific Company for the loan of a Corning glass filter and general assistance with the photometer.

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Precipitation of Calcium in the Presence of Ammonium Molybdate and Iron

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OF LATE much interest has been aroused in the determination of the calcium and phosphorus ratio in nutrition work. According to a method presented at a meeting of the Association of Official Agricultural Chemists (2) one must weigh out two charges, one for calcium and one for phosphorus. The calcium is precipitated as the oxalate by 2.5 per cent oxalic acid and 3 per cent ammonium oxalate and digested, sodium acetate is added, and the precipitate is allowed to stand 4 hours and is titrated in the usual way. The phosphorus is determined by titrating as the molybdate. Another method for calcium and phosphorus has been published by Washburn and Shear (3), who make the solution acid with hydrochloric acid, add oxalic acid, heat, add ammonium hydroxide, digest, cool, filter, and weigh. Phosphorus is determined on the filtrate from the calcium determination.

TABLE I. DETERMINATION OF CALCIUM

Sample	A. O. A. C. Method ^a %	Proposed Method %	Sample	A. O. A. C. Method ^a %	Proposed Method %
1 Skim milk, grain, bone		1.48	4 Soybean meal		0.30
		1.48			0.35
		1.50			0.32
		1.50			0.31
		1.52		0.34	0.32
		1.47			
	1.51	1.49			
2 Miscellaneous grains and meat meal		0.139	5 Dried skim milk		1.26
		0.139			1.27
	0.13	0.139	1.21	1.27	
3 Fish meal		7.15	6 Meat scrap		10.25
		7.42			10.41
		7.42			10.31
		7.32			10.15
		7.34		10.34	10.38

^a In University of Maryland Feed Control Laboratory, R. E. Baumgardner, chemist.

The following procedure, worked out here, has been successful for the determination of calcium and phosphorus. The phosphorus is first removed by precipitation as ammonium phosphomolybdate and the calcium is determined in the filtrate. By this procedure the calcium is precipitated quantitatively in the presence of ammonium molybdate and iron, under certain conditions.

Procedure for Phosphorus

Weigh out a charge of exactly 5 grams of the finely ground sample in an evaporating dish and add about 0.5 gram of sodium carbonate. Heat the dish slowly, then at a dull red heat until a carbon-free ash is obtained. Then add 30 cc. of concentrated nitric acid and 5 cc. of concentrated hydrochloric acid, and heat the dish over a water bath to dissolve all soluble matter.

Transfer carefully to a 250-cc. volumetric flask and make up to volume. The remaining part of the procedure is the same as in the A. O. A. C. volumetric method (1). A considerable excess of molybdate is used in all cases. The filtrate and washings from the phosphorus determination are used for the determination of calcium. Calcium and phosphorus may thus be determined on the same sample with one weighing.

Procedure for Calcium

Make the filtrate from the phosphorus, about 250 cc., slightly alkaline with ammonium hydroxide, using a piece of litmus paper in the solution as an indicator. Then acidify the solution with acetic acid added a few drops at a time, the litmus paper again serving as an indicator. Concentrated acetic acid may be used and an excess of 2 or 3 cc. does no harm. A precipitate at this point should be disregarded, so long as the litmus paper shows

that the solution is acid. Add an excess of ammonium oxalate in a solution with constant stirring, and boil the solution containing the precipitate until the precipitated calcium oxalate settles readily. Allow to stand overnight. Filter the calcium oxalate and wash free of soluble oxalates with water. Remove the filter paper from the funnel, hold it over a beaker, and wash the calcium oxalate into the beaker with a stream of water. Replace the filter in the funnel and dissolve the remaining calcium oxalate into the beaker with alternate washings of dilute sulfuric acid and hot water. Titrate in the usual way with standard permanganate.

Table I shows results obtained on samples containing varying percentages of phosphorus and calcium.

To ascertain whether this method of analysis is reliable in the presence of iron, 5 cc. of 0.1 *N* ferrous ammonium sulfate were added to the acid solution of sample 1 containing calcium and phosphorus. The solution was then boiled. The remaining part of the procedure is the same as above. The iron had no appreciable effect on the calcium determination.

Table II gives the results in the presence of the amount of iron indicated above.

TABLE II. CALCIUM IN PRESENCE OF IRON

In Solution %	Found %
1.51	1.48
	1.47
	1.48
	1.48
	Av. 1.48

As a further check upon the accuracy of the method, samples were made up as shown below. The phosphorus was precipitated according to the A. O. A. C. volumetric method (1), beginning at the point where the solution is made just alkaline with ammonium hydroxide. The calcium was determined on the filtrate from the phosphorus determination according to the method herein described.

SOLUTION USED. 0.1 *N* calcium nitrate, prepared by dissolving chemically pure calcium carbonate in nitric acid. This solution was checked carefully as to calcium content.

0.1 *N* iron solution prepared from ferrous ammonium sulfate and oxidized with nitric acid. This solution contained 1.861 grams of iron per liter.

0.1 *N* acid sodium ammonium phosphate solution, 6.97 grams per liter.

Ammonium molybdate solutions, A. O. A. C. volumetric method (1).

Table III shows results obtained in determining calcium in the presence of ammonium molybdate and ammonium molybdate and iron. Suitable blanks were run on all reagents.

Discussion

The precipitate which is thrown down in the filtrate from the phosphorus determination by the ammonium hydroxide may not be completely dissolved when the solution is acidified with acetic acid, but will disappear when the sample is heated after adding ammonium oxalate.

No iron is precipitated while the solution is boiled after the addition of ammonium oxalate, probably because the oxalate of iron formed is slightly ionized.

When the sample contains considerable iron, the solution above the precipitated calcium oxalate will be decidedly greenish in color.

The calcium oxalate precipitated from samples high in iron has the same appearance as that from samples in which no iron is present. It was not, however, tested for iron.

The solution in which the calcium was precipitated had a volume of about 250 cc., and contained from 0.25 to about 2 grams of molybdic oxide in the form of ammonium molybdate.

There was no visible evidence of the reduction of the molybdate by the ammonium oxalate.

When considerable amounts of magnesium are present, double precipitation of the calcium oxalate would no doubt be necessary.

TABLE III. CALCIUM IN PRESENCE OF AMMONIUM MOLYBDATE AND IRON

Sample	0.1 N Calcium Nitrate Added Cc.	0.1 N Acid Sodium Ammonium Phosphate Added Cc.	0.1 N Iron Solution Added Cc.	Ammonium Molybdate Added (about 5% MoO ₃) Cc.	Calcium Present Gram	Calcium Found Gram
1	10.00	25.00	0.00	25.00	0.0200	0.0201
2	10.00	25.00	0.00	25.00	0.0200	0.0201
3	20.00	10.00	0.00	15.00	0.0400	0.0402
4	20.00	20.00	0.00	25.00	0.0400	0.0400
5	25.00	25.00	0.00	30.00	0.0500	0.0501
6	25.00	25.00	25.00	30.00	0.0500	0.0504
7	25.00	10.00	10.00	20.00	0.0500	0.0503
8	25.00	10.00	25.00	20.00	0.0500	0.0501
9	50.00	10.00	10.00	20.00	0.1000	0.1005

Acetic acid and ammonium oxalate dissolve the precipitate produced by adding ammonium hydroxide and ammonium molybdate to a solution containing the aluminum ion. To bring about this solution, heating is necessary. It would be

interesting to know if calcium could be quantitatively precipitated by the foregoing method in the presence of a considerable quantity of aluminum.

The amount of calcium found and of calcium present agreed within the limits of analytical error.

Summary

Both calcium and phosphorus are determined on the same charge. Calcium may be accurately determined by precipitating it as the oxalate and titrating with potassium permanganate after removing the phosphorus as ammonium phosphomolybdate.

Moderate amounts of iron do not interfere.

It is evident that ammonium molybdate does not interfere with the quantitative precipitation of calcium in the presence of a moderate amount of acetic acid and ammonium oxalate.

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Transposition of Silver Thiocyanate by Sodium Chloride

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IN 1916 Curtman and Harris (1) pointed out that when a mixture of silver thiocyanate and silver iodide is treated with a 5 per cent solution of sodium chloride and the mixture is boiled for several minutes, only the silver thiocyanate is transposed. The difference in the behavior of the silver salts under these conditions was made the basis for a qualitative method for rapidly detecting thiocyanate in the presence of iodide. In this investigation, the purpose was to determine the optimum conditions for effecting a maximum transposition of silver thiocyanate by sodium chloride solution, and to ascertain whether or not the test of Curtman and Harris was capable of affording quantitative indications.

Experimental

PREPARATION OF SILVER THIOCYANATE. To 10 ml. of 0.25 N silver nitrate solution were added 3 ml. of concentrated nitric acid. The whole was diluted to about 50 ml. and heated to boiling, and with constant stirring exactly the desired amount of potassium thiocyanate was added dropwise. The mixture was then allowed to boil gently to coagulate the precipitate. After standing for a short time, the precipitate was transferred completely to a filter, and washed free from silver.

TRANSPOSITION OF SILVER SALT. The precipitate and paper were transferred to a beaker and treated with a definite volume of *M* sodium chloride solution. The mixture was boiled for the requisite time, and then filtered as rapidly as possible. The precipitate and paper were washed free from thiocyanate, and the combined filtrate and washings were collected. (Throughout this investigation *M* sodium chloride was used instead of the 5 per cent solution used in the original investigation of Curtman and Harris, the former being practically equivalent to the latter.)

QUANTITATIVE DETERMINATION OF THIOCYANATE. The thiocyanate in the filtrate and washings was determined by precipitating it as cuprous thiocyanate, dissolving the latter in nitric

acid, and determining the copper iodometrically in the usual manner.

CONTROL. The sodium thiosulfate was standardized against the potassium thiocyanate solution as follows: To 10.00 ml. of potassium thiocyanate solution (equivalent to about 100 mg. of thiocyanate ion) 60 ml. of *M* sodium chloride were added, and the thiocyanate was determined as above described. (Duplicate determinations were made by boiling the thiocyanate and sodium chloride for 5 minutes to determine whether there was any loss due to decomposition or boiling. None was discovered.) The per cent of transposition was then calculated as follows:

$$\text{Per cent transposition} = \frac{\text{Na}_2\text{S}_2\text{O}_3 \text{ determined}}{\text{Na}_2\text{S}_2\text{O}_3 \text{ control}} \times 100$$

The results of numerous determinations of the per cent of transposition are given in Table I.

TABLE I. TRANSPOSITION DETERMINATIONS

AgCNS in Terms of CNS ⁻ Mg.	Volume of NaCl Ml.	Time of Boiling Min.	Transposition %	Mg.
Series A				
100	60	2	81.2	..
100	60	3	91.6	..
100	60	5	94.3	..
100	60	10	94.4	..
Series B				
100	25	5	51.9	..
100	40	5	91.1	..
100	60	5	94.3	..
100	80	5	94.8	..
100	100	5	97.5	..
Series C				
30	60	5	96.5	28.9
50	60	5	96.5	48.2
100	60	5	94.3	94.2
150	60	5	61.2	91.9

Discussion

In Series A the time of boiling was varied while the other factors were kept constant. The results indicate that the transposition is reasonably complete after 5 minutes, and that further boiling increases the transposition but slightly. Series B was run in order to discover the optimum volume of sodium chloride. The results of this series are plotted in Figure 1. The curve is seen to level off at about 60 ml. Accordingly, a volume of 60 ml. was chosen as the standard in this work. Series C shows the effect of using varying amounts of silver thiocyanate. Up to a certain point all of the silver thiocyanate is transposed but, after this point has been reached, the per cent of transposition drops, while the amount transposed remains practically constant. We must conclude, therefore, that the sodium chloride solution becomes saturated with respect to CNS^- . Therefore, the larger the quantity of silver thiocyanate, the larger must be the volume of chloride solution required to transpose it.

The foregoing conclusion is in harmony with the mass action law. The amount of silver thiocyanate transposed is governed by the solubility products of silver chloride and silver thiocyanate taken simultaneously:

$$\begin{aligned} C_{Ag^+} \times C_{CNS^-} &= S_1 \\ C_{Ag^+} \times C_{Cl^-} &= S_2 \\ C_{CNS^-} &= S_1/S_2 \times C_{Cl^-} \end{aligned}$$

From the solubility products of silver thiocyanate and silver chloride, calculated from their solubilities (2), the number of milligrams of CNS^- in 60 ml. was obtained. The values are: 36 mg. at 25° C. and 245 mg. at 100° C. The experimental value is 94 mg. of CNS^- , the temperature being well above room temperature but certainly falling below 100° C. during the process of filtering off the silver chloride and untransposed silver thiocyanate.

Summary

The most satisfactory conditions for the transposition of silver thiocyanate by M sodium chloride are: For every 100 mg. of thiocyanate as silver thiocyanate, 60 ml. of M sodium

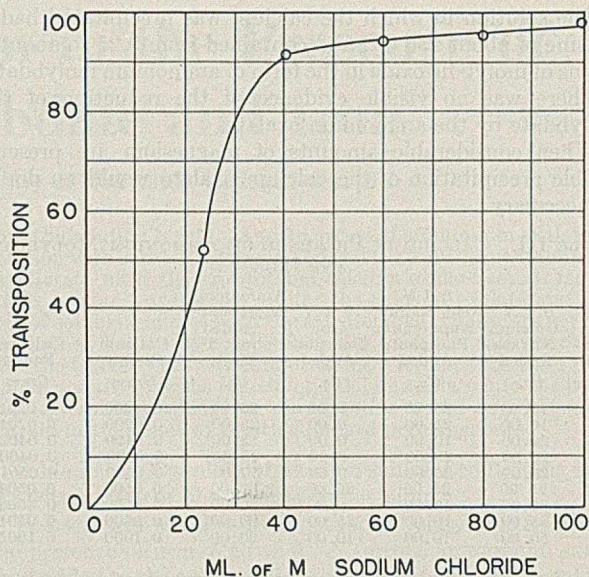


FIGURE 1. PER CENT TRANSMISSION PLOTTED AGAINST MILLILITERS OF M NaCl

chloride solution are required, and the mixture must be boiled for at least 5 minutes.

Under the above conditions a transposition of about 95 per cent of the thiocyanate is obtained.

Acknowledgment

The authors wish to thank L. J. Curtman for suggesting this topic for investigation, as well as for his valuable advice throughout the work.

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Automatic Cooling Device for Thyatron-Controlled Thermostats

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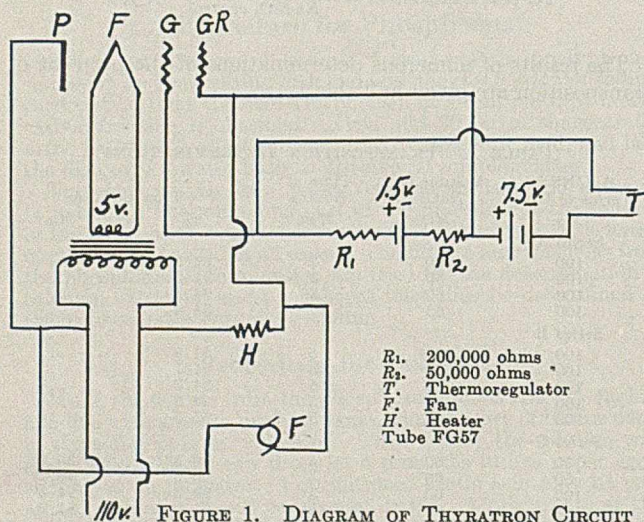


FIGURE 1. DIAGRAM OF THYATRON CIRCUIT

THE thyatron control unit, which is often used to replace the relay control unit for thermostats, is adaptable for automatic cooling as well as heating by the principle employed in a relay circuit described in an earlier paper (1).

The terminals of the fan circuit are connected in the heater circuit in such a manner that the fan and heater form a parallel circuit with the thyatron and heater. When the current is flowing through the tube the fan is shunted out of the circuit because of the high resistance of the fan motor. When no current is flowing through the tube the current will flow through the fan-heater circuit, causing the fan to run and giving only a very small dissipation of energy from the heater.

Figure 1 shows the conventional thyatron circuit with this adaptation.

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Preparing Samples of Canned Dog Food for Proximate Chemical Analysis

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DURING the course of routine chemical analysis of commercial canned dog foods, difficulty was encountered in obtaining representative samples of the food for proximate chemical analysis. Since there is no official method for the analysis of canned dog foods, an attempt was made to apply to these foods the official method of the Association of Official Agricultural Chemists (1) for the analysis of canned meat products. This was found to be impossible, however, since the official method of sampling canned meats calls for initial grinding of the contents of the can in a food chopper. Pieces of intestine, green bone, and cartilage which are present in many dog foods will not pass through a food chopper or will pass through unground; furthermore, separated layers of oil in the cans are lost in the grinding process or are not thoroughly incorporated into the bulk of the food. If a small sample of the food prepared in this manner is used for analysis, a serious error due to inaccurate sampling may result. It is obvious, therefore, that the existing official methods of analysis of the A. O. A. C. cannot be applied to canned dog foods, and that a new method must be devised.

If the food is dried first, no difficulty is encountered in grinding and the material may be thoroughly mixed so that small samples may be used for analysis. The salient features of the method proposed in this paper are the initial, thorough mixing of the fresh food, the use of large samples for the determination of moisture, and the subsequent use of these dried samples for the determination of ash, ether extract, crude protein, and crude fiber. Results of moisture determinations made by the method herein described and of other proximate analyses made on the composite samples are presented to show the duplicability of results.

Procedure

The contents of four cans of the dog food to be analyzed were emptied into the bowl of a small Hobart mixer by cleanly cutting the lid off the can, punching a hole in the bottom, and shaking the contents out in one piece. The cans were inverted and the separated oil was allowed to drain into the bowl. Any fat or oil adhering to the sides of the can was wiped out with a piece of the solid food on the end of a spatula. The food was beaten in the mixer at slow speed of the wire beater until the mass was broken up, and then at high speed for 2 minutes. The material adhering

to the sides of the bowl was pushed to the bottom with a spatula and the beater was again run at high speed for 2 minutes. The oil was thus emulsified and the larger particles were evenly distributed throughout the mass.

Three samples of this material (approximately 100 grams each) were spread evenly in thin layers on the bottom of previously tared flat-bottomed evaporating dishes 139 mm. in diameter and 32 mm. deep. The weight was determined as rapidly as possible on a heavy-duty laboratory balance with a sensitivity of 10 mg. The samples were dried at $102^{\circ} \pm 0.5^{\circ} \text{C.}$ in an electric air oven to constant weight (12 to 24 hours); allowed to cool in a desiccator, and rapidly weighed, and the percentage of moisture was calculated from these weights. The samples were combined, ground to pass through a 40-mesh sieve, thoroughly mixed, and dried at 102°C. for 3 hours to remove the moisture taken up from the air during the grinding. The material was cooled in a desiccator and stored in tightly stoppered bottles. All subsequent proximate analyses were made on these composite samples.

In some dog foods, the presence of large amounts of fat prevented the passage of the material through the sieve, no matter how finely it was ground. Thus it was difficult to ascertain whether or not the sample was finely enough ground to be used for crude-fiber and ether-extract determinations. In this case a small portion of the ground food was extracted with ether and sifted; if it still did not pass through the 40-mesh sieve, the original sample was reground as finely as possible.

The results of moisture determinations made on 23 brands of commercial canned dog food by this method are given in Table I, as well as results of other proximate analyses made on the composite samples by the official methods of the A. O. A. C. (1).

Discussion

The homogeneity of the samples of canned dog food prepared by this method is demonstrated by the excellent agreement between samples in Table I. These analyses, with the exception of the moisture determinations, were made on the composite dry sample and the percentage composition was calculated on the fresh basis from the average moisture content of the three individual samples.

