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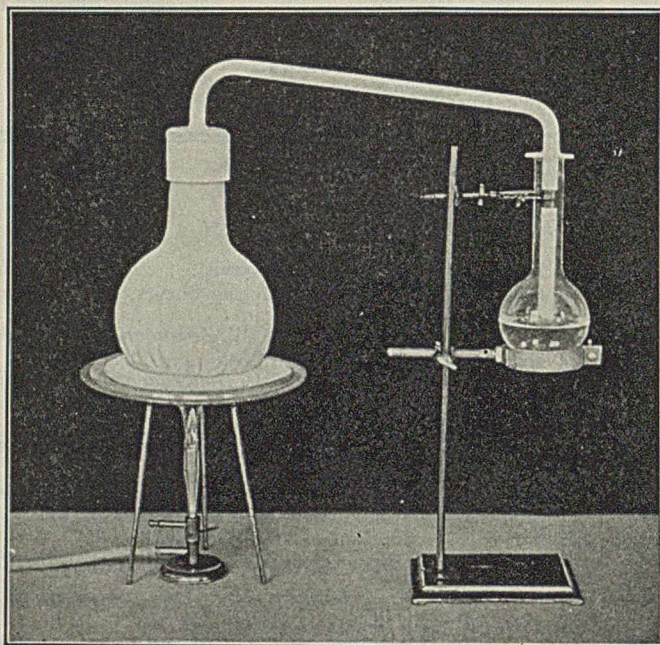
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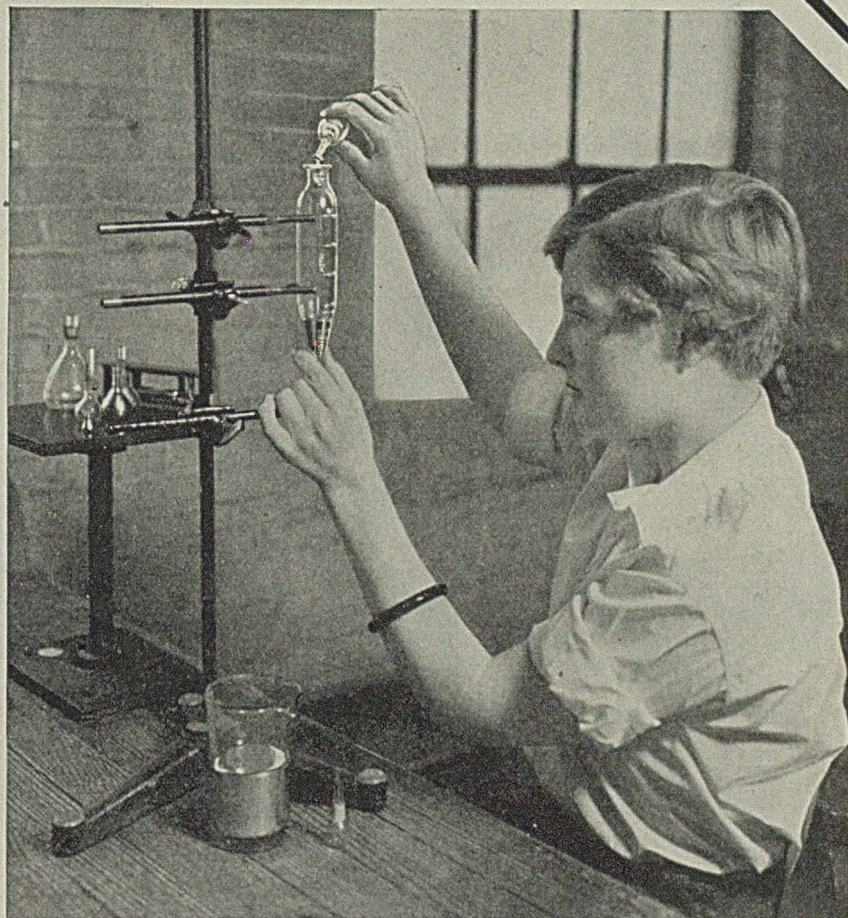
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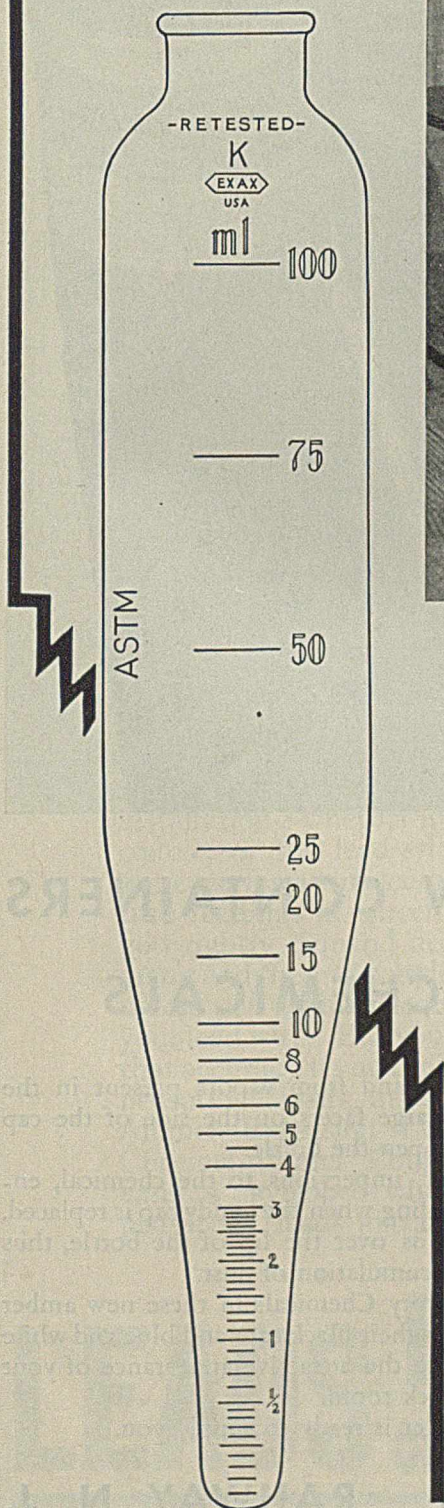
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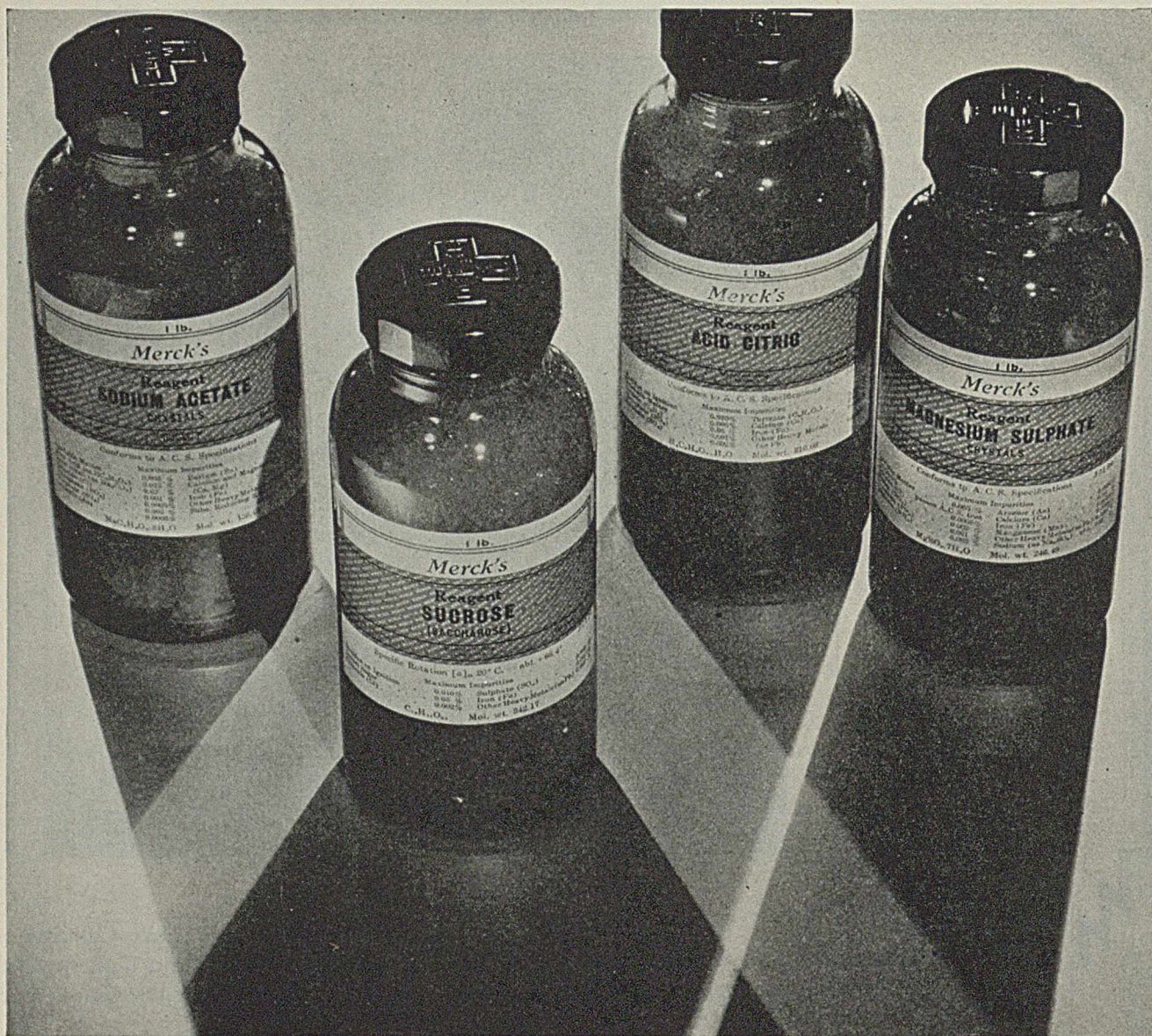
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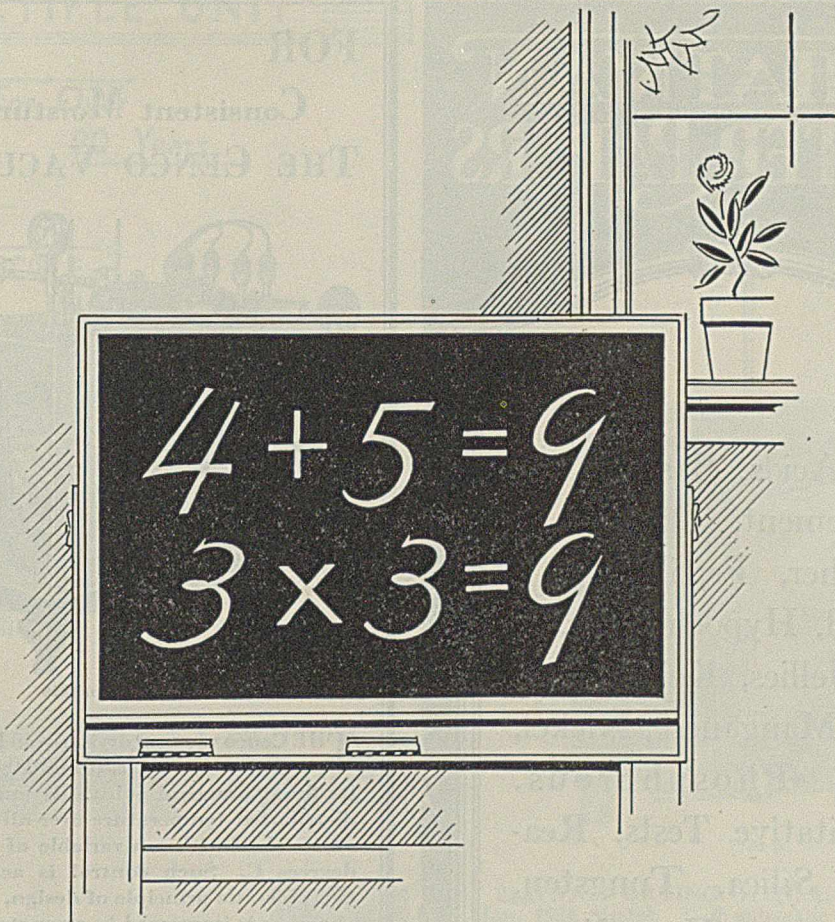
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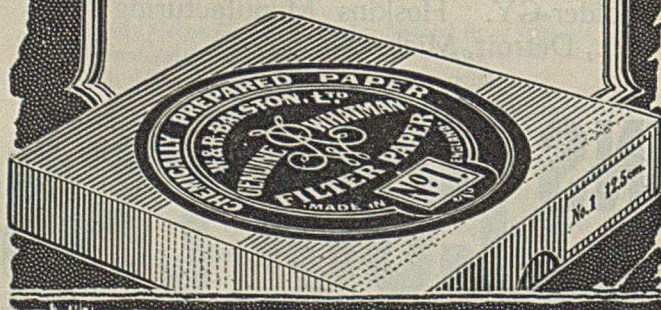
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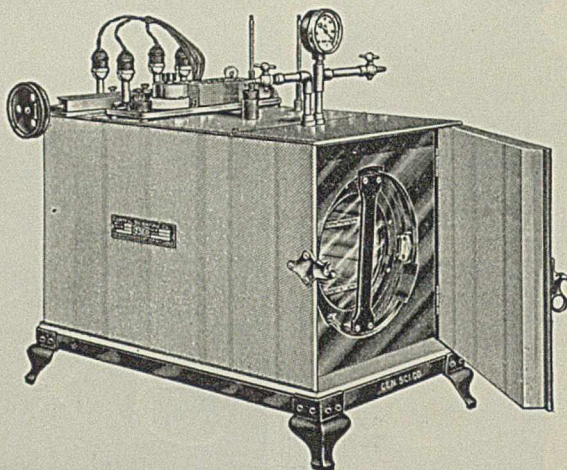
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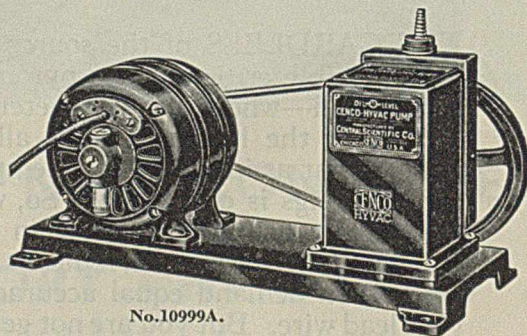
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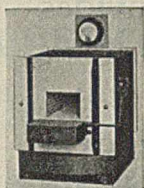
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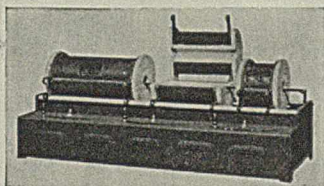