Since canned dog food, when spread in thin layers, dries to a very porous mass, the residual moisture content may be con-

TABLE I. ANALYSIS OF COMMERCIAL CANNED DOG FOODS

Brand Number	Moisture			Ash		Crude Protein		Crude Fat		Crude Fiber	
	Sample 1 %	Sample 2 %	Sample 3 %	Sample 1 %	Sample 2 %	Sample 1 %	Sample 2 %	Sample 1 %	Sample 2 %	Sample 1 %	Sample 2 %
1	46.27	46.30	46.43	1.70	1.70	13.82	13.98	25.39	25.42	0.85	0.86
2	66.25	66.37	66.42	4.20	4.20	13.41	13.46	3.86	3.87	1.31	1.38
3	68.07	68.20	68.28	3.83	3.83	8.45	8.51	4.49	4.66	0.84	0.87
4	69.88	69.89	69.93	5.15	5.15	9.61	9.65	3.51	3.53	0.77	0.79
5	70.04	70.30	70.30	4.79	4.80	8.85	8.93	1.66	1.68	1.12	1.13
6	70.06	70.20	70.48	2.80	2.82	11.31	11.39	4.76	4.87	0.68	0.71
7	70.50	70.20	70.57	2.79	2.81	10.18	10.19	2.74	2.74	0.84	0.86
8	71.10	71.28	71.79	2.22	2.27	9.11	9.13	4.83	4.84	0.67	0.68
9	71.15	71.18	71.22	3.77	3.82	7.31	7.41	2.28	2.32	1.33	1.38
10	71.33	71.46	71.48	1.40	1.42	10.40	10.44	6.12	6.13	1.62	1.65
11	71.56	71.57	71.67	1.76	1.77	12.16	12.28	3.68	3.68	0.79	0.80
12	71.84	71.91	71.91	0.85	0.85	8.36	8.42	3.24	3.24	0.51	0.54
13	72.48	72.52	72.88	1.09	1.11	11.41	11.48	3.79	3.79	0.88	0.88
14	73.04	73.22	73.48	2.48	2.49	10.77	10.79	3.34	3.48	0.77	0.84
15	73.26	73.45	73.73	2.78	2.81	7.09	7.19	2.00	2.07	0.84	0.88
16	73.88	73.89	74.02	3.31	3.31	10.70	10.73	2.40	2.40	0.93	0.94
17	74.81	75.06	75.21	2.65	2.66	6.20	6.24	1.85	1.85	0.88	0.88
18	75.71	75.72	75.86	3.21	3.21	9.16	9.18	2.15	2.15	0.78	0.80
19	76.39	76.66	76.71	1.80	1.80	9.44	9.47	0.45	0.46	1.19	1.24
20	76.30	76.81	76.86	2.26	2.27	5.61	5.65	1.24	1.25	0.98	0.99
21	76.95	76.99	77.18	0.90	0.91	6.56	6.94	0.80	0.81	2.12	2.24
22	77.46	77.53	77.57	0.96	0.96	7.30	7.48	1.55	1.56	1.10	1.19
23	79.48	79.49	79.69	1.35	1.36	4.65	4.67	0.80	0.82	0.84	0.85

sidered negligible in a substance containing 70 to 80 per cent moisture. Even though the fresh material is thoroughly mixed, a large sample should be used for the moisture determination in order to obtain a representative share of the larger particles. After this material has been dried, ground, and thoroughly mixed, it is homogeneous and small samples can be used safely for other analyses.

Ether-extract determinations were made on samples stored in tightly stoppered bottles at room temperature for 12 weeks. No appreciable difference was noted between these values and those obtained from the freshly prepared samples. As the other constituents may be considered stable, it appears that these samples may be stored for at least 12 weeks without appreciable change in the values obtained by proximate chemical analyses. These samples, however, are extremely hygroscopic and should not be unduly exposed to the air.

The Dog Food Division of the Institute of American Meat Packers (2) has recommended a method for the preparation of samples and determination of moisture content of canned dog food in which the food is first dried sufficiently to permit grinding and the moisture content is calculated. The food is then ground, mixed, and subsampled to determine the residual

moisture content. This method is open to the criticism that dog foods which have been dried sufficiently to grind easily are often hygroscopic enough to take up considerable amounts of moisture from the air during the grinding, rendering the subsampling inaccurate. Thus the accuracy of the method is dependent upon the humidity of the air and the moisture content of the food during the grinding process. In the method proposed in this paper, this possible source of error is eliminated by determining total moisture before the food is ground.

The use of the composite dry sample, obtained from the moisture determination for the other proximate analyses, eliminates to a great extent the errors which usually accumulate in the value obtained for nitrogen-free extract.

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RECEIVED February 2, 1938.

Syringe Attachment for Accurate Volumetric Work

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BY PROVIDING suitable stops for measuring linear displacement, the hypodermic syringe is capable of exceptional accuracy in volumetric measurement, thus replacing the volumetric pipet, as has been shown by Krogh and Keys (1, 2).

A modified arrangement as shown in Figure 1 has the ad-

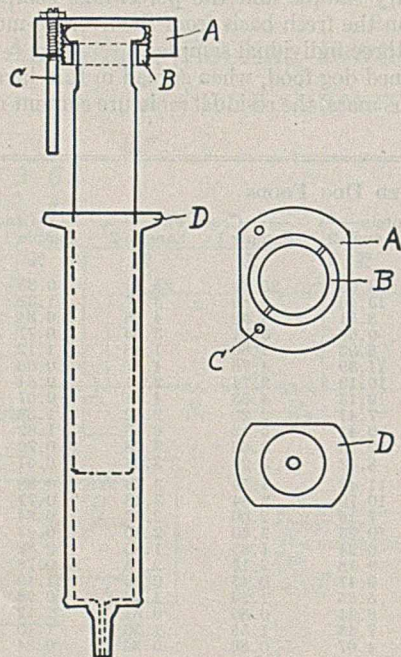


FIGURE 1

vantage of readily eliminating any air bubbles produced during filling and is also more convenient to handle in use. It is simple in construction and may be attached to the ordinary syringe. The shape of the flange, *D*, at the top of the ordinary syringe makes it very convenient to use as a stop.

The adjustable rod, *C* (Figure 1), is threaded into a metal cap, *A*, which fits over the end of the plunger and is held in position after calibration by a lock nut. The top of the plunger and the top flange of the syringe should be ground on a flat glass plate with fine silicon carbide before assembly. Naturally this grinding should be as nearly at right angles to the axis of the syringe as possible. The cap, *A*, is held on the plunger by a threaded collar, *B*, and a suitable washer of fiber or soft metal.

In use the syringe is slowly filled until by a slight rotation the end of the rod may slip over the projecting flange. The excess liquid is then discharged. The exact volume is then ready for discharge and by a slight reverse rotation the rod slips over the side of the flange.

The syringe is excellently adapted to blood chemical analyses, where the exact volume of blood may be measured at the time of taking the sample and added directly to the tungstic acid or other precipitating fluid. In drawing blood it is almost impossible to avoid the formation of some gas bubbles or foam. By taking slightly more than the desired sample, and then inverting the syringe, the bubbles together with the excess sample can be discharged into absorbent cotton.

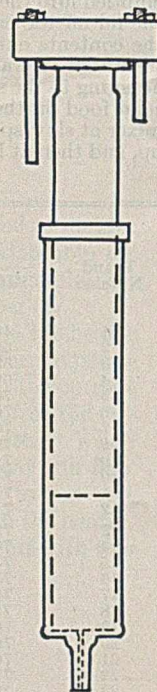


FIGURE 2

A cleaner delivery results from using a needle with the syringe, and because of the small size droplets produced accuracy is more readily obtained. A 16- or 18-gage needle gives drops small enough for ordinary work where 5-cc. samples or larger are used.

Calibration is readily made with distilled water by weighing the discharged sample and adjusting the threaded rod which may then be locked in position by the locking nut.

By providing two rods of different lengths as shown in Figure 2, the syringe may be made to deliver three different volumes, one for each rod and one for their difference in length—for example, with rods for 2 and 5 cc., a 3-cc. volume may be obtained by going from the 5-cc. position to the 2-cc. position.

Such a syringe appears to have the following advantages over a pipet, many of which have been already listed by Krogh:

1. It is much faster to use, since there is no drainage time.
2. Volatile or poisonous liquids may be handled without danger.
3. Considerably greater accuracy is attainable. Using well-constructed 10-cc. syringes, calibration is readily carried out to 1 mg. or 0.001 cc. of water. For samples smaller than 2 cc., greater accuracy can be obtained by using smaller syringes.
4. Fluids of increased viscosity or poor drainage are measured without increased error.

Literature Cited

- (1) Krogh, A., *IND. ENG. CHEM., Anal. Ed.*, 7, 130 (1935).
- (2) Krogh and Keys, *J. Chem. Soc.*, 1931, 2436.

RECEIVED January 31, 1938.

Apparatus for Evaporating Solutions on Electrodes

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SOME methods of quantitative spectrographic analysis involve the evaporation of definite amounts of solutions directly on electrodes. Need for an apparatus by means of which several evaporations could be carried out simultaneously and conveniently by one operator developed in the author's laboratory when a number of samples of drinking waters were to be analyzed spectrographically for fluorine. The apparatus, which was built for that purpose and is described below, is useful also in other work involving the analysis of solutions by spectrographic means.

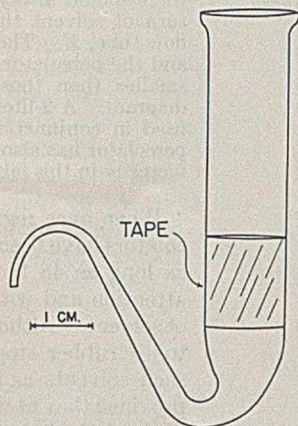


FIGURE 1. GOOSENECK PIPET

Figure 1 shows the gooseneck form of the pipets, made from 12-mm. glass tubing, that are used in the apparatus. Each pipet will hold at least 2 cc. of solution without leaking from the tip. However, the solution can be forced out at the tip by placing a finger over the large end of the pipet and pressing down. The slight piston action of the finger in the pipet then forces the solution out. A strip of adhesive tape around the body of each pipet keeps them from slipping when placed in a wooden clamp.

The arrangement of the pipets, electrodes, and other parts of the evaporator is shown in Figure 2, where twenty electrodes and a unit of twenty pipets are mounted in position for the evaporation of solutions. Twenty other pipets removed from the apparatus show more clearly the arrangement of the parts. The electrodes fit in holes in the copper bar, A, and setscrews hold the

electrodes firmly in place. A piece of heavy copper sheet, B, bent to form a flat-bottomed trough that is open at the two ends, is fastened in an inverted position on the bottom of the copper bar. The bar is about 2.8 cm. (1.125 inches) square by 37.5 cm. (15 inches) in length.

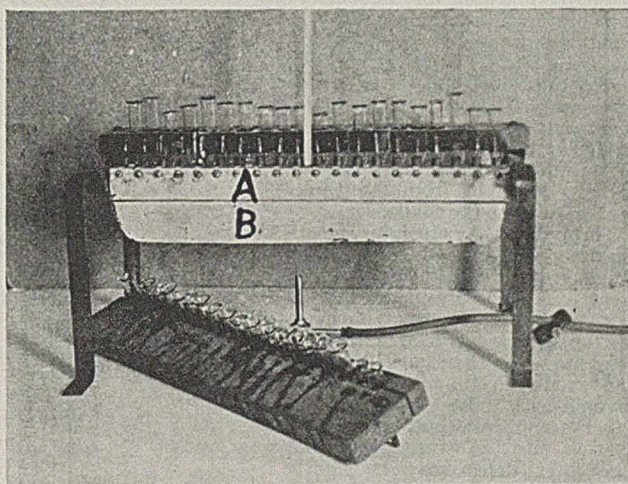


FIGURE 2. EVAPORATOR

In using the apparatus, the electrodes and pipets are put in place, then measured representative portions of the solutions to be analyzed are introduced into the gooseneck pipets. The bar is then brought to the proper temperature by regulation of the microburner, and the solutions are forced dropwise from the pipets and onto the electrodes where the evaporations take place. At the finish of the process, about 2 drops of pure solvent are placed in each pipet in order to transfer the last part of each solution to its electrode.

The rate of evaporation depends principally on the bar temperature, which is usually maintained high enough for rapid evaporation without boiling or spattering of the solutions from the electrodes.

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An Automatic Continuous Percolator

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DURING the course of investigations of a number of plant materials, it was found necessary to percolate the ground plants thoroughly with a solvent such as ether or petroleum ether. Large Soxhlet extractors are rather expensive and often do not work so efficiently or smoothly as the small ones. When nearly complete extraction is desired, the usual process of percolation is laborious and time-consuming. To overcome these difficulties, an automatic percolator was constructed which is simple, compact, inexpensive, and efficient, and, when once regulated, will operate for long periods without requiring attention and with very little loss of solvent.

The apparatus is illustrated in the diagram.

The percolator, *A*, which holds the material to be extracted, was made by cracking off the bottom of a bottle of appropriate size and grinding down the sharp edge on a flat glass plate with a little silicon carbide powder and water. The condenser, *B*, is an efficient and compact distilling condenser. Tube *D* should be 10 mm. or more wide to permit the unobstructed passage of solvent vapor from the three-neck flask, *C*, to the condenser.

To operate the percolator the apparatus is assembled as shown in the diagram, a small piece of cotton being packed loosely in the bottom of the percolator so that it covers the top of tube *F*. The material to be extracted is then packed loosely and evenly in the percolator and covered with a few sheets of filter paper to prevent particles from floating into the overflow tube, *E*. The filter paper may be lightly weighted down if necessary. Solvent is poured into the percolator so that it percolates through the material to be extracted and does not run into the flask through the overflow tube. Enough solvent should be poured through the material so that the three-neck flask is about half full. The percolate runs down into the flask through tube *F*, which

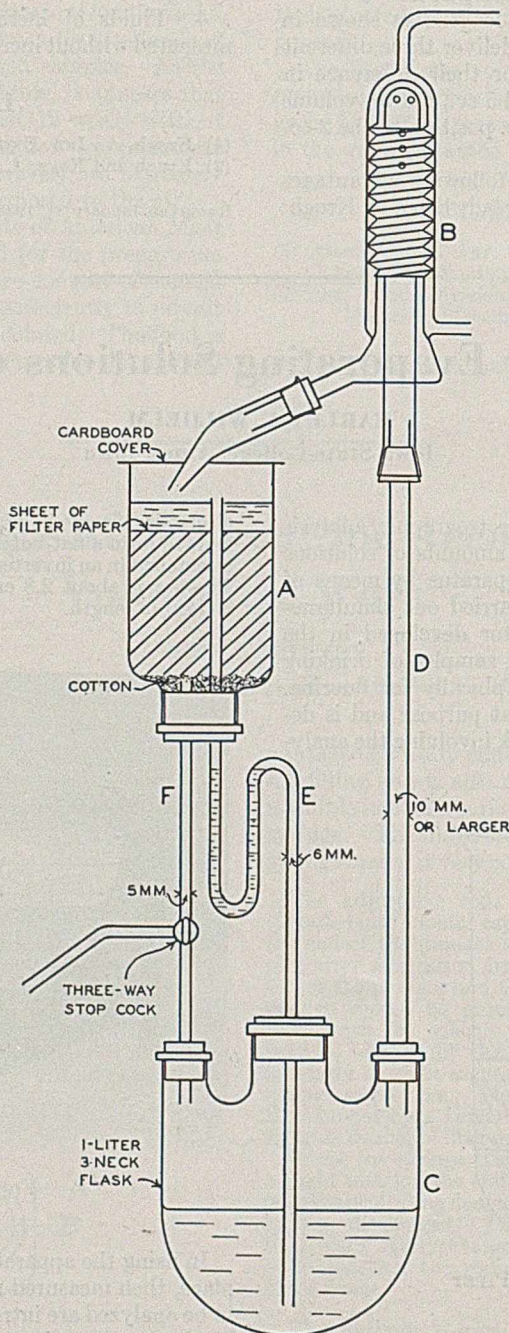
contains a stopcock and a side arm through which the percolate may be sampled at any stage of the percolation. The rate of percolation is also controlled by adjusting this stopcock. The three-neck flask is heated on a steam bath (when using ether or petroleum ether). The solvent vapors ascend tube *D* and are condensed in the condenser, and the fresh solvent distills into the top of the percolator through the adapter, which is inserted through a hole in the cardboard cover of the percolator. The bottom of the adapter should be kept above the level of liquid in the percolator.

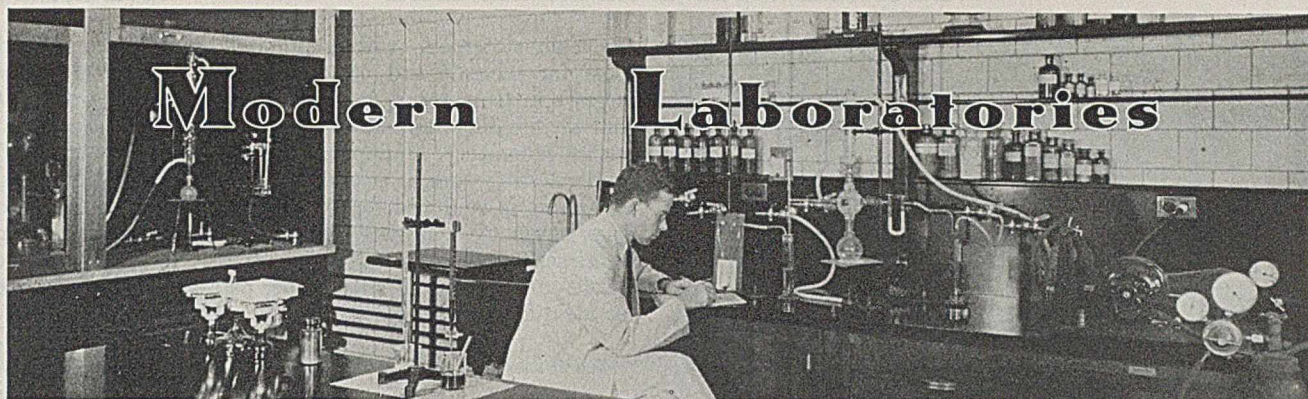
In warm weather it has been found advantageous to use a compact vertical worm condenser in conjunction with the recovery condenser, *B*, in place of the adapter shown in the diagram. If the solvent distills into the percolator faster than it percolates through tube *F* into the flask, the excess will overflow into tube *E* and be returned to the flask. A small, very loose plug of cotton may be placed at the top of tube *E* to filter the returning solvent free from floating particles, but care should be taken not to obstruct the overflow of solvent.

The rate of distillation and the rate of percolation are regulated so that the solvent distills into the percolator slightly faster than the liquid runs into the flask from tube *F*; there should always be a slight return of solvent through the overflow tube, *E*. The three-neck flask and the percolator may be larger or smaller than those shown in the diagram. A 2-liter three-neck flask used in conjunction with a 3-liter percolator has also been used satisfactorily in this laboratory.

When once regulated, the percolators have been in operation for as long as 48 hours without any attention and with very little loss of solvent. Although it is possible to use rubber stoppers even with such solvents as petroleum ether, provided they fit well into the neck of the flask, it is desirable to use special stoppers that do not swell so much.

RECEIVED April 26, 1938.





New Research Laboratory, Columbia Chemical Division of the Pittsburgh Plate Glass Company

THE continued expansion of the research activities of the Columbia Chemical Division of the Pittsburgh Plate Glass Co. made imperative an increase in space and facilities. Therefore, an addition to the laboratory, considerably larger than the original building, was erected.

The older building consisted of three floors, one floor being below the surface of the ground at the front but above ground at the rear because of the sloping surface. Four floors were desired in the new building, and in order to preserve the architectural integrity of the combined building it was necessary to place one of the new floors partially below ground. Viewed from the street, therefore, the building appears to consist of two stories. The construction is of brick, colonial in effect with its limestone trim. The reinforced concrete floors are carried on steel I-beams. All glazing is plate glass.