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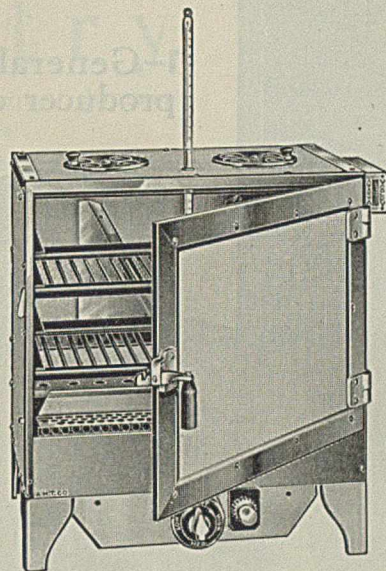
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Cl0005%
NO ₃001%
SO ₄001%
Fe0005%
H. M. (as Pb)0005%

NH₄Cl

MAXIMUM LIMITS OF IMPURITIES

Insoluble in H ₂ O005%
Nonvolatile015%
Neutrality	Passes Test
PO ₄0003%
SO ₄002%
Ca & Mg ppt002%
Fe0005%
H. M. (as Pb)0005%

$(\text{NH}_4)_2\text{SO}_4$

MAXIMUM LIMITS OF IMPURITIES

Insoluble in H ₂ O005%
Nonvolatile010%
Neutrality	Passes Test
Cl0005%
NO ₃001%
PO ₄0005%
As0005%
Fe0005%
H. M. (as Pb)0005%

NH₄NO₃

MAXIMUM LIMITS OF IMPURITIES

Insoluble in H ₂ O005%
Nonvolatile010%
Free Acid	Passes Test
Cl0005%
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Measurement of Quality in Rubber Goods by Physical Tests

ARTHUR W. CARPENTER, B. F. Goodrich Company, Akron, Ohio

THE expression "measurement of quality" as applied to rubber goods seems at first thought to be quite definite; unfortunately, it conveys to different persons widely divergent ideas. Engineers in dealing with various materials often interpret the word "quality" as being synonymous with strength. Such usage is quite common in the rubber industry, and stocks possessing high tensile strength may be designated as high quality. A rubber compounder, on the other hand, may consider the quality of a rubber compound to be related to the percentage of pure rubber contained in the mixture. Thus, compounds having only small amounts of other materials added to the rubber would be considered high grade though they might be inferior in strength. Purchasers of rubber products have in the past shared both of these viewpoints, but today the more enlightened consumers understand the expression "high quality" to indicate the relative excellence of an article in performance of the intended service. This seems a more rational interpretation since, in the last analysis, satisfactory service is the prime objective and may or may not be affected by either great strength or high rubber content.

While quality of rubber articles in terms of strength or rubber content is comparatively easy to measure in the laboratory, and fairly satisfactory methods have long been more or less standardized, adequate laboratory evaluation of service behavior is quite another matter. Definition of quality on the basis of performance in service has therefore necessitated the development of new test methods. The older tests for particular properties which are still indispensable for the control of uniformity have been supplanted in product evaluation to a considerable degree by tests directly related to the service conditions. Just as the varieties of articles and types of service cover a tremendous field, so too these performance tests are exceedingly diverse and may

Physical tests of rubber products may be classed in two groups—those which measure fundamental physical properties and those which determine service value. Performance tests of the latter class present many difficulties in their proper design and in the interpretation and correlation of the results. Often the value of a performance test is lost because of careless and incomplete mechanical analysis of the factors involved in the test and in the service of the article. Some of these factors are discussed and a number of performance tests are described. Data are presented showing the effect of the dual plastic and elastic nature of vulcanized rubber on the testing of indentation hardness. A time study is given of actual rate of stretching dumb-bell specimens in standard tensile testing.

be quite simple for some products or highly specialized and complex for others. Some rubber articles are really structures requiring as complicated engineering as the building of a skyscraper, and the play of forces within them in service may be more complex and less capable of complete analysis than the stresses in the skyscraper. Testing such products involves more than merely the measurement of quality of the rubber compounds. Careful and complete analysis of both the structure and the service is necessary, after which development of a suitable test is worthy of the very best engineering thought.

TYPES OF PHYSICAL TESTS

The physical tests ordinarily made on rubber products may be considered as being in one of two classes, the first consisting of those which are designed to measure fundamental physical properties, and the second, those tests which aim to determine service value. Obviously no such classification can be rigid, for in many cases a certain particular physical property may govern the fitness of an article for service. The first class would include measurement of dimensions, of specific gravity, of tensile strength and ultimate elongation or the stress-strain relationship, of compressive strength and the relation between load and deflection, of hardness and resilience, of permanent set, color, dielectric strength, coefficient of friction, and the like. In the second class would be included tests for aging, adhesion, resistance to abrasive wear including tearing and cutting, fatigue tests of various kinds involving repeated applications of stress producing either extension, compression, or flexure, as well as a countless variety of service tests which represent attempts to imitate the actual service under laboratory conditions in such a way that accelerated results may be secured.