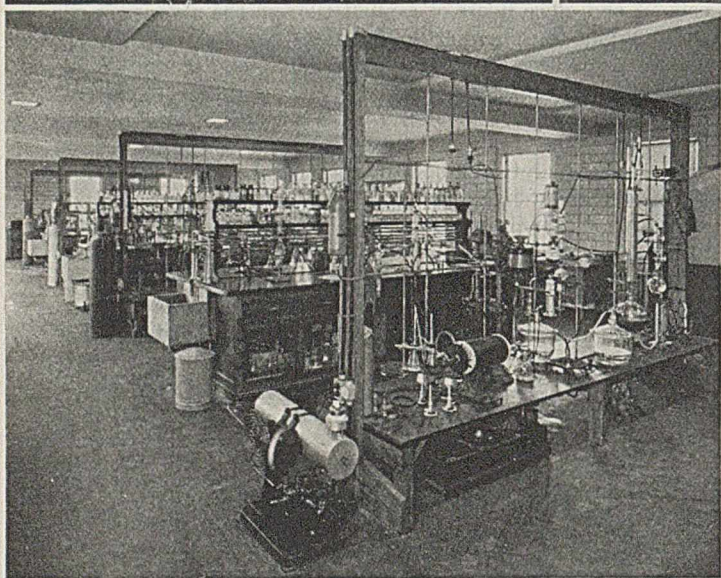
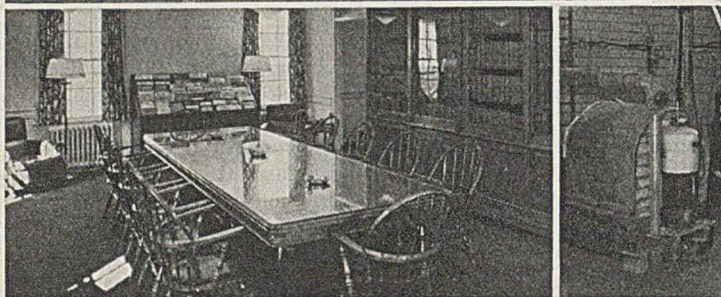
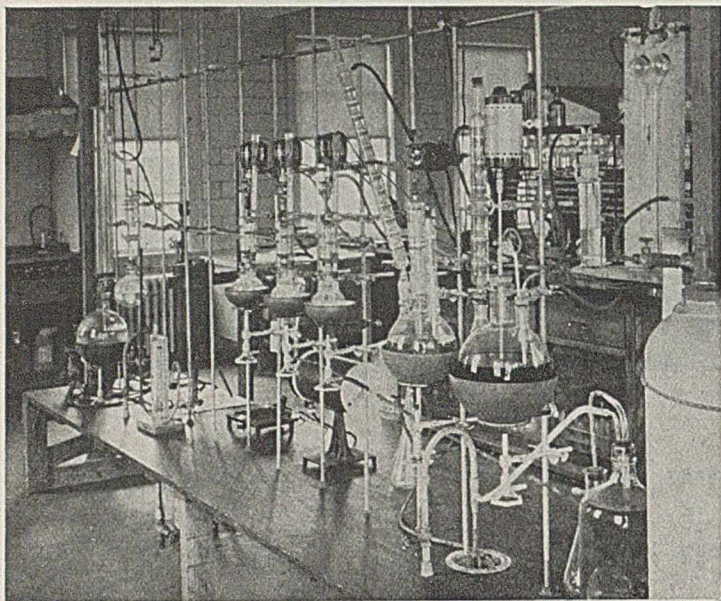
The main entrance leads to a foyer on the second floor partitioned in Lumite glass block. Besides clerical offices, this floor has the research director's office, the library, a smaller laboratory, and the analytical laboratory. The library and the research director's office have ceilings covered with acoustic tile to diminish extraneous sound. The floor above, divided into two large rooms, houses the inorganic and physical section, the organic section, and a smaller room for the microanalytical laboratory. The large rooms have a series of alternating laboratory tables and equipment racks.

The laboratory tables are divided along the center by a waste trough, shelving, and service lines, and have Alberene stone sinks at each end. Table tops are of treated birch. Services at each table include hot and cold water, 90-pound compressed air, 110-volt alternating current, and 220-volt direct current. Except for the lead fittings at each desk, all waste lines are of Duriron for corrosion resistance. The equipment racks are provided with a stainless-steel rod system and steam lines in addition to the other services. In the new building the laboratory floors are of resilient mastic cement and office floors of asphalt tile; in the older part of the building the floors are of painted concrete with rubber mats, backed with sponge rubber in much-used places. The new building has matt-glazed ivory tile as the wall surface. Luminaries are recessed flush with the ceiling and utilize 300-watt lamps.

The microanalytical laboratory is separated from the main laboratory room by glass partitions, so that the required standards of dustlessness can be maintained. Air coming in from the outside is heated by a thermostatically controlled radiator unit and filtered through glass wool before entering the laboratory. The laboratory is of the standard Pregl type, utilizing a Kuhlmann balance and equipped for the usual microchemical determinations. The balance is mounted on a rubber ball suspension¹ which has proved very satis-

¹ Kirner, *IND. ENG. CHEM., Anal. Ed.*, 9, 300 (1937)





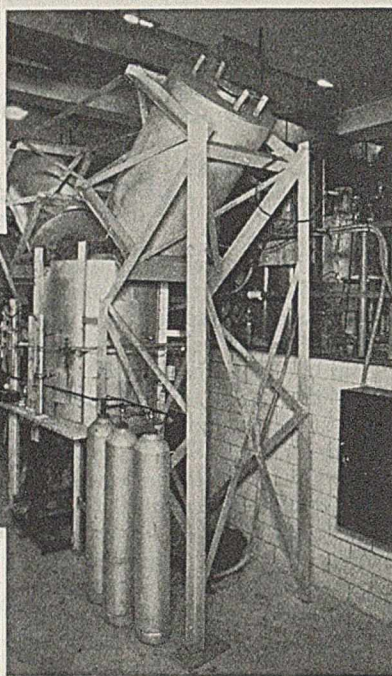
factory. When excavations were being made for the newer building, a retaining wall, an integral part of the older building, was battered down by a 4-ton steel ball swung by a steam shovel with concussions that made the whole building tremble. It was possible, however, to carry on the micro-weighings with no noticeable aberration while the pounding was going on.

The first floor, also equipped with racks and laboratory desks, is reserved for industrial projects requiring the handling of materials on a slightly larger scale. This floor holds

the main storeroom, with a fireproof, specially ventilated room for solvents and other inflammable material. Any increase in temperature in this room actuates controls that shut the fire door and release carbon dioxide. The technical service laboratory, equipped for rubber compounding and similar testing work, is also located here. A physical testing laboratory is equipped for pH determination (colorimetric, glass, antimony, and hydrogen electrodes) and identification by refractive index (Abbe refractometer). Other items include a light- and dark-field microscope, petrographic microscope for identification work, and photomicrographic and photo-

graphic equipment. A tool room on this floor contains a lathe, drill press, work bench, and glass-blowing table.

The basement, extending only under the newer section of the building, is devoted to pilot-plant work. Part of it has a ceiling height of 15 feet, as compared with 9 feet for the rest of the building, to accommodate larger pieces of equipment. This floor is equipped with a high-pressure (25-pound) gas line for furnacing operations, 440-volt alternating current, and 140-pound steam.



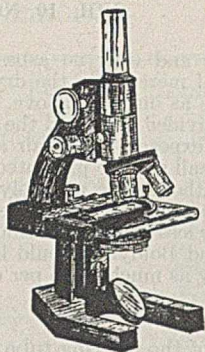
The attic of the building is used for storage purposes, but the building is so constructed that the roof may be raised and another floor added when expansion is indicated.

All floors are connected by an elevator, and much of the equipment is mounted on wheels so that it may be taken to any part of the building via the elevator without any trouble. A large centrifuge and a motor-generator set providing low-voltage high-amperage current for electrolytic work are included in the equipment of this type.

Much special equipment, such as high-pressure autoclaves and bombs designed in this laboratory, is in use.

Ventilation throughout the building is accomplished mostly through the hoods, which are of the open-face type. Fifteen to twenty air changes of the entire building an hour are exhausted through the hoods and auxiliary louvres by blowers in the attic operating through a Durimet duct system. Fresh air enters the building through louvres in the outside wall, and is passed through finned-tube heating units before entering the building.

Full use of many of the modern forms of glass are made throughout the laboratory, including, besides the uses mentioned, such things as tempered glass for special hoods and safety laminated glass shields, bound with metal edges, for surrounding hazardous operations. These shields, easily supported by laboratory clamps, are also used for the walls of thermostats housing potentially hazardous experiments.



Microchemistry

Ethanolamine in the Determination of Mercury

In Inorganic and Organic Compounds and Pharmaceutical Preparations

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BECAUSE of the increasing use of mercury compounds in medicine and other fields, the determination of mercury in its organic and inorganic salts and its organometallic compounds is becoming more and more important.

Many methods for the determination of mercury in organic compounds are recorded in the literature. In several procedures the organic compound is heated with lime or sodium carbonate and the liberated mercury is distilled onto gold foil or wire or into a gold cup, so that it may be weighed as an amalgam. Some procedures have been adapted to work on a micro scale. Other methods employ oxidative decomposition in sealed or open vessels, using such agents as nitric acid, bromine water, permanganate, dichromate, persulfates, iodine, etc. After the mercury has been converted to the ionic form it may be handled by any of the well-known methods for determining ionic mercury. Some organic compounds when treated with sodium and alcohol give up their mercury as metallic mercury, which may be estimated in various ways. In the case of some organic compounds direct electrolytic determination of the mercury is possible.

During the development of the use of monoethanolamine for the determination of halogens in organic compounds (2, 3) the observation of Meltsner, Wohlberg, and Kleiner (1) that the amine would reduce mercury salts in aqueous solution suggested its use in the quantitative determination of mercury. It has been found possible to determine mercury quickly and accurately in inorganic salts, oxides, organic salts, organic mercuric halides and nitrates, Mercurochrome, pharmaceutical ointments and tablets containing mercury compounds, and some compounds of the type R_2Hg , by the use of monoethanolamine. In some compounds containing halogen as well as mercury, the two may be determined simultaneously.

The general procedure adopted for salts, oxides, Mercurochrome, and pharmaceuticals containing such compounds consists of simply heating the solid sample with the amine for 5 minutes, whereupon the mercury is reduced to the metallic state and appears as a single globule below the liquid amine. The excess amine is quickly removed by filtration, and the globule is washed with water, transferred to a halogen filtration microtube, and weighed as such after a simple drying procedure. Alternatively, the globule of mercury is dissolved in nitric acid and titrated by means of thiocyanate.

Compounds which do not respond to the above treatment in a reasonable length of time may be handled by exactly the same method as that used for halogens (2). This procedure involves the use of monoethanolamine, sodium, and dioxane.

In some cases the substitution of diethanolamine for monoethanolamine enables the mercury to be determined without using the general halogen procedure. The apparatus has been kept very simple and inexpensive, and the procedure is simple and rapid.

Both procedures have been used successfully on micro, semimicro, and macro scales. Samples of pure compounds varying from about 3 to 370 mg. have been handled with practically no variation in technic or apparatus.

The inorganic compounds used were the best analytical grade obtainable and were dried by a suitable procedure. The organic salts were prepared from the corresponding sodium salts and were recrystallized several times from a suitable solvent. The organometallic compounds were purchased and further purified. Pharmaceutical preparations were used as purchased from drugstores.

Materials

The monoethanolamine, $NH_2-CH_2-CH_2OH$, used for the reduction of the sample was commercial material which was distilled in an all-glass outfit at atmospheric pressure. The diethanolamine, $NH(CH_2-CH_2OH)_2$, occasionally employed was commercial material distilled at reduced pressure in an all-glass outfit. The dioxane used as a solvent for removing the base of pharmaceutical ointments was commercial material. The dioxane used with monoethanolamine and sodium for liberating mercury bound directly to carbon was made halogen-free when halogen was to be determined in the organic compound simultaneously. For this purpose it was refluxed with monoethanolamine and sodium and then distilled (2). Acetone employed for washing and drying was dried over calcium chloride and distilled. The sodium was halogen-free.

Apparatus

For the reduction of the sample a 25×200 mm. Pyrex test tube may be used with entire success. A test tube of the same dimensions but with a pear-shaped bulb at the bottom is somewhat more convenient, as the mercury globule will lie in the narrow part of the pear and thus enable the washing and filtration to be carried out more easily. A simple cold-finger reflux condenser serves to prevent loss of amine. The apparatus is thus essentially the same as that employed by the author for determining halogens on a micro scale (2). For filtration the usual Pregl micro halogen arrangement is used.

Method of Weighing Samples

The samples are weighed in small open weighing bottles made by cutting down specimen vials 8 to 10 mm. in diameter and polishing the cut ends. The weighing bottles are most conveniently handled by means of a pair of metal forceps, the prongs of which are bent to fit the cylindrical bottle. Solid samples are introduced into the bottles by means of a small spatula.

TABLE I. CONSECUTIVE WEIGHTS OF FILTER TUBES OBTAINED BY THE DRYING PROCEDURE

	<i>Mg.</i>		<i>Mg.</i>
	Macrobalance ^a		
1	5975.85	5	5975.80
2	5975.85	6	5975.90
3	5975.85	7	5875.80
4	5975.85	8	5875.85
	Microchemical Balance ^b		
1	5356.891	
2	5356.895	
3	5356.906	
4	5356.893	

^a 5-minute aspiration, 10-minute standing at balance.
^b 10-minute aspiration, 15-minute standing at balance.

Standardization of Volumetric Solutions

For standardizing the 0.02 *N* and 0.05 *N* thiocyanate solutions used for volumetrically determining the mercury in some samples, the best grade of calomel was used. A weighed sample of calomel was reduced to metallic mercury by means of monoethanolamine. The mercury was dissolved and titrated with the solution to be standardized.

All the details for the reduction and titration are given below. This method of standardization was adopted after the success of the reduction procedure had been established. As a further check on the standardization procedure, the mercury from the sample of calomel was determined gravimetrically as described below before it was dissolved for titration.

Method I

SALTS, OXIDES, AND MERCUROCHROME. Slip the weighing bottle containing the sample into the digestion tube, add 3 to 5 ml. of monoethanolamine, and attach the cold finger. Suspend the digestion tube loosely from a clamp and gently boil the amine with a microburner for at least 5 minutes. In some cases colloidal mercury begins to appear as soon as the amine strikes the salt. At the boiling temperature the colloidal mercury quickly disappears and the reduction is probably complete in a very short time, but at least 5 minutes' boiling should be allowed. The mercury appears as a single globule at the bottom of the test tube or at the narrow part of the pear. Cool the tube and contents rapidly to below 100° C. by lowering the tube into a beaker of cold water, and wash down the condenser with water. After removing the condenser, add more water to bring the total volume to 15 or 20 ml. to reduce the viscosity of the amine. In some cases, but not usually, an insoluble material may appear on dilution.

When only mercury is to be determined, remove the liquid from the tube by the use of the filtration arrangement designed by Pregl for the determination of halogens, but employ a blank tube without any filtering medium. This reduces the filtration time to a matter of seconds. Correct placing of the lower end of the siphon tube facilitates removing the liquid without disturbing the mercury. Wash the globule several times with small amounts of water and suck this over as above. In each case all but a fraction of a milliliter of the wash liquid may be easily removed.

Finally bring the globule over to the prepared micro halogen filter tube by lowering the siphon over the globule and gently applying suction. If the globule breaks into several smaller globules as it falls on the mat of the filter tube, assemble these by gently tapping the tube so that the particles roll around and come into contact with each other. Wash the globule several times with water and finally several times with dry acetone. Remove the filtering tube from the suction flask and thoroughly wipe it with moist flannel. Then place it in the filtering arrangement with a perfectly dry suction flask, attach a cotton filter tube, and aspire a gentle current of air through the tube for 5 minutes. Finally place the tube near the balance and weigh it after 10 minutes. For microwork 10-minute aspiration and 15-minute standing are advisable. The filter tubes are of the type used for handling the silver halides, and have coarse sintered-glass disks and thick asbestos mats. The mats should be firmly pressed with the blunt end of a glass rod to make the upper surface as hard as possible. The tubes are prepared for use by washing with water and dry acetone and drying as indicated above.

Some years ago Willard and Boldyreff (4) tried a somewhat similar method of handling metallic mercury, but used macro-

Gooch crucibles with sintered bottoms and with no asbestos. They claimed a loss of about 1.3 mg. of mercury in the drying process, which was essentially the same as outlined above. In their case the mercury was in a finely divided form and the loss was probably due to the large surface exposed to the air as it streamed through the crucible. The small surface presented by the single globule of mercury in the author's case probably accounts for the failure to note such a loss. Fairly good results were obtained on a micro scale, where the loss of any such amount of mercury as mentioned by Willard and Boldyreff would have thrown the percentage of mercury off by as much as 25 per cent in some cases.

The fact that reproducible weights of the filtering tube can be obtained by the described method of washing and drying is demonstrated by Table I. Between the consecutive weighings, the tubes were washed and dried as previously outlined.

The mercury may be determined volumetrically if desired.

Wash the globule of mercury in the digestion tube as directed, dissolve it in a few drops of concentrated nitric acid, and add a few milliliters of water. To ensure the absence of nitrous acid and mercurous mercury, add 5 per cent potassium permanganate solution dropwise until the permanganate color persists for 5 minutes. Destroy the excess permanganate with dilute hydrogen peroxide solution. Before titration with thiocyanate add 1 to 1 nitric acid and ferric alum indicator. The mercury ion may be titrated with 0.02 *N* or 0.05 *N* thiocyanate solution, depending upon the scale of the work. On a micro scale the titration may be carried out in the digestion tube, but on a macro scale it will be necessary to transfer the mercury solution (or globule) to an Erlenmeyer flask for titration. The transfer is most readily accomplished by using the Pregl filtration arrangement. For this purpose place a two-hole rubber stopper in the Erlenmeyer with a blank filter tube and apply suction to the other hole of the stopper. Rinse the digestion tube and siphon well to bring over the last trace of mercury solution.

Other methods of estimating the mercury may be used after it has been obtained in the ionic condition.

Reactive halogen in organic or inorganic mercury compound will be present in ionic form in the filtrate obtained in the first filtering and rinsing step. For determination of the halogen, the filtrate is best caught in a 25 × 200 mm. test tube. On acidifying with nitric acid and adding silver nitrate, the halogen may be determined as directed elsewhere (2).

PHARMACEUTICALS, OINTMENTS, AND TABLETS CONTAINING MERCURY SALTS OR OXIDES. Because of the small mercury content fairly large samples are necessary, and hence larger weighing bottles are used. The only modification of procedure necessary is with the ointments, where the ointment base must be removed after the reduction. To get rid of the ointment base, omit the rinsing of the digestion tube and condenser with water at the end of the digestion period, and filter off the liquefied ointment base and ethanolamine while still hot. Use the same filtering arrangement as in the previous case. Dissolve the last amount of base in hot dioxane or other suitable solvent and remove it by the filtration procedure. Then handle the globule in the usual manner.

With tablets the only new problem is the removal of the filler. No modification of the procedure for salts is necessary, as the filler is easily sucked away from the globule by the rinsing procedure before the globule is transferred to the filter tube.

Table II gives typical results obtained with a variety of compounds and preparations containing mercury.

Method II

ORGANIC COMPOUNDS OTHER THAN SALTS. Most mercury compounds in which mercury is directly attached to a carbon atom cannot in general be reduced to metallic mercury by

TABLE II. DETERMINATION OF MERCURY IN ORGANIC AND INORGANIC COMPOUNDS AND PHARMACEUTICAL PREPARATIONS

Compound	Sample	Method	Mercury Found		Theory %	Compound	Sample	Method	Mercury Found		Theory %	
			Mg.	%					Mg.	%		
Mercurous chloride	10.924	I	9.297	85.11	84.98	Phenylmercuric nitrate	41.61	I-D	24.60	59.12	59.06	
	9.588	I	8.163	85.14	15.02(Cl)		92.00	II	54.35	59.08		
	124.20	I	105.50	84.95			101.40	I-D	60.05	59.22		
	127.75	I	108.55	84.97		Phenylmercuric chloride	11.445	II	7.335	64.09	64.07	
	194.20	I	165.05	84.99			24.74	II	15.90	11.34(Cl)		11.38(Cl)
	368.35	I	312.90	84.95			35.26	I-D	22.62	64.15		
	120.25	I	V ^a	14.96(Cl)			99.05	I-D	63.45	64.06		
131.20	I	V ^a	14.93(Cl)					11.38(Cl)				
Mercuric chloride	112.10	I	82.80	73.82	73.88	Di- <i>p</i> -tolylmercury	35.40	II	18.19	51.38	51.42	
	139.30	I	102.85	73.84	26.12(Cl)		39.32	II	20.20	51.37		
	180.15	I	V	73.91			12.637	II	6.514	51.54		
			26.08(Cl)		139.60		II	71.80	51.43			
					32.72		I-D		51.37			
Mercuric oxide	40.48	I	V	92.67	92.61	Mercurochrome (H. W. D., dried)	156.85	I	41.55	26.49	26.73	
	203.45	I	V	92.68			134.60	I	35.70	26.52		
Mercuric iodide	121.50	I	53.52	44.05	44.14		175.55	I	46.65	26.57		
				55.90(I)	55.86(I)	195.40	I	V	26.56			
	156.50	I	69.10	44.15		Ammoniated mercury ointment, 5% with petrolatum base	752.90	I	28.52	3.79		
			55.83(I)		933.60		I	35.40	3.79			
Mercurous iodide	116.80	I	71.61	61.31	61.25		554.45	I	20.70	3.73		
				38.60(I)	38.75(I)	637.90	I	24.18	3.79			
	136.80	I	83.93	61.35		734.10	I	V	3.79			
Mercuric oxalate	44.50	I	30.93	69.51	69.45	Calomel ointment, 5%	1342.0	I	53.68	4.00		
	180.70	I	125.50	69.45			1023.4	I	41.31	4.03		
				69.45					V ^b	4.02		
Mercuric <i>p</i> -toluate	9.928	I	4.226	42.97	42.62	1131.4	I	V	3.99			
	20.05	I	8.55	42.64		1234.6	I	V	3.99			
	96.00	I	40.90	42.60		Calomel tablets	265.20	I	53.07	20.01		
Mercuric benzoate	3.227	I	1.463	45.34	45.32		291.60	I	58.11	19.93		
	46.23	I	20.95	45.32			161.10	I	31.83	19.76		
	93.55	I	42.43	45.38				V ^b	19.92			
Mercuric phthalate	11.185	I	6.159	55.06	55.01	374.30	I	76.29	20.38			
	50.88	I	28.00	55.03		221.70	I	44.71	20.22			
	108.70	I	59.80	55.01				V ^b	20.25			
Mercuric succinate	35.36	I	22.40	63.35	63.35	389.20	I	78.65	20.21			
	67.10	I	42.50	63.34								
Mercuric cyanide	115.65	I-D	V	79.36	79.41							
	105.40	II	V	79.46								

^a Mercury from sample used for standardization of thiocyanate. ^b Mercury determined volumetrically after first determining it gravimetrically.

monoethanolamine in a reasonable time, if at all. However, a number of types of organic mercury compounds may be handled successfully by using the general procedure as employed for halogens in organic compounds (2). This involves the use of sodium, monoethanolamine, and dioxane in the same type of apparatus as in Method I.

Reflux the sample with 3 to 5 ml. of monoethanolamine and 2 to 3 ml. of dioxane. For microwork add about 0.2 gram of sodium in small pieces from time to time, and for larger samples use correspondingly larger amounts of sodium. The mercury set free by the reduction amalgamates with unreacted sodium and appears at the end of a half-hour, refluxing as a small hard pellet at the bottom of the tube. After the heating period, remove the liquid contents of the tube as usual and thoroughly wash the pellet with water in the tube. Cover it with about 5 ml. of water and boil the water until the amalgam no longer evolves hydrogen, showing that all the sodium has been destroyed. This usually takes about 5 minutes. From this point on the procedure is the same as in Method I.

Halogen may be determined simultaneously as in Method I.

Merely substituting diethanolamine for the monoethanolamine of Method I and refluxing for 30 minutes will give a

quantitative reduction of some organic mercury types. Analyses done in this way are designated as I-D in Table II.

Summary

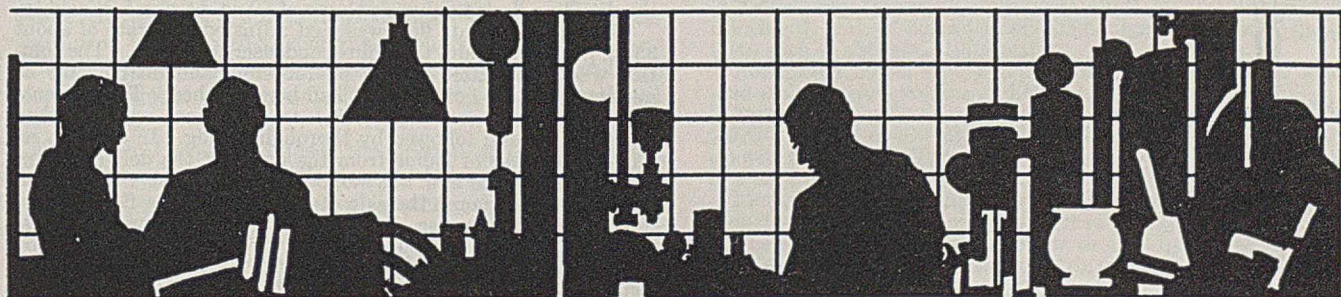
A simple and rapid method for the determination of mercury in inorganic and organic compounds and in pharmaceutical preparations has been developed. The process has been put on both a gravimetric and volumetric basis. The halogens may be determined simultaneously. The method may be used on a qualitative basis for the detection of mercury in inorganic or organic compounds.

The author was unsuccessful in trying to apply either Method I or Method II to a sample of Merthiolate kindly supplied by Eli Lilly and Company.

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Iodometric Microdetermination of Selenate in the Presence of Selenite

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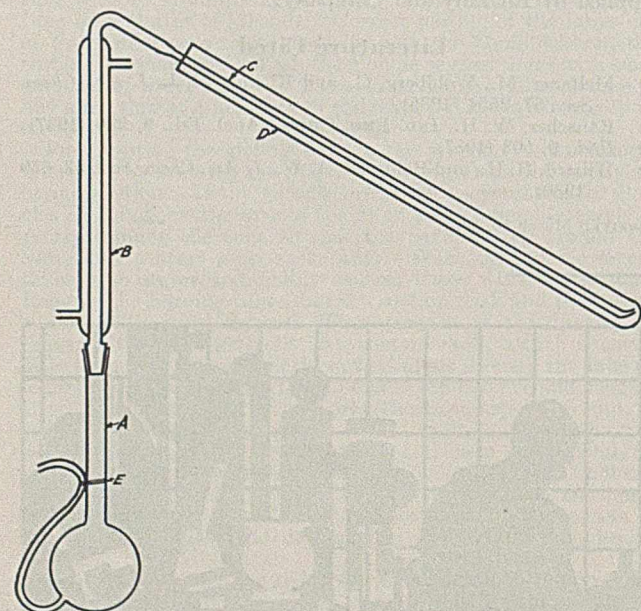
GOOCH and Evans (3) studied the conditions necessary for an iodometric method of determining selenate in the presence of selenite, based on the reaction $H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + Cl_2 + H_2O$, which takes place when the mixture is distilled. The chlorine evolved is absorbed in potassium iodide solution, and the liberated iodine is titrated with standard thiosulfate solution. Moser and Prinz (5), in an extensive investigation of several methods for the determination of selenium, showed that reliable results can be obtained by Gooch and Evans' procedure. In analyzing mixtures containing only a few milligrams of selenate radical in the presence of about 0.10 gram of selenite radical, the authors were not able to obtain satisfactory results by the procedure of Gooch and Evans. The experimental details of a satisfactory procedure, modified to include the use of a reflux condenser in the distilling operation, are described below. Dolique (1), who used such a modification in analyzing 0.20-gram selenate samples, states that the method is accurate to about 0.5 per cent.

Experimental

The distilling apparatus used in this work is shown in the diagram.

The distilling flask was a 125-cc. round-bottomed flask to which a ground-glass joint of 12-mm. bore was sealed at *A*. A side tube was sealed into the bottom, as shown, to provide a convenient way of passing carbon dioxide through the apparatus. In order to prevent accidental breakage of the seal, the side tube was fastened securely at *E* with a few turns of wire. The reflux condenser tube in *B* was of 7-mm. bore and 22 cm. long, and the delivery tube, *C*, of 4-mm. bore and 50 cm. long. A tube, *D*, 17 mm. by 45 cm., was used as a container for the potassium iodide solution used to absorb the chlorine. A film of concentrated sulfuric acid served to seal the ground-glass joint. An ebullition tube 1-mm. bore was used to promote quiet boiling.

A selenic acid solution used as the selenate standard was prepared by the method described by Thomsen (6). Por-



tions of this solution when treated with hydrochloric acid and saturated with sulfur dioxide showed negative results for selenous acid. The selenate radical concentration was determined gravimetrically by reducing to free selenium with sulfurous acid according to the method of Gutbier, Metzner, and Lohmann (4). About 50 grams of sample solution were used in order to yield about 0.075 gram of selenium. The selenium obtained was weighed with a semimicrobalance, using certified weights. Duplicate analyses agreed within 0.2 per cent. In all the work given in this paper, the selenate samples were measured with a weight buret.

TABLE I. DETERMINATION OF SELENATE

Selenate Used Mg.	Selenate Found Mg.	Error	
		Mg.	%
81.78	81.74	-0.04	-0.05
76.02	76.02	±0.00	±0.00
18.62	18.60	-0.02	-0.1
18.24	18.20	-0.04	-0.2
8.24	8.27	+0.03	+0.4
2.03 ^a	2.02	-0.01	-0.5
1.69	1.68	-0.01	-0.6
1.06	1.07	+0.01	+0.9
1.05 ^b	1.04	-0.01	-0.9
1.03 ^b	1.05	+0.02	+1.9
0.51	0.50	-0.01	-2
0.37 ^c	0.36	-0.01	-3
0.27 ^a	0.26	-0.01	-4
0.27	0.28	+0.01	+4

Foreign substance added: ^a 0.10 gram SeO_2 ; ^b 2.0 grams Na_2SO_3 ; ^c 0.20 gram SeO_2 .

Conductivity water and reagent quality chemicals were used throughout. Blanks were run to detect possible traces of iodate in the potassium iodide. Since the hydrochloric acid concentration remains essentially constant in the distillation process, it was possible to show indirectly the absence of active impurities in this reagent. This was done by adding a second sample of selenate directly to the distillation residue of the previous determination, and then proceeding as usual. No significant variations were detected in any case.

Sodium thiosulfate solution (0.01, 0.025, and 0.005 *N*) was standardized against standard potassium iodate solution. The titration end points were determined by means of the "dead stop" potentiometric method as given by Foulk and Bawden (2). The apparatus used was definitely sensitive to 0.01 cc. of 0.005 *N* iodine in a volume of 100 cc. A motor-driven stirrer was used in all titrations.

Procedure

The receiver was filled within about 10 cm. of the top with a solution containing about 2.5 grams of potassium iodide, and placed in position. Sufficient concentrated hydrochloric acid and water were then added to the measured selenate sample in the distilling flask to give a volume of 60 cc. having 5 *N* acidity.

The carbon dioxide flow was next adjusted to a rate of about 35 cc. per minute, and the reflux condenser turned on. The solution was then heated with a microburner, and distilled for 20 minutes after the boiling point had been reached. The contents of the receiver were transferred to a 250-cc. wide-mouthed Erlenmeyer flask, followed by thorough rinsing. In order to remove any traces of iodine from the inside of the delivery tube, the carbon dioxide flow was stopped and a wet rag was momentarily touched against the side of the hot distilling flask to produce sufficient decrease of internal pressure to cause the rinse water to be drawn into the delivery tube, whereupon the carbon dioxide was again turned on to force the liquid out. In order to duplicate the acidity conditions of the thiosulfate standardiza-

tions, 2 cc. of 6 *N* hydrochloric acid were then added to the liberated iodine solution, followed by immediate titration with thiosulfate.

The results of a series of determinations are given in Table I. The quantities given are in terms of selenate radical.

Discussion

Table I shows that reliable results were obtained over a wide range of selenate samples. Equally good results were obtained when 6 *N* instead of 5 *N* hydrochloric acid was used in the distillations. Detectable positive errors, due to the volatilization of selenium tetrachloride, were found in running blanks containing 0.10 gram of selenium dioxide in 7 *N* acid, while with 8 *N* acid positive errors corresponding to 0.4 mg. of selenate radical were found. As shown, comparatively large

amounts of sodium sulfate do not interfere. Foreign materials which are either active oxidizers or reducers under the given experimental conditions must obviously be absent, including bromide and iodide, since these further reduce the selenious acid formed to elementary selenium.

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Determination of Zinc

A Colorimetric Micromethod

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THE colorimetric method presented here for the determination of zinc in soil and agronomic products was developed to meet the special requirements of an investigation of the physiological effects of zinc in soil on crops growing therein, but should be applicable to the determination of zinc in many materials. Of the various methods which have been previously devised for the determination of small quantities of zinc, probably the most convenient is the turbidimetric procedure which depends upon the formation of colloidal zinc potassium ferrocyanide. This method, recently revised by Boggs and Alben (3), was found by the writer to give good results when only approximate values were required. Using a photoelectric cell to measure turbidity, the writer found that the opacity of the colloidal suspensions increased markedly with a short time of aging of the freshly prepared potassium ferrocyanide reagent. Other unexplained factors operated to cause vagaries in the results obtained. The method of Todd and Elvehjem (9), in which zinc is precipitated as zinc ammonium phosphate and calculated from a subsequent colorimetric determination of the phosphate, was found to be unsuccessful for the small quantities of zinc isolated from samples of soil. A search was made for a method that could be used to measure reliably some small differences in the zinc content of the soils and vegetation in question.

The zinc present in soil may be brought into solution by fusion with potassium pyrosulfate and separated from interfering elements by means of hydrogen sulfide as most recently employed by Boggs and Alben (3). This procedure was adopted in the present work. The zinc in plant materials may be brought into solution by ashing at 450° to 500° C. and extracting the ash with hydrochloric acid as in the procedure used by Hibbard (4), or the ash may be fused with potassium pyrosulfate to render the zinc soluble. The zinc may then be isolated by means of hydrogen sulfide as recommended by Hibbard.

Theoretical considerations of the mechanism of combination between 8-quinolinol and the ions of heavy metals led Ráy and Bose (7, 8) to experiment with other related compounds for use as analytical reagents. Among these was quinaldic acid. These authors obtained excellent results when this compound was used as a precipitant for the gravimetric de-

termination of zinc. Later, they adapted the use of quinaldic acid to a micromethod (5, 6).

The findings of Ráy and Bose suggested that it might be possible to prepare a colored derivative of quinaldic acid which not only would precipitate zinc quantitatively but could also be used for a colorimetric determination. Colored derivatives are obtained from many organic compounds upon the introduction of one or more nitro groups into the molecule. This was found to be true of quinaldic acid. The method of Besthorn and Ibele (2) for the preparation of 5-nitroquinaldic acid was employed, and two isomeric compounds were produced, a considerable quantity of 8-nitroquinaldic acid being formed. Only the 5-nitro acid was found to precipitate zinc in weakly acid solutions. This acid possesses a pale yellow color of insufficient intensity for colorimetric measurement. When it is treated with stannous chloride, however, a water-soluble reduction product is formed which has a deep orange color well suited for colorimetric comparisons. The following procedure was devised for the determination of quantities of zinc ranging from 0.05 to 1.00 mg.

Reagents and Apparatus

The method of Besthorn and Ibele (2) was employed for the preparation of 5-nitroquinaldic acid from quinaldic acid obtained from the Eastman Kodak Company. The compound thus prepared crystallized from water, and after being dried at 105° C. it retained two molecules of water of crystallization. The reagent used in this procedure consisted of 0.75 gram of this compound dissolved in 100 ml. of warm 95 per cent ethyl alcohol. One milliliter of the solution was equivalent to approximately 1 mg. of zinc.

Ammonium hydroxide, approximately 3 *N*, was prepared by diluting 1 part of concentrated ammonium hydroxide (sp. gr. 0.90) with 4 parts of distilled water.

Acetic acid, 50 per cent, was prepared by diluting glacial acetic acid with an equal volume of distilled water.

Stannous chloride solution consisted of 12.5 grams of SnCl₂·2H₂O dissolved in 100 ml. of hydrochloric acid (sp. gr. 1.21) and diluted to 500 ml. The solution was preserved by the addition of a little metallic tin.

Methyl red indicator solution was made by dissolving 0.1 gram of methyl red in 100 ml. of 95 per cent ethyl alcohol.

The colorimeter used was like that devised by Yoe and Crumpler (11), but contained a photoelectric cell circuit of greater sensitivity as suggested by Wood (10).

TABLE I. INFLUENCE OF TIME OF DIGESTION UPON COMPLETENESS OF PRECIPITATION OF ZINC

Digestion Period Min.	Zinc Added Mg.	Zinc Recovered Mg.
10	0.10	0.090
10	0.10	0.080
15	0.10	0.10
15	0.10	0.095
30	0.10	0.10
30	0.10	0.11
24 hours	0.10	0.10
24 hours	0.10	0.095
10	0.50	0.494
10	0.50	0.494
15	0.50	0.499
15	0.50	0.500
30	0.50	0.500
30	0.50	0.501
24 hours	0.50	0.498
24 hours	0.50	0.499

TABLE II. EFFECT OF EXCESS REAGENT ON PRECIPITATION OF ZINC BY 5-NITROQUINALDIC ACID

Excess of Reagent %	Zinc Present Mg.	Zinc Recovered Mg.
25	0.20	0.200
25	0.20	0.198
144	0.20	0.200
144	0.20	0.197
213	0.20	0.200
213	0.20	0.199
340	0.20	0.200
340	0.20	0.202
25	0.50	0.501
25	0.50	0.502
144	0.50	0.502
144	0.50	0.499
213	0.50	0.500
213	0.50	0.500
340	0.50	0.500
340	0.50	0.498

Analytical Procedure

The quantity of zinc to be taken for a determination will vary with the type of colorimeter to be employed. Quantities ranging from 0.05 to 1.00 mg. were easily within the range of the colorimeter described above. The zinc, having been previously separated from interfering substances by a method such as the one suggested by Boggs and Alben (3), was brought into solution by means of hydrochloric acid, and was then determined by the following procedure:

An aliquot containing 0.05 to 1.00 mg. of zinc is pipetted into a 30-ml. beaker. The volume is brought to 5 to 10 ml. by evaporating or diluting as necessary. A drop of methyl red indicator is added and the solution made just alkaline with 3 *N* ammonium hydroxide. Acetic acid is added until the solution is distinctly acid (1 to 2 drops). The solution is heated to near boiling and 5-nitroquinaldic acid solution is added in slight excess of that necessary to bring about complete precipitation. The beaker and contents are allowed to stand on the hot plate for 30 minutes without boiling. The precipitate is filtered off by means of an asbestos filter stick, and the beaker and filter are washed five times with boiling water from a wash bottle. The precipitate is dissolved in 5 ml. of hot stannous chloride solution, and heated to boiling. Any asbestos that may be present is filtered off and the solution is cooled to room temperature, and compared in the colorimeter with standards prepared by the same procedure from solutions containing known quantities of zinc. The standard and unknown must be at the same temperature at the time of reading.

When a photoelectric colorimeter is used for the determination, it is convenient to make use of a graph prepared from readings made on standard solutions. The colorimeter readings in microamperes are plotted as ordinates, and the quantities of zinc employed as abscissas. A curve is thus obtained which may be used for reading off the quantity of zinc corresponding to any reading of the colorimeter. This expedient eliminates the necessity for preparing standards every time that determinations are to be made.

The precision which may be obtained by this method in the measurement of the zinc in standard solutions is illustrated by the close agreement between values in Table II.

Conditions Influencing Precipitation

ACIDITY. The zinc salt of 5-nitroquinaldic acid dissolves readily in solutions of the more highly ionized acids, but remains insoluble in solutions having pH values in the range 2.5 to 8.0.

In order to determine the range of hydrogen-ion concentration within which precipitation might be complete, a series of experiments was carried out with 0.5-mg. portions of zinc in the form of the chloride. A standard solution was prepared by dissolving 1 gram of c. p. metallic zinc in hydrochloric acid and diluting to 1000 ml. One hundred milliliters of this solution were diluted to 1000 ml. and several 5-ml. portions were pipetted into 30-ml. beakers. Various acidities were obtained by adding different quantities of hydrochloric acid, acetic acid, and ammonium hydroxide to different beakers, using methyl orange, methyl red,

and phenolphthalein indicators to cover a wide range of pH values. The zinc was then precipitated and determined by the above procedure. The filtrates from which the precipitates were separated were immediately cooled and their pH values determined employing a glass electrode (Beckman pH meter).