The need for laboratory tests capable of giving information rapidly from which the behavior in service of rubber articles

can be reliably predicted and the difficulties which have arisen in such use of present tests have been frequently emphasized. Bierer and Davis (1) pointed out the failure of

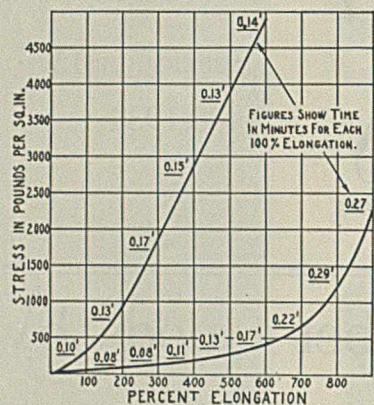


FIGURE 1. RATE OF STRETCHING OF DUMB-BELL SPECIMENS BETWEEN ONE-INCH BENCH MARKS

over the older tests. Dinsmore (2) has given a number of instructive examples showing the inadequacy and unreliability of the usual laboratory methods for the prediction of service performance. He selected stress-strain data, abrasion test results, and certain flexing tests, and referred to aging tests although various other tests might also, as he observed, have been included. He cited the variety of performance testing devices which have been developed in recent years as evidence that the need for better tests is well recognized and pointed out that such modifications as the work of Somerville and Russell (3) on testing rubber at higher

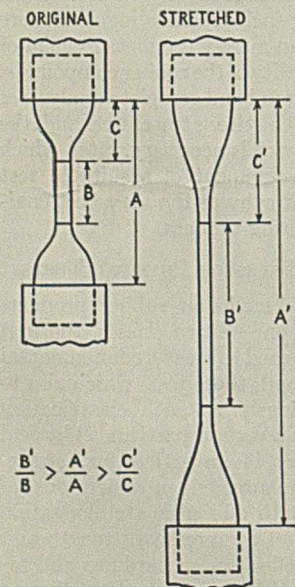


FIGURE 2. EFFECT OF DUMB-BELL ENDS ON RATE OF STRETCHING BETWEEN MARKS

which seems especially worthy of elaboration and emphasis: "More effective laboratory methods may result from careful mechanical analysis of the behavior of rubber products in service. Rubber chemists have naturally failed to appreciate the full value of mechanical studies but they must turn to the physicist for aid in their difficulties. A sound theoretical basis may serve materially to shorten the tedious search for

laboratory and service correlation. Certainly the haphazard development of new tests must lead but slowly to progress."

It would ordinarily be supposed that the oldest tests used for rubber products would have been thoroughly investigated and completely analyzed from a mechanical point of view. Two of these tests which were probably carried over from the field of the testing of metals are the measurement of tensile strength and elongation and the determination of hardness. Both of these have been used for more than a quarter of a century by rubber men and have been studied extensively. The lack of completeness of these studies can be illustrated by some data which were recently secured. In measuring tensile strength and elongation, it has usually been agreed that either

a uniform rate of application of load or a uniform rate of stretching is desirable for producing duplicable test conditions. Since machines for applying load uniformly would be considerably more complicated than those designed for uniform rate of jaw separation, the latter have quite generally been used. How serious any departure from uniform loading or uniform stretching might be in its effect on

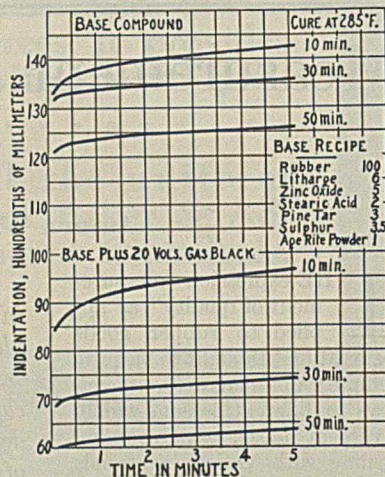


FIGURE 3. EFFECT OF DURATION OF LOADING OR UNIFORM STRETCHING ON INDENTATION HARDNESS (Pusey and Jones plastometer)

temperatures and that of Somerville, Ball, and Edland (5) on autographic stress-strain curves of rubber at low elongations, are steps in the right direction. Dinsmore further suggests that, since rubber is partly plastic and partly elastic slow deformation emphasizes its plastic properties while fast deformation develops more elasticity. High temperatures appear to increase the plasticity effect at slow speed and elasticity effect at higher speeds. Degree of vulcanization is also an important factor. He considers it likely that this dual nature of rubber is important in many tests, mentioning particularly stress-strain, fatigue, adhesion, and possibly abrasion. Finally, he expresses another thought