The results obtained are shown graphically in Figure 1. The precipitation of zinc is found to be complete within the range of pH 2.5 to 8.0. The use of acetic acid and methyl red indicator as recommended in the procedure gives acidities lying well within these limits.

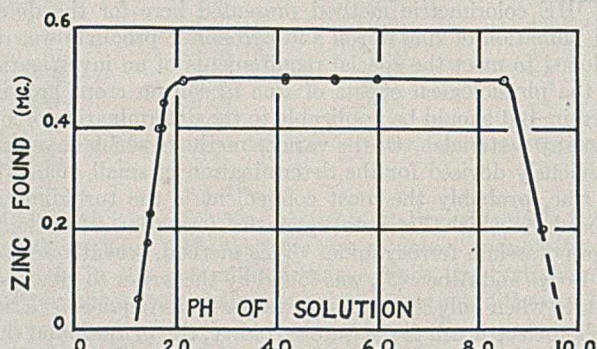


FIGURE 1. INFLUENCE OF HYDROGEN-ION CONCENTRATION ON PRECIPITATION OF ZINC

TIME OF DIGESTION. The time of digestion necessary for complete precipitation was determined as follows:

Two series of solutions of zinc chloride containing 0.5 and 0.1 mg. of zinc, respectively, were treated with an excess of 5-nitroquinaldic acid after adjustment of acidity, and were digested on the steam bath for periods ranging from 10 minutes to 24 hours. The precipitates were then filtered off, and their zinc contents determined as previously described.

The figures in Table I indicate that precipitation had reached a maximum value after digesting for 15 minutes. In most instances the supernatant solutions were still turbid at the end of this time, and digestion for 30 minutes resulted in clear solutions. It might be deemed best, therefore, to digest for 30 minutes to reduce the possibility of fine particles passing through the filter.

ADSORPTION OF EXCESS REAGENT. Two series of precipitations were carried out with 0.5- and 0.2-mg. portions of zinc, with acidities and digestion periods as given in the procedure. 5-Nitroquinaldic acid was added in excesses amounting to 25, 144, 213, and 340 per cent greater than the theoretical amounts needed for complete precipitation. The precipitates were filtered off and determinations made by the procedure given. The results (Table II) show that the precipitates did not adsorb appreciable quantities of the excess

TABLE III. EFFECT OF AMMONIUM CHLORIDE ON PRECIPITATION OF ZINC

NH ₄ Cl Concentration <i>N</i>	Zinc Present <i>Mg.</i>	Zinc Recovered <i>Mg.</i>
0.0	0.20	0.195
0.0	0.20	0.200
0.15	0.20	0.200
0.15	0.20	0.200
0.70	0.20	0.200
0.70	0.20	0.198
1.0	0.20	0.193
1.0	0.20	0.190
0.0	0.50	0.500
0.0	0.50	0.497
0.15	0.50	0.500
0.15	0.50	0.500
0.70	0.50	0.503
0.70	0.50	0.495
1.0	0.50	0.475
1.0	0.50	0.480

TABLE IV. EFFECT OF CONCENTRATION OF ACID ON DEPTH OF COLOR

Acid Concentration <i>N</i>	Colorimeter Reading ^a <i>Microamperes</i>	Zinc Equivalence <i>Mg.</i>
0.24	82.1	0.20
0.48	82.0	0.20
0.60	81.8	0.21
0.72	82.0	0.20
0.84	82.1	0.20
1.08	83.0	0.17
1.20	85.5	0.15
1.40	89.5	0.10
0.24	63.8	0.50
0.48	63.6	0.50
0.60	64.0	0.50
0.72	63.8	0.50
0.84	63.6	0.51
1.08	65.2	0.47
1.20	67.0	0.42
1.40	69.2	0.39

^a Represents per cent of light transmitted by colored solution.

reagent, regardless of the quantity of precipitant used. Evidently the excess of 5-nitroquinaldic acid is readily removed by the hot wash water. The close agreement between these values also indicates the degree of precision obtained with this reagent.

INTERFERING SUBSTANCES. Interfering substances are liable to be of frequent occurrence since many metals are precipitated under the conditions of this method. Tests showed that 5-nitroquinaldic acid forms insoluble precipitates with silver, lead, mercury, copper, iron, manganese, cobalt, and nickel in weakly acid solutions. With respect to its nonspecificity as an analytical reagent, 5-nitroquinaldic acid is similar to 8-quinolinol (1).

It is necessary to separate zinc from any or all the metals listed above before an accurate determination can be made by this method. This is best accomplished by means of hydrogen sulfide as already mentioned. The zinc sulfide so obtained is brought into solution by means of hydrochloric acid. It was found that ammonium chloride formed by neutralizing acid in such solutions with ammonium hydroxide may inhibit complete precipitation of the zinc within the digestion period of 30 minutes. Results given in Table III show the concentrations of ammonium chloride that may be tolerated. Complete recovery of zinc may be accomplished in the presence of ammonium chloride in concentrations as high as 0.7 *N* but not from solutions of higher concentration. Before making determinations by this procedure it is best, therefore, to avoid the use of large quantities of acid in dissolving the precipitates of zinc sulfide. Similar concentrations of sodium chloride also inhibit complete precipitation, so that sodium hydroxide offers no advantage over ammonium hydroxide for the neutralization of the acid.

Conditions Influencing Color Intensity

High concentrations of acid were found to decrease the depth of color, as shown by Table IV. Portions of 5-nitroquinaldic acid solution equivalent to 0.5 and 0.2 mg. of zinc, respectively, were pipetted to beakers, and the alcohol was evaporated by warming gently. Concentrated hydrochloric acid was added in increments to different beakers, and the solutions were treated with equal quantities of a hot solution of stannous chloride. The resulting solutions were nearly colorless at higher acid concentrations but were distinctly colored at the lower concentrations. Most of the solutions, however, developed full color intensity upon being diluted to volume in the tube of the colorimeter. The results show that the intensity of color was not appreciably influenced by differences in concentration of acid within the range 0.24 *N* to 0.84 *N*. The quantity of hydrochloric acid found adequate for dissolving and reducing the precipitates obtained in this

method gives a normality of 0.24 upon dilution for the colorimeter. Hence, the acidity is sufficiently low for accuracy.

Variation in temperature of the solutions at the time of reading was found to have considerable influence on the depth of color. At high temperatures the solutions are more intensely colored than at room temperature, and considerable error may occur in determinations if readings are made with standard and unknown at different temperatures.

The intensity of color of the solutions of reduced 5-nitroquinaldic acid was found to be independent of the concentrations of stannous chloride over the range 0.075 to 0.40 per cent SnCl₂·2H₂O.

The color of the solutions is stable. The solutions tested were found to give the same readings after standing for 24 hours as they gave immediately after reduction.

Spectral Absorption of the Colored Solutions

Spectrophotometric measurements made on solutions of 5-nitroquinaldic acid reduced by stannous chloride showed that such solutions absorb light in the visible portion of the spectrum between 4000 and 6000 Å., and transmit almost completely the higher wave lengths. The violet, blue, and lower half of the green bands are absorbed by concentrated solutions, while the upper half of the green band and the yellow and red bands are transmitted. It is apparent, therefore, that filters which transmit the violet, blue, or the lower half of the green bands of the spectrum may be used in colorimeters with this reagent.

Discussion

The range of quantities of zinc conveniently determinable by the technic described in the analytical procedure was found to be 0.05 to 1.0 mg. Quantities as large as 2 mg. have been determined by the same procedure. It was necessary, however, to dilute the colored solutions to concentrations suitable for the photoelectric colorimeter. When such dilutions were carried out, an extra 5-ml. portion of stannous chloride solution was added, so that sufficient acid was present to prevent hydrolysis of the stannous chloride. Omission of this precaution sometimes resulted in turbid solutions. The range of quantities of zinc determinable by this method is, therefore, limited to 0.05 to 2.0 mg. Extension of the range to larger or smaller quantities would require further modifications of technic.

5-Nitroquinaldic acid is expensive to prepare by present methods. Quinaldic acid was selling for \$3.60 per 10 grams at the time it was purchased for this work. Since the yield on nitration is less than 50 per cent of the theoretical, the reagent seems rather costly for use other than for microdeter-

minations, although it should serve admirably for gravimetric macrodeterminations. The cost of reagent for a single microdetermination is estimated to be about 2.5 cents, which is not prohibitive.

Summary

A procedure which has been successfully used for the colorimetric microdetermination of the zinc content of agronomic materials is described. The method is applicable for the determination of quantities of zinc ranging from 0.05 to 1.0 mg.

After a preliminary separation of the zinc from interfering elements, 5-nitroquinaldic acid is used as a precipitating agent. The precipitate is filtered from the excess reagent, and converted into an orange-colored, water-soluble compound by reduction with stannous chloride. The intensity of color is measured by means of a photoelectric colorimeter.

Precipitation of zinc by 5-nitroquinaldic acid is complete within a range of pH 2.5 to pH 8.0 after digestion for 30 minutes. Ammonium chloride and sodium chloride in concentrations greater than 0.7 *N* inhibit the complete precipitation of the zinc.

The intensity of color of the reduction product of 5-nitroquinaldic acid is independent of the acid concentration at acidities lower than 0.8 *N* and of the concentration of stan-

nous chloride. The intensity of color increases appreciably with rise in temperature of the solutions, making it necessary to carry out all readings at the same temperature.

Acknowledgment

The writer wishes to acknowledge with gratitude the support given by the American Zinc and Chemical Co. for the performance of this work.

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A Copper Tube Preheater

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MANY references occur in the literature to the construction and use of preheaters or "catalyzer tubes" for burning oxidizable impurities present in air and commercial oxygen gas. The following is a description of a preheater for

use in microanalyses of carbon and hydrogen. In addition to being very efficient, it has the advantages of simplicity, extreme ruggedness, and low cost of construction.

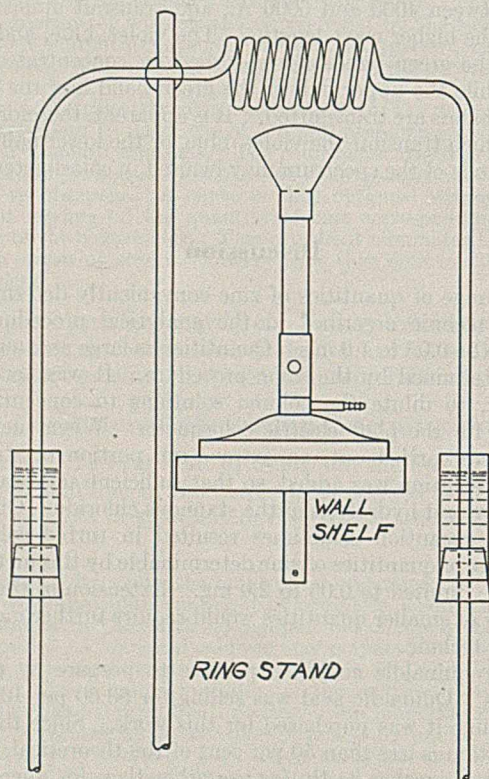
The preheater is made from a 1-meter length of commercial copper tubing approximately 5 mm. in outside diameter with walls 1 mm. thick. Because it has been found convenient to stand the preheater on the shelf at the back of the desk, this length is greater than may otherwise be needed. At a distance of 30 cm. from the inlet end (see figure), the tubing is wound several times around a pipe of small diameter (1 cm.), forming a compact coil. The coil is clamped in a horizontal position at burner height. At either end of the coil, the tubing is bent downward at right angles and slightly towards the front of the desk in order to clear the shelf. The inlet and exit ends are attached with rubber connections to the pressure regulator and purifying line, respectively. To prevent the rubber connections from being overheated, the two ends are surrounded by water jackets. These consist of 6-cm. lengths of 20-mm. glass tubing fitted at their lower ends over rubber stoppers of proper size. The jackets are conveniently filled with water from a wash bottle, once a week being sufficiently often even when the apparatus is in constant use.

The coil is heated with a Pittsburgh burner and wing top. When first prepared, after flushing out with grease solvents, the copper tube is heated to redness over its entire length with a stream of oxygen passing through. On further heating the coil becomes filled with copper oxide scale, thus providing efficient contact with the entering gas.

Two such preheaters have been in daily use in this laboratory for over 6 months without developing leaks through corrosion at the heating surface.

In order to test the efficiency of this type of preheater, a number of blanks were run using compressed air directly from the laboratory line. Although this air was saturated with colloidal oil and other organic impurities, negligible blanks were obtained. This is probably the most rigorous test possible of the efficiency of the preheater in converting the organic vapors into absorbable products.

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The Cathode Ray-Tube Polarograph

Theory of Method

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THE polarograph as developed by Heyrovský and his co-workers is an instrument well known to electrochemists and analysts. The theory and applications have been summarized in several monographs (1, 2). The recording of current-potential curves of a dropping mercury electrode may be accomplished in a number of ways. Heyrovský gives adequate reasons for preferring the photographic method, such

as performance of the record, etc. It would seem natural to utilize the cathode ray oscillograph for this purpose, but in practice a number of difficulties arise. Oscillograph practice requires rapid recurrence of the phenomenon if a persistent stationary image is desired. It is true that transient images can be photographed, but this procedure would nullify the advantage of a continuous picture of what is going on. If we attempt to sweep through the range of potentials very rapidly in order to produce a persistent stationary pattern, the question arises whether the electrode equilibria can keep pace with the rapidly changing potentials.

The authors have found a solution to this problem and the instrument based on this method yields values identical with those based upon the conventional Heyrovský method.

Theory

Let curve *OAHBC* of Figure 1 represent an idealized Heyrovský polarogram for a certain ion. The potential, *V*, corresponding to point *H*, is the *Halbwellenpotential* and represents a characteristic identifying value, for the given ion. Now imagine a small sinusoidal alternating potential of peak value, ΔV , applied in series with the main potential, *V*. The current, *I*, will now vary about the mean value, *H*, to produce a wave, *S*, of the same wave form and frequency, but with an amplitude which depends upon the steepness of curve *AHB*. If the main direct current potential, *V*, is now shifted the sine wave, *S*, will become distorted at its upper or lower portion because of intersection with the nonlinear portions of the curve at *B* or *A*. If this curve, *S*, is continuously viewed on an oscillograph screen it will be almost perfectly sinusoidal and undistorted when and only when *V* has

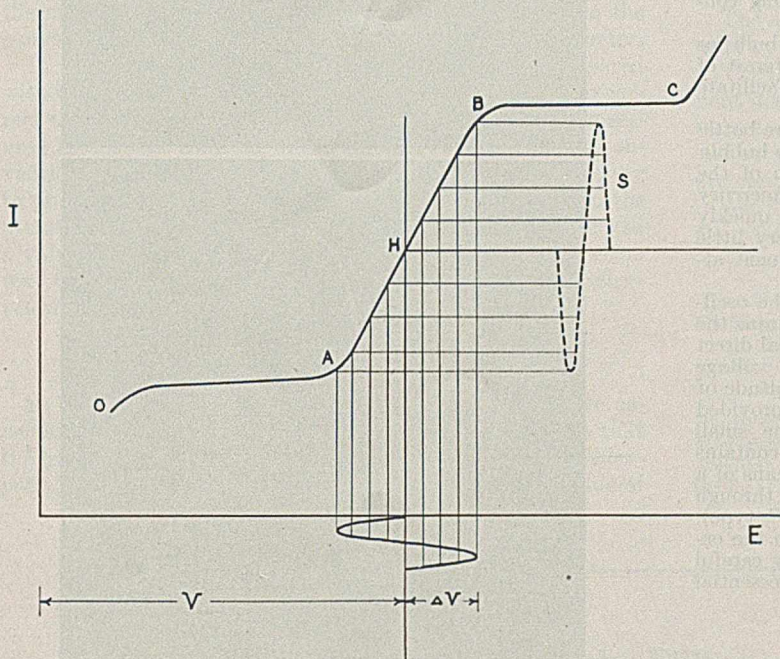


FIGURE 1

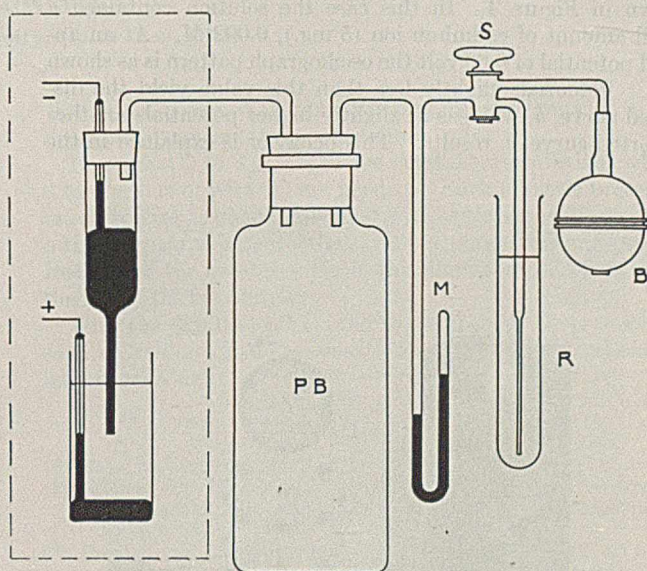
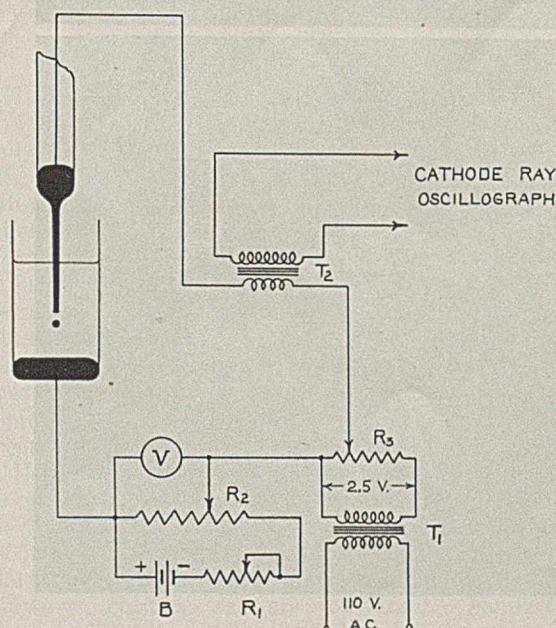


FIGURE 2. CIRCUIT (LEFT) AND DIAGRAM OF APPARATUS (RIGHT)

a value corresponding to the mid-point of the current-potential curve (at H). Conversely, the appearance of such undistorted waves, as V is varied from zero to the maximum value of deposition potentials, will serve to detect and identify the characteristic potentials.

The Instrument

The circuit is shown in Figure 2, left. Battery B supplies the potentials through regulating resistor R_1 and voltage divider R_2 . The voltmeter, V , indicates the applied potential. The small alternating potential in series with the direct current potential is supplied by step-down transformer T_1 and voltage divider R_3 . The lead to the dropping mercury cathode passes through the high-gain, low primary-impedance transformer, T_2 . The secondary of this transformer is connected to the vertical deflector plates of the cathode ray oscillograph. If the oscillograph is not provided with a built-in amplifier or one of sufficient gain (3000 to 5000 \times) it must be preceded by a voltage amplifier stage. The horizontal deflector plates are driven by the usual sweep circuit and in most cases means are provided for locking in the sweep with the phenomenon under investigation (synchronizing control).

The authors have eliminated the customary leveling bulb for supplying mercury to the dropping electrode in the interest of compactness and convenience of manipulation and to facilitate careful electrical shielding of the electrode assembly.

Figure 2, right, shows a simple arrangement of pressure bottle PB , rubber bulb B , and two-way stopcock S with a micro bubble regulator, R . Manometer M gives a rough indication of the driving air pressure. Actually, the rate of dropping of mercury is the best criterion of satisfactory operation, and this is quickly adjusted by means of the stopcock by-pass. Since very little mercury is used, the air reservoir requires very infrequent attention.