which seems especially worthy of elaboration and emphasis: "More effective laboratory methods may result from careful mechanical analysis of the behavior of rubber products in service. Rubber chemists have naturally failed to appreciate the full value of mechanical studies but they must turn to the physicist for aid in their difficulties. A sound theoretical basis may serve materially to shorten the tedious search for laboratory and service correlation. Certainly the haphazard development of new tests must lead but slowly to progress." It would ordinarily be supposed that the oldest tests used for rubber products would have been thoroughly investigated and completely analyzed from a mechanical point of view. Two of these tests which were probably carried over from the field of the testing of metals are the measurement of tensile strength and elongation and the determination of hardness. Both of these have been used for more than a quarter of a century by rubber men and have been studied extensively. The lack of completeness of these studies can be illustrated by some data which were recently secured. In measuring tensile strength and elongation, it has usually been agreed that either a uniform rate of application of load or a uniform rate of stretching is desirable for producing duplicable test conditions. Since machines for applying load uniformly would be considerably more complicated than those designed for uniform rate of jaw separation, the latter have quite generally been used. How serious any departure from uniform loading or uniform stretching might be in its effect on the final results is irrelevant in connection with the present question of mechanical analysis. Presumably, the tensile testing machines were intended to give uniform stretching since care has been taken in all specifications to require a uniform and standard rate of jaw separation. A study was made of the actual rate of the stretching of dumb-bell rubber samples between one-inch bench marks when tested in a type L-6 Scott tester. The machine was first carefully checked under load to be certain that the speed of lower jaw travel was uniform and independent of load. Stop-watch measurements of the time required for each 100 per cent elongation between the marks were made by two observers. The data are shown in Figure 1. The time for 100 per cent increments of extension between the bench marks is not uniform for a high-rubber stock having low modulus but increases from 0.08 minute at the start to a maximum of 0.29 minute. In the case of a high-modulus tread stock, the rate is very much more uniform. Evidently, then, the rate of elongation measured with bench marks and dumb-bell samples is influenced by the modulus of the sample. It is believed that the explanation rests in the stretching of the enlarged ends outside of the bench marks. When under sufficient stress these also yield, relieving the elongation of the portion between the marks. This effect is illustrated in Figure 2. While A increases to A' , B and C do not increase to B' and C' in the same ratio, and the extension of C lowers the rate of extension of B .

A simple study of two instruments for measuring indentation hardness again illustrates the lack of complete analysis in the case of even this very old test. It also adds weight to Dinsmore's view of the importance of the dual plastic and elastic nature of vulcanized rubber. Differences in relative