Figure 3 shows a photograph of the instrument. The oscillograph is on the right. The main case on the left contains the circuit and controls. The voltmeter indicates the critical direct current potentials. The left-hand dial controls the voltage divider, R_2 . The right-hand dial, R_3 , governs the magnitude of the alternating current potential. Toggle switches are provided for the battery and alternating current supply. The small copper case mounted on the right side of the instrument contains the electrode assembly and can be tightly closed by means of a copper door. The electrode connections pass directly through the wall through insulated connectors ("banana plug" type). The case is grounded during operation. Connection to the oscillograph is made through shielded cable. Reasonably careful shielding and the absence of loose, rambling wires are essential for satisfactory operation.

Operation

A typical polarogram as obtained by this instrument is shown in Figure 4. In this case the solution contained a small amount of cadmium ion (5 mg.), 0.002 M . At an applied potential of 0.63 volt the oscillograph pattern is as shown in *a*. Potentials slightly less than this value yield the distorted curve, *b*, whereas at slightly higher potentials another distorted curve, *c*, results. This behavior is explained in the

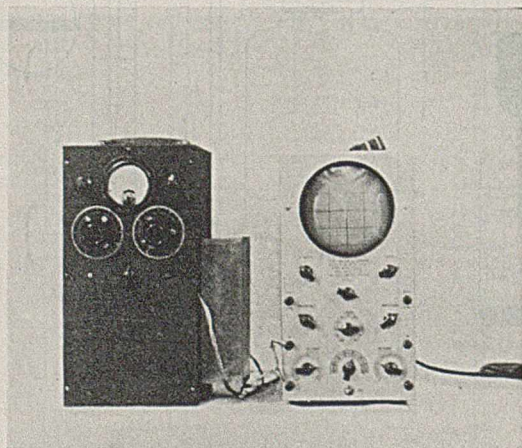


FIGURE 3

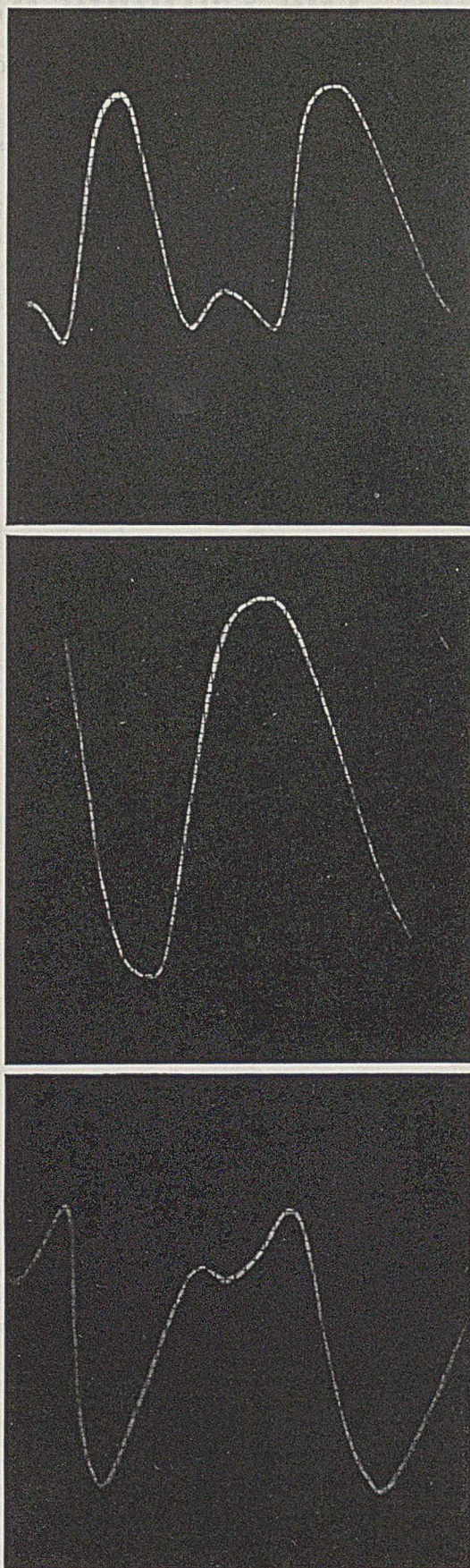


FIGURE 4. TYPICAL POLAROGRAM

discussion of Figure 1. On a complete analysis the operator merely increases the potential, V , manually from zero to the maximum and notes the potentials at which symmetrical waves appear. The process can be repeated as often as desired. For feeble curves (traces of ion) the gain control may be stepped up in order to miss none. Under these circumstances the maxima due to large amounts of other ions will produce high deflections, beyond the edge of the screen, but the instrument is not damaged as a delicate galvanometer would be.

The entire pattern disappears when a mercury droplet falls from the capillary. A new curve appears almost immediately, and the momentary interruption is not disturbing, inasmuch as the general technic requires fairly slow dropping rates.

The observed potentials are very reproducible and vary by only a few millivolts—0.627 to 0.629 in the above case. Furthermore they are identical with the values obtained in the conventional way—with a voltage divider and galvanometer.

In all cases in which the new instrument was compared with the "manual" method it was absolutely necessary to correct the observed potentials for the anode potential as measured against the solution with a calomel electrode in the conventional way. Authorities (1, 2) agree that this is necessary to obtain the standard value for each ion as recorded in the literature. Thus for zinc ion (0.001 M) the authors observed a value of -1.110 volts, and the anode potential correction was 0.041 volt yielding -1.069 volts for the *Halbwellenpotential*. The accepted value is -1.06 volts.

Discussion

So far no mention has been made of the quantitative aspects of the instrument. Reference to Figure 1 will show that the final deflection of the cathode ray beam at the *Halbwellenpotential* depends upon the gain of the amplifier, the value of

V , and the height of the "Heyrovský curve" for the particular ion under observation. The gain of the amplifier may be held constant and ΔV adjusted to some predetermined value. Investigations are in progress for the determination of suitable values of the voltage under various conditions of operation, so that quantitative estimation may be accomplished with the instrument.

The complete instrument, including the oscillograph but not labor, costs \$150.

Summary

Current voltage curves taken with an oscillograph using a small series alternating current potential yield patterns which are interpretable on the basis of the conventional Heyrovský method.

The polarograms are viewed continuously and require no photographing or recording.

The actual identification is in terms of the same potentials used by the classical methods.

The introduction of the small alternating current component does not give rise to any complications; the observed values are the same as those obtained with direct current.

The analysis can be repeated indefinitely and the results are continuously visible to the operator.

Sensitivity control is not hampered by possible damage to the recording instrument.

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Electrolytic Silver Wool in the Filling of Microcombustion Tubes

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IN PREPARING the universal combustion tube filling of Pregl for use in carbon and hydrogen analysis, it is generally recommended (2, 3) that loosely wound silver wire rolls or wads be used. There are obvious mechanical difficulties in this procedure in preparing a closely packed and uniformly distributed filling, and in addition the wire does not offer the maximum surface per unit weight. Recently Elek (1) has advocated the use of rolls of silver gauze because of their greater surface.

It has been found in this laboratory that a "silver wool" produced by electrolysis of metallic silver has several advantages over silver wire. Finely divided silver wool may readily be prepared electrolytically according to well-known methods for purifying silver. A description of a simple electrolytic cell is given by Richards (4). By varying the current through the cell, the crystal size of the deposit can be controlled. In this way crystals have been obtained having a diameter of 0.005 to 0.05 mm. and length of 3 to 8 mm. When removed from the electrolytic cell, the crystals are in the form of closely interwoven clusters, and are conveniently handled with pincers in filling the combustion tube. The interwoven clusters facilitate the uniform packing of the tube. Satisfactory

results are obtained without the preliminary ignitions in hydrogen and oxygen, thus saving time.

In general 2 to 3 grams of the crystals are sufficient where 4 to 5 grams of wire (2) are needed. Such crystals present a much greater surface than silver wire of the same dimensions, owing to many imperfections visible under the microscope. Because of the greater surface, the silver wool often outlives the rest of the tube filling.

Thus the qualities attributed to electrolytic silver wool are such as to warrant its preparation and use in microchemical laboratories in preference to the wire form.

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RECEIVED February 14, 1938.

Mechanism of Absorption of Oxides of Nitrogen by Lead Peroxide in Microcombustions

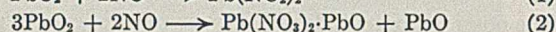
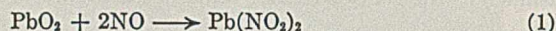
W. R. KIRNER, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

IN CONNECTION with the direct gasometric microdetermination of oxygen in nitrogen-containing organic compounds, developed in this laboratory (14), it was necessary to make a study of the reaction which occurs when oxides of nitrogen, formed during the combustion of such substances, are absorbed by the lead peroxide present in the combustion tube. It is the purpose of this paper to describe the quantitative study made of the reaction of nitric oxide and also nitrogen peroxide with lead peroxide.

There is very little information in the literature regarding the specific oxides of nitrogen which are formed during the combustion of nitrogen-containing compounds. Some investigators (2, 4, 5, 11, 12, 16) believe nitrogen peroxide is the ultimate oxide formed, whereas others (15, 17) favor nitric oxide and still others (21) believe that nitrous oxide is also likely to be present. Many other investigators make no attempt to distinguish between these oxides, and in discussing their reactions merely refer collectively to oxides of nitrogen.

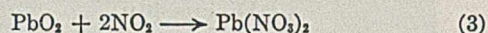
The literature is likewise not specific as to the mechanism of the reaction between the various oxides of nitrogen and lead peroxide. Dennstedt and Hassler (5) claim that nitric oxide can pass over lead peroxide without being absorbed, whereas Auden and Fowler (1) state that a basic lead nitrate is formed, the reaction starting at a temperature as low as 15° C., and attaining a maximum above 130° C., with only traces of nitrite being formed. Sabatier and Senderens (23) demonstrated that nitric oxide on reaction with metallic peroxides formed nitrogen peroxide, the metallic peroxide being reduced.

In aqueous suspension and in the absence of air they claimed that nitric oxide and lead peroxide first formed lead nitrite, which was later converted to a basic nitrite. Moser, however (19), illustrates the reaction between nitric oxide and lead peroxide with the following equations:



Müller and Barck (20) state that nitric oxide is completely absorbed by lead peroxide at room temperature, forming lead nitrite, as in Equation 1, and that at temperatures above 200° C. oxygen begins to be liberated from the lead peroxide. Lindner (17) found that at 180° C. 0.465 gram of lead peroxide absorbed nitric oxide at first rapidly and then more slowly, and after 6 days had taken up 32 cc. According to Equation 1 the lead peroxide should have absorbed 87 cc., and, according to Equation 2, 29 cc.

Kopfer (16), Dennstedt and Hassler (4), Friedrich (11), and Hermann (12) believe that nitrogen peroxide reacts with lead peroxide, forming lead nitrate according to the following equation:



The work to be described was undertaken because the literature failed to yield specific information, required in connection with the investigation previously mentioned, regarding these questions.

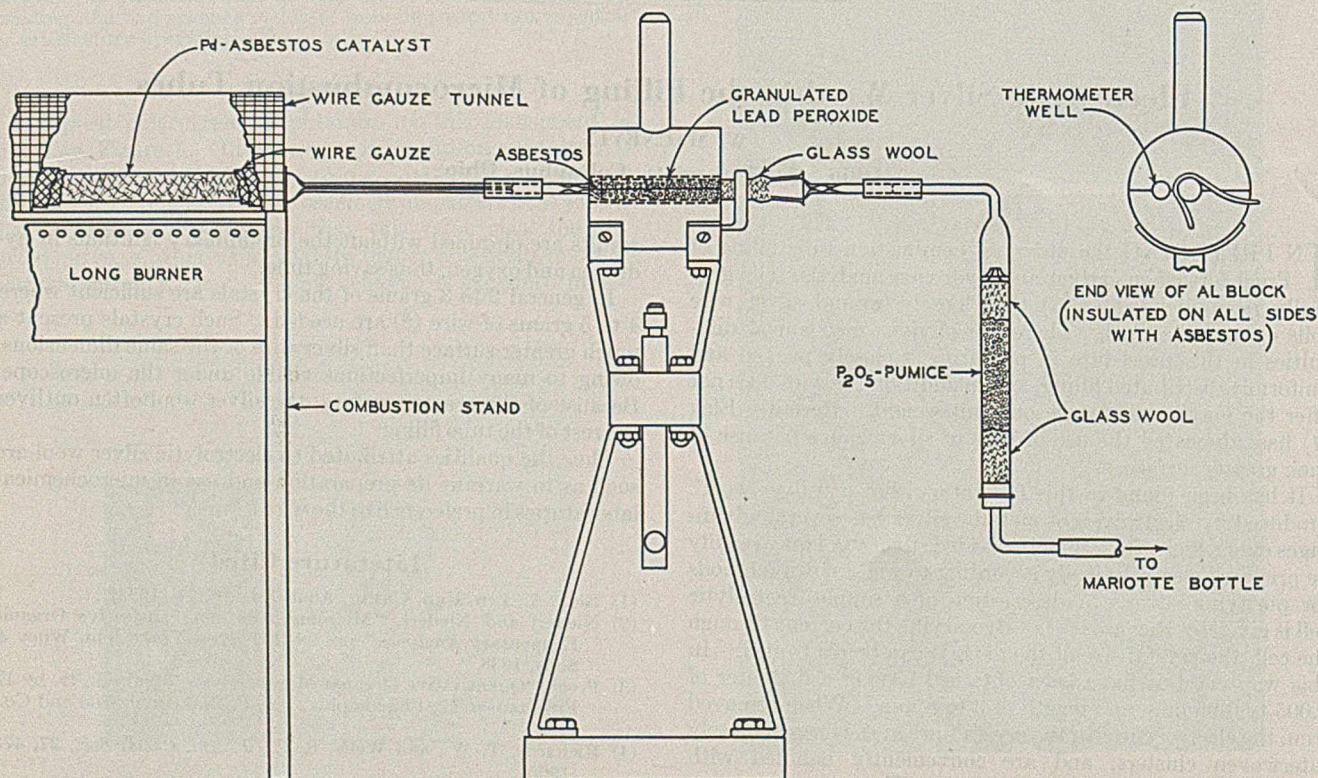


FIGURE 1. THE COMBUSTION TRAIN

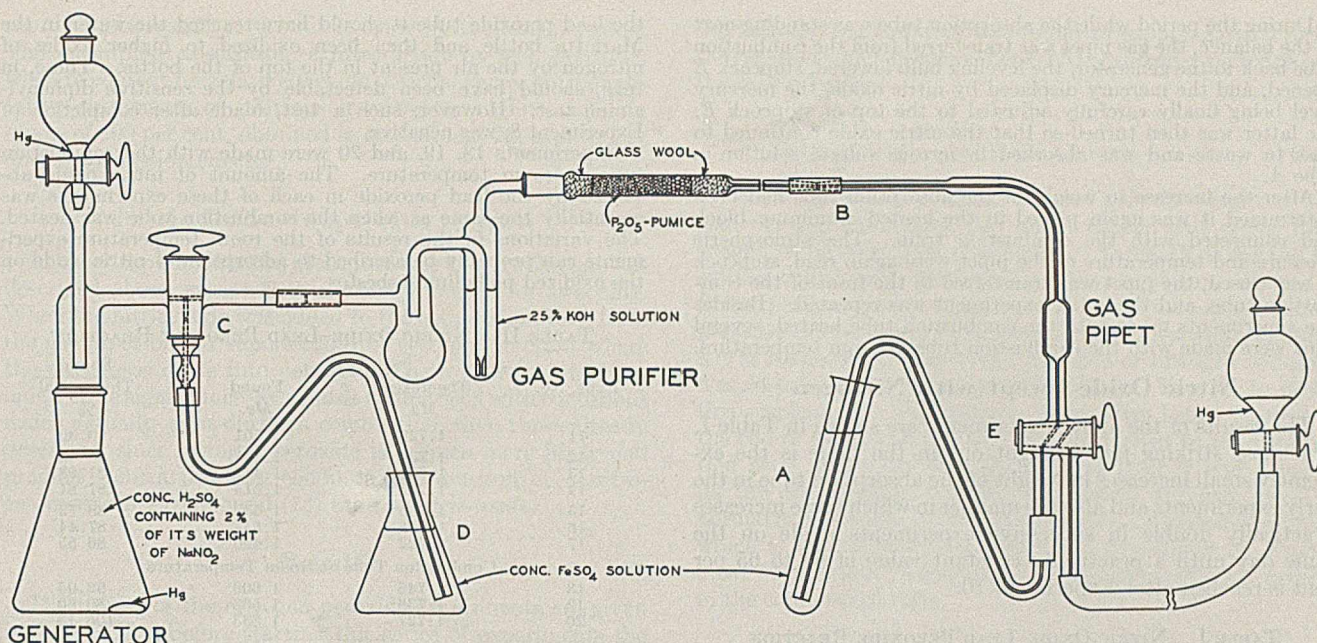


FIGURE 2. APPARATUS FOR PREPARATION OF NITRIC OXIDE

The combustion train (Figure 1) was identical to that devised by Pregl for the carbon and hydrogen microdetermination, except that the side-arm combustion tube had an 8-cm. 0.1-mm. capillary sealed to the exit end. The purpose of this capillary was to transfer the effluent gases, as rapidly as possible, to the weighed micro absorption tube containing purified lead peroxide which was kept at a temperature of about 185° C. by means of an aluminum block heated by a microburner. The gas flow was maintained at 3.0 to 3.5 cc. per minute by means of the pressure regulator and Mariotte bottle.

In the experiments using nitrogen for sweeping, the pressure regulator and bubble counter were filled with the sodium β -anthraquinone sulfonate-sodium hydrosulfite mixture recommended by Fieser (10) for removing oxygen. In filling the gasometer with nitrogen (water pumped), the gas was taken from a high-pressure cylinder and passed through a Milligan gas-washing bottle containing the oxygen absorbent. When oxygen was used for sweeping, the pressure regulator was filled with dilute potassium hydroxide and the bubble counter with 40 per cent potassium hydroxide. From the bubble counter the gases traversed a small U-tube, containing Ascarite and P_2O_5 -pumice, and then entered the side arm of the combustion tube. The combustion tube contained only a 40 per cent palladium-asbestos catalyst, the same that was used in the previous work on the simultaneous determination of carbon, hydrogen, and oxygen (13). No silver was present in the combustion tube, as statements have appeared in the literature (3, 9), although unconfirmed (4, 7, 12, 20), that silver is capable of reducing oxides of nitrogen to elementary nitrogen.

Preparation of Nitric Oxide

The nitric oxide was prepared by the method of Emich (6) in the apparatus illustrated in Figure 2. In the first work the air in the apparatus was displaced by generating nitric oxide for some time, the waste gas being absorbed in concentrated ferrous sulfate solution in tube A. In the later work the air in the apparatus was removed by evacuating the entire generator and purifying train with a water pump connected through a large U-tube, containing phosphorus pentoxide, attached at B. Nitric oxide was then generated until it had displaced the vacuum. The apparatus was again evacuated and refilled with nitric oxide before the gas pipet was attached. Then the nitric oxide was passed through the calibrated gas pipet (volume = 2.003 cc.), for some time before taking the experimental sample. The nitric oxide was absolutely colorless.

Combustion Procedure

Before starting the actual experiments the lead peroxide absorption tube was conditioned by placing it in the heated aluminum block and passing nitrogen (or oxygen) through it for some

time. Then, using technic identical to that of an actual run, but with no nitric oxide added, wiping-weighing experiments were made so as to determine the weight characteristics of the absorption tube. The weight of the absorption tube could be duplicated to within ± 0.003 mg. in these blank determinations. In these experiments the absorption tube was placed in the heated aluminum block and connected to the combustion train and the gas was allowed to flow through it for 45 minutes after first passing through the heated combustion tube. Then the aluminum block was removed and the absorption tube allowed to cool for 10 minutes, with the gas still passing through it, after which it was disconnected from the combustion train, taken to the balance room, wiped, fitted with tight-fitting pins to hinder diffusion and allowed to stand outside the balance for 10 minutes, then placed in the balance and weighed at the end of an additional 5 minutes.

In an actual experiment the combustion tube was heated and gas passed through it for some time. Then the absorption tube was put into the heated aluminum block and attached to the combustion train, and the procedure described above was followed, so as to get the initial weight of the absorption tube. During this time the nitric oxide generator was made air-free. After being weighed the absorption tube was placed in the heated aluminum block and connected to the combustion train, but the water from the Mariotte bottle was not started until later. The atmospheric pressure and temperature in the immediate vicinity of the gas pipet were read, the stopcock on the latter was closed, and the pipet was rapidly disconnected from the generator and attached to the front end of the combustion tube by means of a rubber stopper. During the experiment the generator was stoppered at B and stopcock C turned so that the nitric oxide, which continued to generate slowly, went to waste and was absorbed in ferrous sulfate solution in flask D.

The siphon tube of the Mariotte bottle was then lowered, so that the flow of gas started and was maintained at the proper rate. Then the leveling bulb was raised to a height of 7 to 8 cm. above the horizontal arm of the pipet and the scratched stopcock, E, was opened cautiously so that the mercury entered the pipet and slowly and regularly displaced the nitric oxide, 10 to 15 minutes usually being required. When the mercury reached the end of the horizontal capillary of the pipet, which extended into the combustion tube, stopcock E was closed. The nitric oxide which had entered was then swept through the combustion tube and into the absorption tube and continued until 45 minutes had elapsed from the time of starting the nitric oxide. At the end of this time the aluminum block was removed and gas passed for an additional 10 minutes, after which the absorption tube was removed, taken to the balance room, wiped, fitted with tight-fitting pins, and weighed after the appropriate interval. A total of 150 to 175 cc. of gas was passed through the absorption tube during the 55-minute interval.

During the period while the absorption tube was standing next to the balance, the gas pipet was transferred from the combustion tube back to the generator, the leveling bulb lowered, stopcock *E* opened, and the mercury displaced by nitric oxide, the mercury level being finally carefully adjusted to the top of stopcock *E*; the latter was then turned so that the nitric oxide continued to pass to waste and was absorbed in ferrous sulfate solution in tube *A*.

After the increase in weight of the absorption tube had been determined it was again placed in the heated aluminum block and connected with the combustion train. The atmospheric pressure and temperature of the pipet were again read, stopcock *E* was closed, the pipet was transferred to the front of the combustion tube, and the entire experiment was repeated. Besides the experiments made with the combustion tube heated, several runs were made with the combustion tube at room temperature.

Nitric Oxide Swept with Nitrogen

The results of the above experiments are shown in Table I. The most striking fact brought out in the table is the extremely small increases in weight of the absorption tube in the early experiments and also the manner in which these increases practically double in successive experiments made on the same day until a practically constant value of 64 to 65 per cent is reached after Experiment 10.

TABLE I. NITRIC OXIDE-LEAD PEROXIDE REACTION

Expt. No.	Time for addition Min.	Pressure Mm. Hg	Temp. ° C.	Nitric Oxide		Weight added Mg.	Increase, PbO ₂ Absorption Tube Mg.	%
				Volume added N. T. P. Cc.				
1	10.5	731.3	25.7	1.762	2.361	0.024	1.02	
2	7	732.2	25.0	1.768	2.369	0.048	2.03	
3	10	732.5	25.0	1.769	2.370	0.104	4.39	
4	7	736.5	23.5	1.787	2.395	0.090	3.76	
5	7	736.4	23.8	1.785	2.392	0.183	7.65	
6	12	741.0	24.9	1.790	2.399	0.227	9.46	
7	18	740.6	25.9	1.783	2.389	0.499	20.89	
8	14	740.4	26.3	1.780	2.385	0.709	29.73	
9	23	740.2	27.0	1.775	2.379	0.824	34.64	
10	14	740.2	28.0	1.769	2.371	1.262	53.23	
11	13	739.2	29.4	1.759	2.357	1.561	66.23	
12	12	738.0	28.0	1.764	2.364	1.481	62.65	
13	22	738.2	28.6	1.761	2.360	1.412	59.83	
14	12	738.0	29.5	1.755	2.353	1.515	64.39	
15	20	740.5	28.9	1.765	2.365	1.539	65.07	
16	10	740.4	30.0	1.758	2.356	1.511	64.13	
17	11	739.8	30.9	1.752	2.347	1.490	63.49	
Combustion Tube at Room Temperature								
18	10	738.2	26.2	1.775	2.379	1.606	67.51	
19	13	738.0	27.7	1.766	2.367	1.503	63.50	
20	14	737.6	29.0	1.757	2.355	1.833	77.83	

^a The horizontal spaces separate experiments made on succeeding days.

A possible explanation of this behavior is that at the start of the experiments the hot palladium-asbestos catalyst (maximum temperature about 600° C.) almost completely reduces the nitric oxide to nitrogen, so that very little of it reaches the lead peroxide. As more nitric oxide is passed through the catalyst the latter, owing to oxidation, gradually loses its reductive ability, so that after Experiment 10 the nitric oxide is probably passing through practically unchanged. Calculation shows that in Experiments 1 to 10 sufficient nitric oxide could theoretically have oxidized, to palladous oxide, over 20 per cent of the palladium present which is then no longer effective in reducing nitric oxide. Twenty per cent possibly represents the amount of the total palladium present which is sufficiently exposed to undergo a surface reaction. It is known that palladium undergoes oxidation at temperatures of 600° to 700° C. (18) and that nitric oxide is an oxidizing agent at these temperatures and, when reduced by many metals, is quantitatively converted to nitrogen (8, 22). At the start of the experiments the palladium-asbestos had a gray, metallic appearance and after the experiments were completed it was brown, indicating oxidation. The following experiments support the above explanation:

After Experiment 8, 17.2 mg. (12.8 cc. N. T. P.) of nitric oxide are unaccounted for. If this amount had passed through

the lead peroxide tube it should have reached the water in the Mariotte bottle and then been oxidized to higher oxides of nitrogen by the air present in the top of the bottle. These, in turn, should have been detectable by the sensitive diphenylamine test. However, such a test, made after completion of Experiment 8, was negative.

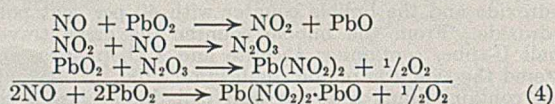
Experiments 18, 19, and 20 were made with the combustion tube at room temperature. The amount of nitric oxide absorbed by the lead peroxide in each of these experiments was essentially the same as when the combustion tube was heated. The variations in the results of the room temperature experiments can probably be ascribed to adsorption of nitric oxide on the oxidized palladium-asbestos.

TABLE II. NITRIC OXIDE-LEAD PEROXIDE REACTION

Expt. No.	Nitric Oxide		Found Theoretical %
	Theoretical Mg.	Found Mg.	
11	1.729	1.561	90.30
12	1.734	1.481	85.42
13	1.731	1.412	81.58
14	1.725	1.515	87.81
15	1.735	1.539	88.72
16	1.728	1.511	87.44
17	1.722	1.490	86.55
Combustion Tube at Room Temperature			
18	1.745	1.606	92.05
19	1.736	1.503	86.60
20	1.727	1.833	106.13

From these results it can be inferred that the catalyst is no longer effective and, whether hot or cold, permits the nitric oxide to pass through it without reaction. It is therefore concluded that when successive experiments yield practically constant increases in weight of the lead peroxide tube, beginning with Experiment 11, the palladium-asbestos catalyst has ceased to react and allows the nitric oxide to enter, unchanged, into the lead peroxide tube.

In searching for an equation to express quantitatively the results of these reactions it was obvious that Equations 1 and 2, given by Moser, are inadequate, since in no case was the increase in weight of the lead peroxide tube equal to the weight of nitric oxide added. The only quantitative data which could be found in the literature for the reaction between nitric oxide and lead peroxide, up to saturation, were those given by Lindner (17), who also pointed out that Moser's equations did not fit his data. Taking Lindner's data and applying them to various equations finally yielded the following:



In this equation a half molecule of oxygen is liberated for each pair of nitric oxide molecules which react with the lead peroxide. Using this equation and calculating the "apparent" amount of nitric oxide which would be absorbed by the 0.465 gram of lead peroxide used by Lindner gives 32.6 cc.; Lindner found that 32 cc. were absorbed.

The above equation includes the mechanism suggested by Sabatier and Senderens and also yields the final product which they claim is formed in aqueous suspension. While Auden and Fowler claim that a basic lead nitrate is formed in this reaction, they give no details of their experimental procedure. Since lead nitrite is said to be extremely unstable, it is possible that during the isolation of their product the basic nitrite was oxidized to basic nitrate. Finally, the formation of a basic nitrite could account for the harmful influence nitric oxide has upon lead peroxide in its effect on the determination of carbon, as pointed out by Lindner.

Using the above equation for the calculation of the results and including only data in which the nitric oxide absorption had become constant, yield the results shown in Table II. The fact that, with the exception of the last experiment, the percentages do not reach 100, may be explained as due to in-

complete absorption of the nitric oxide by the lead peroxide. The incomplete absorption of nitric oxide by lead peroxide, when in contact for relatively short periods, agrees with qualitative statements of previous investigators. The value in excess of 100 per cent, obtained in Experiment 20, is probably due to adsorption effects.

Nitric Oxide Swept with Oxygen

In these experiments the procedure was exactly the same as described above except that oxygen was used for sweeping. When the nitric oxide was added to the combustion tube from the gas pipet brown vapors could be seen at the point where the two gases came into contact. These experiments have much more significance, as regards comparison with conditions which actually exist during a combustion, than those already described, since nitrogen peroxide is a much more likely end product from a properly conducted combustion of a nitrogen-containing compound (14) than is nitric oxide.

Results

The results of the nitrogen peroxide experiments are given in Table III. Before starting this series of experiments the lead peroxide absorption tube was conditioned with oxygen as already described. In contrast to the nitric oxide experiments, the first experiment with nitrogen peroxide yields an increase in weight of the lead peroxide tube which is of the same order of magnitude as the later ones.

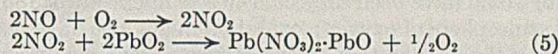
TABLE III. NITROGEN PEROXIDE-LEAD PEROXIDE REACTION

Expt. No.	Time for addition		Nitric Oxide					Increase, PbO ₂ Absorption Tube	%
	Min.	Mm. Hg	Temp. ° C.	Volume added N. T. P. Cc.	Weight added Mg.	NO ₂ Weight added Mg.	Mg.		
1	11	744.8	32.1	1.756	2.354	3.609	3.057	84.70	
2	14	743.8	33.7	1.745	2.339	3.585	3.026	84.40	
3	11	743.6	32.9	1.749	2.344	3.594	3.132	87.15	
4	10	742.6	29.8	1.765	2.365	3.626	3.034	83.68	
5	15	741.8	30.2	1.760	2.359	3.617	3.024	83.61	
6	10	740.8	31.0	1.753	2.350	3.603	3.077	85.41	
Combustion Tube at Room Temperature									
7	12	737.8	28.8	1.759	2.357	3.614	2.627	72.69	
8	12	737.6	29.3	1.756	2.353	3.607	3.108	86.16	
9	10	736.5	30.3	1.747	2.342	3.590	3.262	90.86	
Combustion Tube Heated after Absorption Tube Reattached; No NO Added									
10	0.962	..	

After obtaining the above data the next step was to find an equation which would fit. Since the increase in weight of the lead peroxide tube never equaled the weight of nitrogen peroxide added, which was recently confirmed by Friedrich (11), it was apparent that the reaction is not as simple as Equation 3 above, given by Dennstedt, would indicate. Kopfer and also Dennstedt state that (neutral) lead nitrate is formed according to Equation 3, but they give no experimental proof of the fact, although Dennstedt claims that the lead nitrate could be extracted from the lead peroxide with a 33 per cent alcohol solution and the weight of the material thus extracted agreed with the increase in weight of the lead peroxide when calculated as lead nitrate. However, he did not prove that the residue left on evaporation of the extract was really lead nitrate. Hermann (12) pointed out the possibility of a reaction between lead peroxide and alcohol during this extraction process.

After the entire series of experiments was completed, the water in the Mariotte bottle was again tested for oxides of nitrogen with diphenylamine-sulfuric acid and only a trace found to be present. However, on dissolving the contents of the P₂O₅-pumice protection tube in water, the solution gave a strong test for oxides of nitrogen.

The following equation was found to explain satisfactorily the reaction which occurred between the nitrogen peroxide and the lead peroxide:



According to this equation the net gain in weight of the lead peroxide corresponds to about 85 per cent of the total weight of nitrogen peroxide added. Table IV gives the results of calculations based on the above equation. Since the first experiment made with the combustion tube at room temperature (Experiment 7) yielded a value lower than the rest, it was suspected that nitrogen peroxide or nitrogen tetroxide was adsorbed or absorbed on the catalyst. In order to verify this suspicion the lead peroxide tube, after being weighed at the end of Experiment 9, was again attached to the combustion tube which was then heated and, after it had attained its full temperature, oxygen was passed through as in a normal experiment. The lead peroxide tube gained 0.962 mg., which is somewhat higher than the deficit shown by Experiment 7 but definitely shows that nitrogen peroxide was present in the combustion tube.

TABLE IV. NITROGEN PEROXIDE-LEAD PEROXIDE REACTION

Expt. No.	Nitrogen Peroxide		Found Theoretical %
	Theoretical Mg.	Found Mg.	
1	2.982	3.057	102.5
2	2.962	3.026	102.2
3	2.969	3.132	105.5
4	2.995	3.034	101.3
5	2.988	3.024	101.2
6	2.976	3.077	103.4
Combustion Tube at Room Temperature			
7	2.986	2.627	87.98
8	2.980	3.108	104.3
9	2.966	3.262	110.0

In order to get some information as to whether the above reaction products were nitrites or nitrates, the lead peroxide was removed from the absorption tube after all the above experiments were completed and extracted three times with 75-cc. portions of a 33 per cent alcohol solution. The extracts were filtered and evaporated to dryness at room temperature by blowing filtered air into the beakers containing them. The successive fractions yielded practically white, crystalline residues, the weights of the fractions being, respectively, I = 150 mg., II = 101 mg., III = 22 mg., a total of 273 mg. Summing up the individual increases in weight of the lead peroxide tube in all the experiments and calculating the amount of lead nitrite which would have been formed according to Equation 4 in the nitric oxide-nitrogen experiments yielded 96.83 mg., while in the nitric oxide-oxygen experiments the amount of lead nitrate, formed according to Equation 5, was calculated and yielded 156.24 mg., a total increase in weight of 253.07 mg. If lead nitrate and not lead nitrite was the product ultimately formed in the nitric oxide-nitrogen experiments, the increase in weight would theoretically be 107.19 mg., making the total 263.43 mg., which agrees fairly well with the 273-mg. increase in weight actually found. This confirms roughly Dennstedt's statement that the weight of product isolated by extraction agrees with the increase in weight of the lead peroxide calculated as lead nitrate.

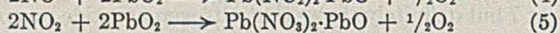
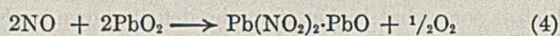
During evaporation of the solvent the substance extracted undergoes some change, for it was found that the residues were insoluble in the solvent originally used to extract them and were also insoluble in distilled water. When put into suspension, acidified with sulfuric acid, warmed to 40° C., and titrated with 0.1 N potassium permanganate only a few drops of the permanganate were reduced, so that only traces of nitrite could be present. It is, of course, possible that a lead nitrite was formed in the nitric oxide experiments and subse-

quently oxidized to nitrate during the conditioning of the lead peroxide tube in preparation for the nitrogen peroxide experiments, or during the latter experiments, at which time the nitrite would have been subjected to a temperature of 185°C. in an atmosphere of oxygen; oxidation might also have occurred during the evaporation of the solvent in the air stream. It also appears that during the evaporation of the solvent, the lead nitrate (if that is what was extracted, which is the opinion of Dennstedt) was converted to a basic nitrate which was no longer soluble in the solvent in which it was originally soluble.

Summary

1. A quantitative study has been made of the reaction between nitrogen peroxide (also nitric oxide) and lead peroxide under conditions similar to those existing in microcombustions.

2. Previous equations given to represent these reactions do not fit the experimental facts. The following equations agree best with the data obtained in the present work:



Equation 4 also agrees with quantitative data obtained by Lindner.

3. The increase in weight of the lead peroxide, calculated as lead nitrate according to Equations 4 and 5, agrees roughly with the weight of product extracted from it by a 33 per cent alcohol solution and confirms Dennstedt's statement to this effect. However, the residue which is weighed does not appear to be lead nitrate, as claimed by Dennstedt, since it is not soluble in the solvent used to extract it, after the original solvent is removed. The presence of nitrite, beyond a trace,

could not be detected in the residue, although it is possible that any nitrite originally formed was oxidized to nitrate before or during attempts at isolation.

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Identification of Sulfanilamide

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RECENTLY quantitative methods for the colorimetric determination of sulfanilamide in biological media have been reported (8, 12, 13, 17). Since these are diazotization procedures and will not differentiate arylamines, a method involving the use of sodium hypochlorite was suggested (17) to distinguish para-substituted amines from other aromatic amines. None of these methods is entirely specific, and since the drug has been found to possess toxic properties and fatalities have been reported as a result of its administration (1, 2, 7, 14, 15, 19), it was considered essential for toxicological purposes to devise microscopic tests by which the presence of sulfanilamide could be conclusively demonstrated.

It has been pointed out (18) that sulfanilamide is a variant vinylog of urea, giving an analogous dixanthyl derivative. This reaction is slow, and crystallization does not occur from solutions containing 100 mg. per cent of the drug when treated according to the method of Fosse (6). Like urea, sulfanilamide undergoes a formal condensation in neutral and slightly alkaline media. The product appears to be a polymer of the urea-formaldehyde type. This reaction is applicable to dilute solutions, the condensation of 10 to 15 gamma of sulfanilamide being visible microscopically. Using one drop (0.04 cc.) of sulfanilamide solution (50 mg. per cent) crystals of 1-amino-2, 6-diiodobenzene-4-sulfonamide (16) may be

prepared. Crystals of the picrate may be prepared through hydrochloride formation, using one drop of 30 mg. per cent solution or less.

Fuller (8) isolated sulfanilamide from urine as the highly insoluble mercury salt. Using 0.50 cc. of aqueous sulfanilamide and 0.30 cc. of standard dilute Nessler's reagent, precipitations occurred in 1 to 5 minutes at and above concentrations of 60 mg. per cent. At a concentration of 40 mg. per cent, a turbidity occurred on standing for 12 hours, whereas at lower concentrations the solutions remained clear. Dilute solutions of the drug may be titrated with mercuric nitrate as in the Liebig method (11) for the determination of urea. The precipitation is such that gravimetric methods may be employed, or the precipitate may be dissolved in dilute acid and the sulfanilamide determined colorimetrically by diazotization procedures. (At concentrations of 0.5 to 2.0 mg. per cent, the mercury does not interfere with the color formation.) Microscopically, the crystals obtained are very small, somewhat transparent, and highly flocculated. It was not found possible to single out crystals of clear definition. However, the precipitation of as little as 10 to 15 gamma of sulfanilamide may be observed, preferably in a dark field.

Sulfanilamide forms a silver salt, but it was not found

practicable to reduce this procedure to microscopic proportions. Like other aromatic amines, sulfanilamide is oxidized with the formation of evanescent colors by the action of ammonium persulfate. This color is stabilized somewhat by the presence of silver ions (3). It is deep pink-yellow at 10 but negligible at 1.0 mg. per cent. The color fades within half an hour.

Boiling solutions of the drug with one-tenth of a volume of concentrated nitric acid gave a faint yellow color which became intensified upon the addition of sodium hydroxide to alkalinity. This color is due to a soluble substance which exhibits a nitrolic acid type of tautomerism. It was very intense for solutions containing 100 grams per cent, intense at 10, but negligible at 1 mg. per cent of the drug. Erdmann's reagent gives the same color phenomena, due presumably to the same nitration processes.

Like aniline, sulfanilamide forms a urea derivative when treated according to the method of Davis and Blanchard (4). It was not found practicable to reduce this reaction to micro dimensions according to the method of Emich (5). Minute amounts of the crystalline substance treated with a drop of acetic anhydride in the cold on a microscope slide are converted to crystals of the acetylsulfanilamide. However, if 2 drops of acetic anhydride are used and the reaction mixture is boiled over a micro flame, needles of the diacetylsulfanilamide separate in cooling. Two or three milligrams suffice for these tests.