FIGURE 4 (RIGHT-HAND CORNER).
AUTOGRAPHIC MACHINE FOR MEASURING
ADHESION

FIGURE 5 (TOP CENTER). COMPRESSION-
DEFLECTION TEST OF A RUBBER
BEARING

FIGURE 6 (RIGHT CENTER). LABORATORY
TEST OF TREAD WEAR

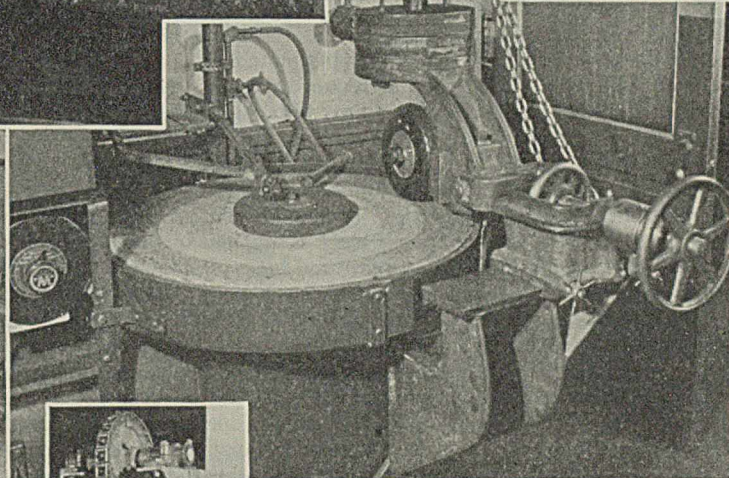
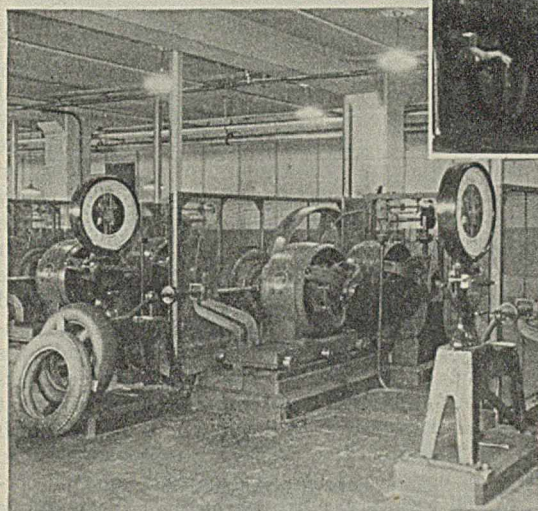
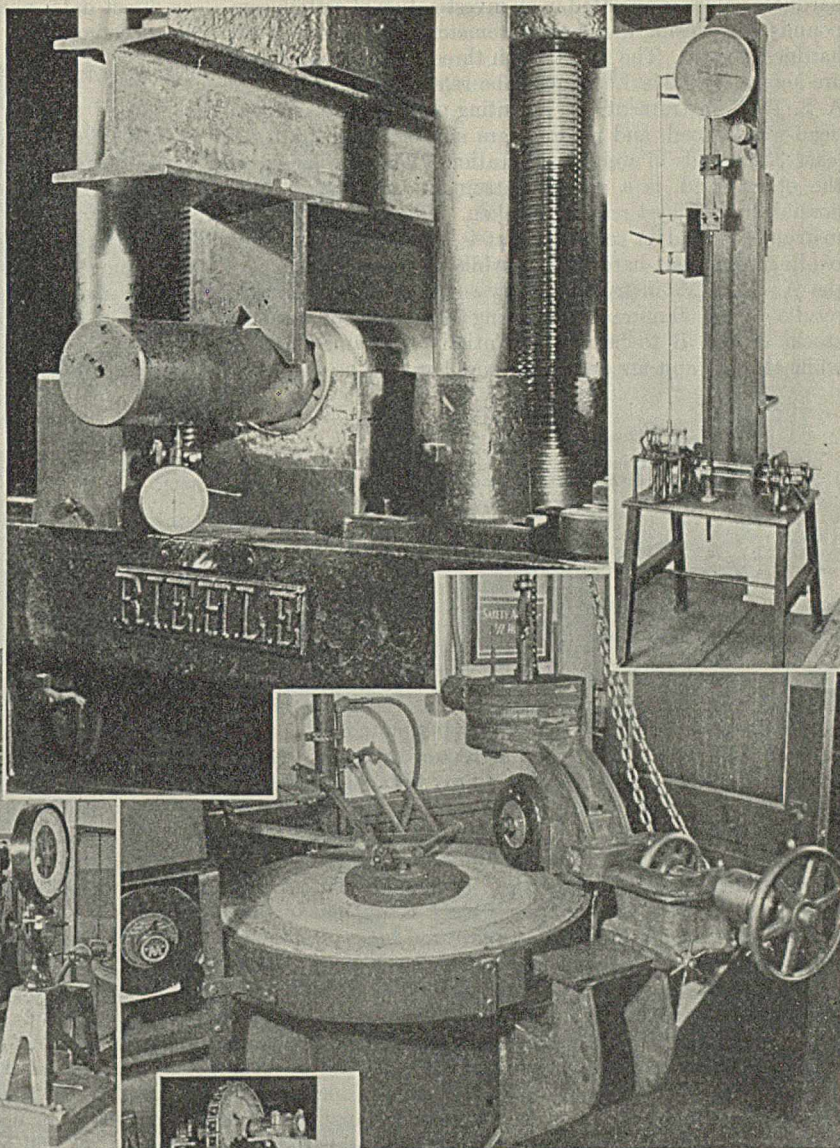
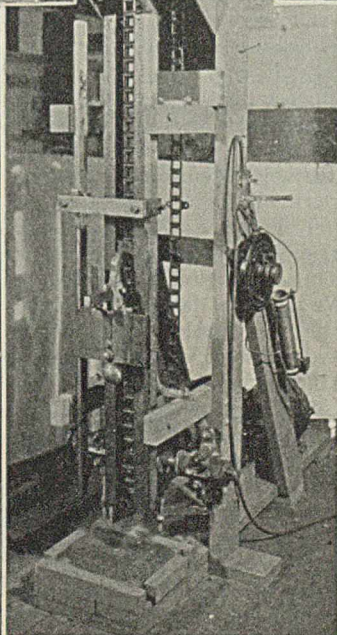
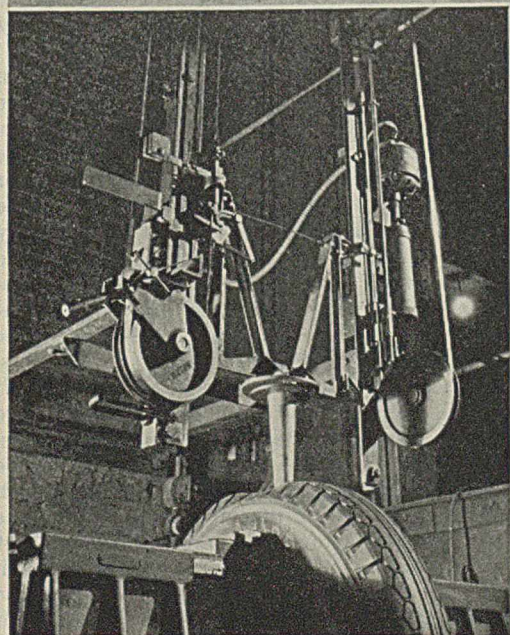