Experimental

FORMOL CONDENSATION. One drop (0.04 cc.) of 100 mg. per cent sulfanilamide solution, 1 drop of 40 per cent formalin, and 1 drop of 10 per cent sodium carbonate were mixed on a microscope slide and the mixture was evaporated to dryness on a water bath. The residue was extracted with 2-drop portions of warm water until free of soluble salts. The product (m. p. 235–240° C. decomposition) appeared as transparent spheres at high magnifications. It was soluble in caustic and warm concentrated hydrochloric acid. The test is sensitive to one drop of 30 mg. per cent solution, or 12 gamma. The product prepared in 0.01 M amounts by the method of Hug (10) appears to be the urea-formaldehyde type, although molecular weight determinations were unsuccessful because of the insolubility of the product. Calculated for $(C_8H_8O_2SN_2)_x$: N = 14.29. Found: N = 14.40.

1-AMINO-2,6-DIODOBENZENE-4-SULFONAMIDE. One drop of sulfanilamide solution (50 to 100 mg. per cent) and 1 drop of iodine monochloride solution were evaporated to dryness. A drop of water was added to dryness and a second drop of hot water was added, stirred, and drawn off with absorbent filter paper. Alkali-soluble, water- and acid-insoluble needles were obtained (m. p. 265° C. decomposition, 16). Purification was repeated when the crystals were colored, and occasionally it was necessary to evaporate the product with a drop of dilute alcohol to obtain good crystals. The iodine monochloride solution was prepared by adding slowly and with stirring 6.6 grams of sodium iodate to 11.0 grams of potassium iodide in 85 cc. of 6 N hydrochloric acid.

PICRATE. One drop of concentrated hydrochloric acid and 1 drop of sulfanilamide solution were evaporated to dryness. The hydrochloride (9, m. p. 235–237° C.) was converted to the picrate by the addition of a small drop of saturated picric acid solution. The test is sensitive to 1 drop of 30 mg. per cent solution: long yellow needles (m. p. 179–180° C.). Calculated for $C_{12}H_{11}O_9N_2S$: N = 17.45. Found: N = 17.28, 17.37.

MERCURY SALT. To one drop (0.04 cc.) of sulfanilamide solution and 1 drop of mercuric nitrate solution, 1 drop of 10 per cent sodium carbonate was added. A highly flocculated, transparent, white precipitate formed. The particles were extremely small. It was not found possible to single out crystals of good definition. The test is best performed in a dark field or against a black background. Macroscopically the substance has a yellow tint. It dissolves in dilute acids and the sulfanilamide amino group may be diazotized.

The mercuric nitrate reagent was prepared by dissolving a small amount in water with sufficient nitric acid to prevent precipitation upon dilution. It was then diluted until, when mixed with an equal volume of 100 mg. per cent sulfanilamide, it gave a pure white precipitate upon the addition of sodium carbonate (10 per cent). At this dilution, addition of sodium carbonate to

the reagent alone imparted only a slightly yellow tinge to the solution.

SILVER SALT. One mole of sulfanilamide (0.400 gram) and 1 mole of silver nitrate were dissolved in 120 cc. of water and 2 drops of concentrated ammonium hydroxide were added. A white precipitation occurred. The reaction mixture was boiled and filtered hot and on cooling white needles separated. The yield was 0.280 gram or 43 per cent. Calculated for $C_8H_7O_2N_2S_2Ag$: Ag = 38.70. Found: Ag = 38.28.

DI-(p-SULFAMIDOPHENYL)UREA. Treatment of sulfanilamide hydrochloride with urea, according to the method of Davis and Blanchard (4) gave poor yields of the product. The yields were increased slightly upon prolonged treatment, with renewal of urea. The product is soluble in caustic, insoluble in acids, and may be hydrolyzed by hot acids, liberating sulfanilamide: white needles (m. p. 270–271° C. decomposition). Calculated for $C_{13}H_{14}O_5S_2N_4$: N = 15.13. Found: N = 15.12, 15.00, 15.12.

DIACETYSULFANILAMIDE. A few small crystals of sulfanilamide treated on a microscope slide with a drop of acetic anhydride were observed to change to the acetylsulfanilamide. Washed with ether, the product (16) melted at 214° C. When 2 acetic anhydride were used and the mixture was boiled over a drop of microflame, crystals of the diacetylsulfanilamide separated on cooling. Washed with ether the product, white needles, melted at 240–242° C. with decomposition.

In macroscopic amounts the sulfanilamide was boiled for 10 minutes in an excess of acetic anhydride. The product did not diazotize. Hydrolysis at 100° C. with 2 N hydrochloric acid liberated sulfanilamide. Recrystallized from dilute alcohol (m. p. 244° C. decomposition). Calculated for $C_{10}H_{12}O_2SN_2$: N = 10.94. Found: N = 10.64.

Summary

The reactions of sulfanilamide with formalin, iodine monochloride, picric acid, and various mercuric salts have been reduced to microscopic proportions and by means of these as little as 10 to 40 gamma of sulfanilamide may be identified. Sulfanilamide has been found to undergo a phenol-like reaction with nitric acid. Ammonium persulfate has been observed to produce evanescent colors with the drug, and this color has been stabilized somewhat by the presence of silver ions. Diacetylsulfanilamide and di-(p-sulfamidophenyl)urea have been prepared.

Acknowledgment

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An Improved Capillary Clamp

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IN MANY microchemical procedures it frequently becomes necessary to measure the diameter of glass tubing or capillaries—the test tubes of the microchemist—with a high degree of accuracy. To make this measurement, the object is placed vertically in the optical axis of the microscope and the diameter is determined with a previously calibrated micrometer eyepiece. If such measurements are made frequently—in routine analyses or in courses on microtechnic (2, 4, 5)—the use of a special capillary clamp is recommended which facilitates the mounting of the object. Such holders have been described (2, 4, 5); Figure 1 shows an improved design. (This capillary clamp is obtainable from the Arthur H. Thomas Co., Philadelphia, Pa.)

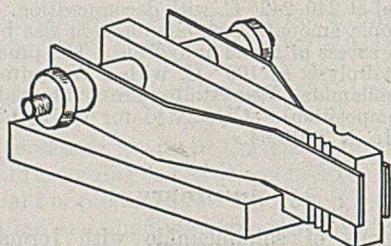


FIGURE 1

The advantages of this inexpensive clamp of nickel-plated brass over previous forms are as follows: The heavy trapezoidal base plate stabilizes the clamp, so that the tendency towards tilting is considerably reduced, even if heavier objects have to be supported, such as Pregl's absorption tubes, in which the dimensions of the capillary endings must be accurately verified (2, p. 227). The dimensions of this base plate are chosen in accordance with the average dimensions of the ordinary rotating microscope stages. The side screws allow a fine adjustment of the pressure exerted by the spring clamps against the capillaries. Objects of different diameters are held safely; the single groove on the back (Figure 1) has a diameter of 2 mm. and serves to clamp tubes of diameters up to 10 mm.; the 3 fine grooves, 0.8 mm. in diameter

and the same distance apart, hold smaller objects of diameters below 2 mm. As the spring exerts only a slight pressure against the horizontal arm, which is 13 mm. high and 4 mm. thick, thin-walled capillaries, 0.3 mm. or less in outside diameter, are not bent, a condition which would interfere with the passage of the light beam, at least in some instances. For extremely fine objects, such as fibers, capillary rods, etc., a thin piece of rubber sheet is placed over the grooves as a cushion. The spring clamps are easily renewed if they lose their elasticity.

The numerous possible applications include: determination of the bore of capillaries used for all qualitative experiments (4, p. 36; 5); observation of the color of liquids in capillaries (coloriscopic capillary, 2, p. 226; 4, p. 93; 5); comparison of three colors by means of the three grooves, thus eliminating any doubtful observations in sensitive color tests where the reagent itself has a slight color (blank tests in Feigl's spot tests); standardization of capillary pipets used in Emich's *schlieren* experiments (4, p. 46; 5, p. 40); holding of needle electrodes during the observation of metallic deposits; and control of further manipulations (1; 2, p. 236).

Recently (3), this clamp has rendered excellent service in determining the extremely small bore at the fine tip of weighing capillaries used when liquids of high vapor pressure or high hygroscopicity are to be weighed for quantitative milligram procedures. According to the experience of the author, the bores must be within the range of 0.03 to 0.05 mm. to prevent any evaporation or moisture absorption during the weighing procedure, since these capillaries should not be sealed.

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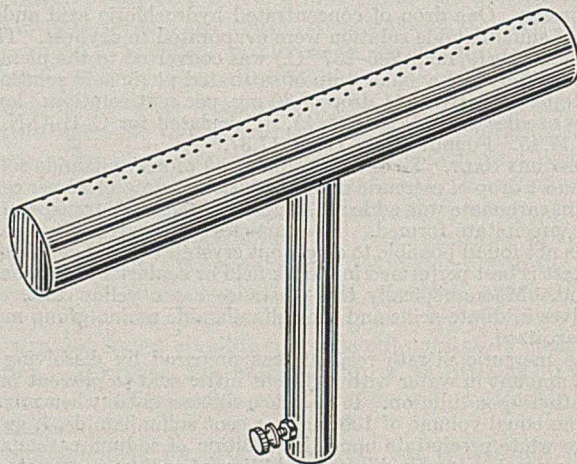
A "Long Burner" Adapter for Bunsen Burners

ALEXANDER KNOLL AND JOHN SCHUKAL, Department of Chemistry, Columbia University, New York, N. Y.

THE adapter pictured here fits over the barrel of a Tirrill or other type of Bunsen burner, and may be used in place of the common "long burner" in the micro and semimicro combustion methods of ultimate organic analysis and for bending glass tubing of large diameter. It is inexpensive and easily regulated as to size of flame and height. It will burn natural gas and water gas satisfactorily.

It consists of a brass pipe of standard 0.094-inch stock, 7 inches long and 1 inch in outside diameter. The ends of the pipe are closed flush by means of two brazed caps. Two rows of thirty-six holes 0.056 inch in diameter and 0.19 inch apart are drilled along the top of the burner piece.

The barrel, of 0.094-inch stock is 4.5 inches long and about 0.5 inch in inside diameter. It is threaded and soldered into the bottom of the burner piece at the center. A set screw near the bottom of the barrel allows adjustment of the height.



RECEIVED March 8, 1938.

The advertisement features two large books standing upright. The book on the left is titled "SCIENTIFIC LABORATORY APPARATUS" and is labeled "CATALOG No. 50". The book on the right is titled "CHEMICAL REAGENTS" and is labeled "CATALOG No. 55". Both books are published by "E.H. SARGENT AND CO. CHICAGO, U.S.A.". In the foreground, a tilted sign reads "SARGENT LABORATORY SUPPLIES, E.H. SARGENT AND COMPANY, 155 EAST SUPERIOR ST., CHICAGO". The background is a circular vignette showing various pieces of laboratory glassware, including flasks, beakers, and a burette.

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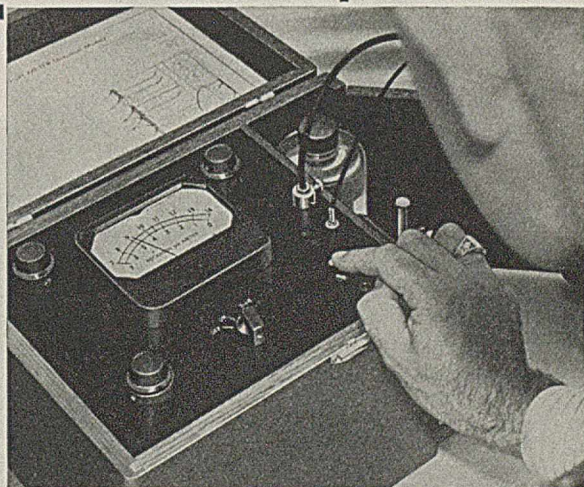
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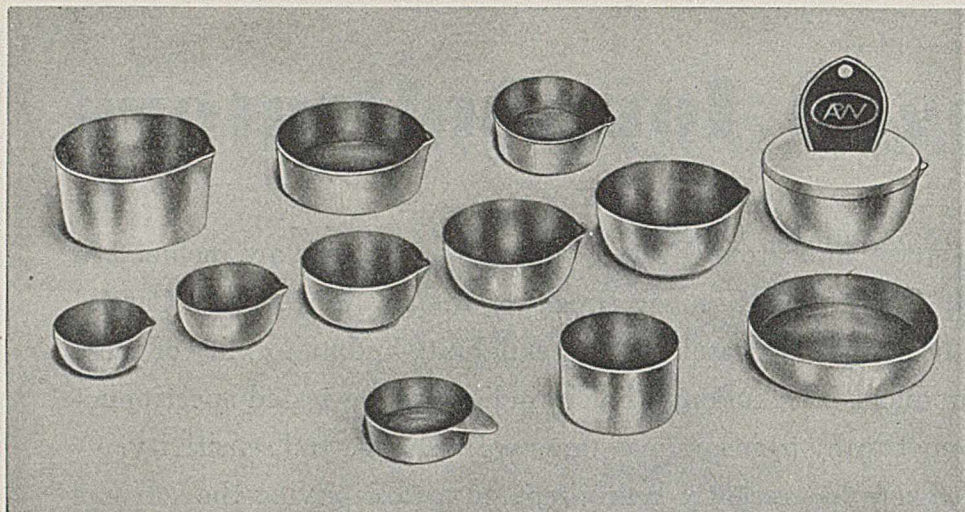
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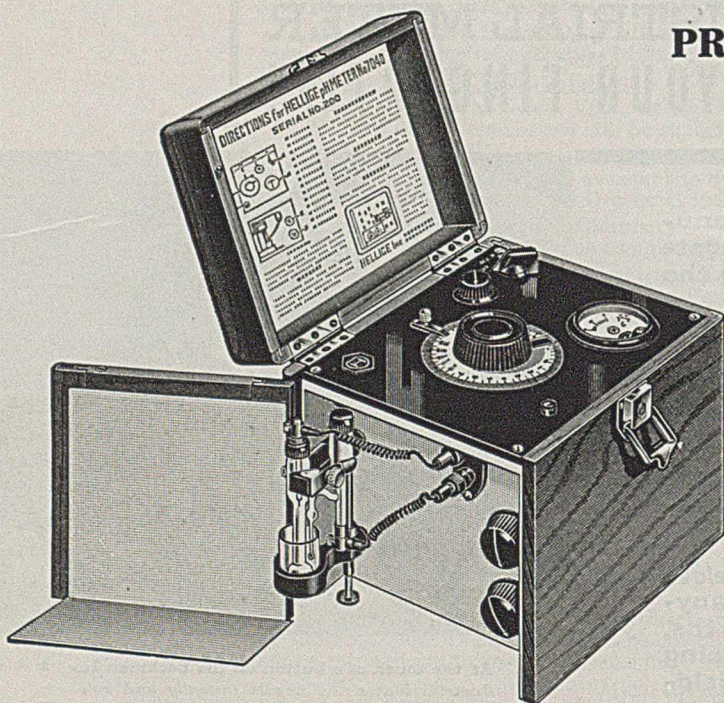
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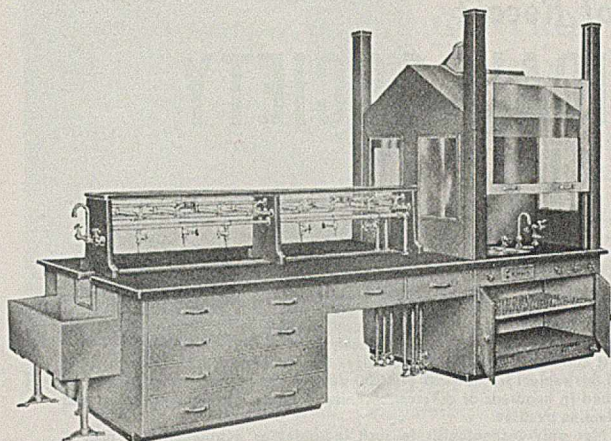
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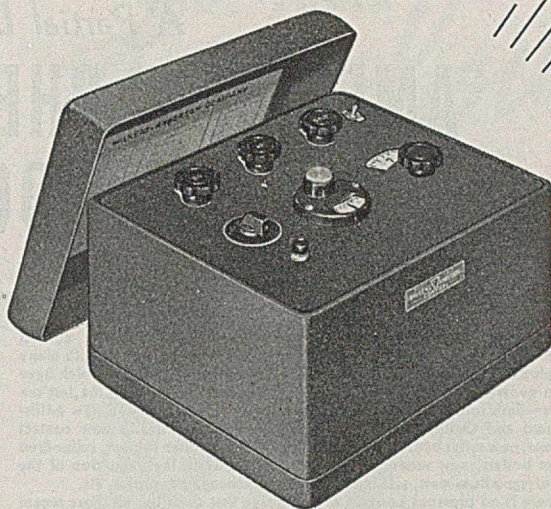
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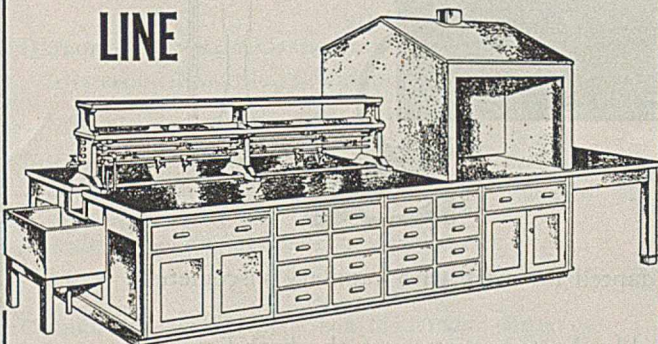
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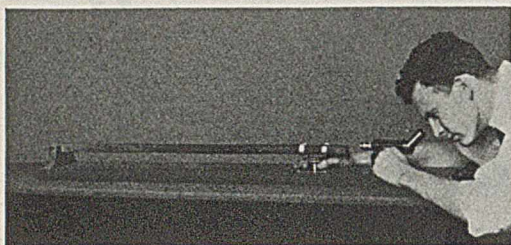
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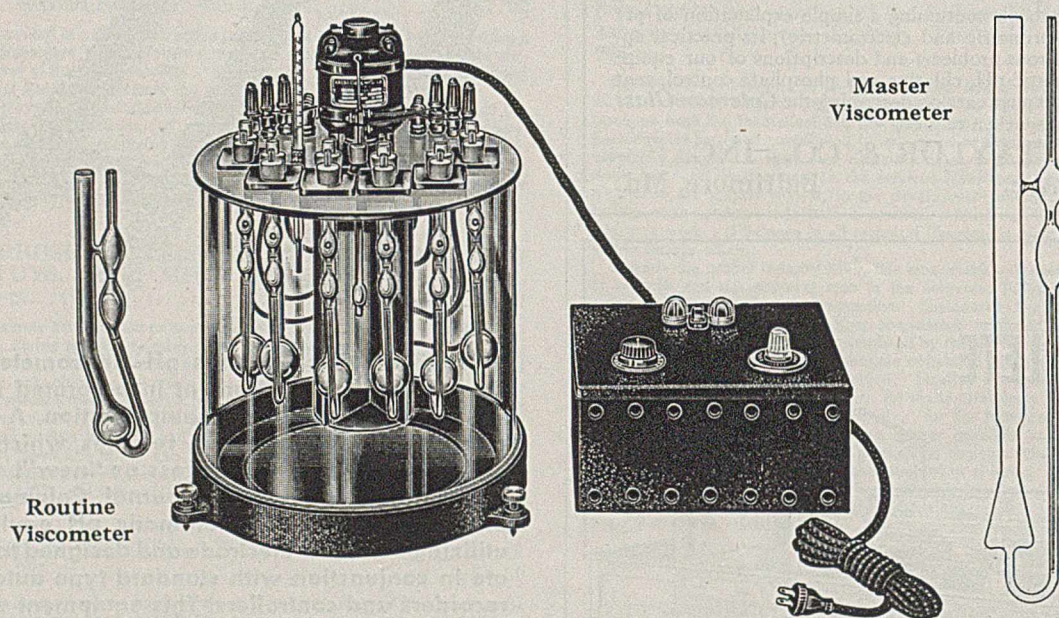
Oil & Gas Journal, Vol. 34, No. 47, April 9, 1936. Page 45.

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