FIGURE 7 (LEFT CENTER). SPRAGUE
DYNAMOMETER FOR TIRE TESTING

FIGURE 8 (LEFT-HAND CORNER).
"GUILLOTINE" TEST OF A TIRE

FIGURE 9 (BOTTOM CENTER). DROP
HAMMER FOR IMPACT TESTS



hardness values were noted in an investigation of certain compounds when using the Shore durometer and the A. S. T. M. hardness tester. The results with three of these compounds are shown in Table I. It must be remembered that, in the A. S. T. M. instrument, the indenting point operates under a dead-weight load, and readings are not taken until after at least 30 seconds of weight application. The durometer, on the other hand, is a spring instrument, and the quickest possible and highest reading is taken. The scales of the two instruments read in reverse; that is, the higher durometer readings represent harder stock while the higher readings of the A. S. T. M. instrument show softer stock. Thus, the results on the 30-minute cures using the A. S. T. M. test show stocks A and B to be of substantially the same hardness while stock C appears decidedly more hard. The durometer

as direct data, must be assembled if the final estimate is to be a good one.

DIFFICULTIES IN CORRELATING LABORATORY AND SERVICE RESULTS

The difficulties which are experienced in correlating laboratory test results with service performance must be attributed to one or both of two causes. Either the tests themselves are improperly designed or the results secured from the tests are not correctly interpreted. Improper design is a frequent consequence of hasty, unsound analysis of the service which fails to give full knowledge and appreciation of all the conditions and forces that are involved. A fundamental requirement of good testing is that the service to be measured shall be first completely and accurately defined before attempting

TABLE I. COMPARISON OF A. S. T. M. AND DUROMETER HARDNESS

Stock	BEST CURE AT 280° F. Min.	SAMPLES AT BEST CURE			A. S. T. M. hardness	Durometer hardness	CURE, 30 MIN. AT 280° F.		
		Tensile strength Lb./sq. in.	Ultimate elongation %	Modulus at 300% elongation Lb./sq. in.			A. S. T. M. hardness	Durometer hardness	Permanent set, stretched ^a
A ^b	15	2650	660	600	125	39	78	50	34
B ^c	45	1570	400	950	69	59	75	57	60
C ^d	30	1070	425	650	69	56	65	58	25

^a 80 per cent of ultimate.

^b Stock A (parts by weight): rubber, 36.5; inner tube reclaim, 36.5; zinc oxide, 6.5; mineral rubber, 11.0; palm oil, 1.3; sulfur, 3.2; accelerator, 5.0; total, 100.0.

^c Stock B: 100 parts A + 82.5 Georgia clay.

^d Stock C: 100 parts A + 82.5 Missouri clay.

test, however, indicates that stocks B and C are of the same hardness and that both are harder than stock A. If we bear in mind that undercures, such as the 30-minute cure of stock B, should be more plastic than correct or overcures, such as those of stocks C and A, the differences with the two instruments can be readily explained on the basis of plastic flow of stock B which affects the A. S. T. M. measurement but not the durometer reading. This is confirmed by the readings at the best cures. A further check (8) was made using a high-rubber stock and a 20-volume gas black compound in three cures, measuring hardness with a Pusey and Jones plastometer which is also a dead-weight indentation instrument. Readings were taken over a somewhat extended period. The results are shown in Figure 3. The curves for the undercured stocks (10 minutes at 285° F.) show plainly the effect of plastic flow, some of which persists even in the overcures (50 minutes at 285° F.) as shown by the slopes of these curves. Hardness of vulcanized rubber compounds thus appears to consist of two parts, one of which is due to resistance to resilient deformation and the other to resistance to plastic deformation. Some methods of measurement include both in the indentation hardness result, and other methods show only the resilient hardness depending on the duration of the application of the load.

The significance of this kind of analysis in making possible better correlation with service has been intentionally omitted from the discussion because much more work will be necessary before it can be fully evaluated. Surely, however, such analysis cannot help but give us better appreciation of the value of the tests which are made and a more accurate understanding of how to use the test data. We must not fail to realize the indirect nature of all laboratory tests nor should we underestimate their value for comparative purposes, even though direct correlation with service is not always clear. Certainly, direct interpretation in terms of service value is not possible for tests such as determinations of stress-strain relationships, permanent set, and adhesion, except in some special instances. Yet, what rubber technologist would be willing to have such useful tools taken from him and would be content to rely on imitations of service and on simple hand tests alone? Service evaluation or prediction represents a judgment on the part of the technologist, and all of the information possible, comparative and indirect, as well

the design of a test. A good example of the lack of such definition is found in the case of abrasive wear, particularly as applied to tread wear of tires. The various conditions and forces involved are so numerous and complex that we frankly admit our shortcomings in respect to their analysis. Yet we attempt to design laboratory abrasion tests and we carry on extensive road testing at enormous expense without really knowing what it is we are trying to measure. Possibly more time and money spent in determining just what road wear consists of and in establishing the relative importance of the various service factors might pay more dividends in the end than all of these expensive test programs. Proof of the serious inadequacy of present analyses of road wear factors is evidenced by the difficulties which different tire manufacturers have in checking one another's road tests, and by the fact that each manufacturer has elaborate sets of road test data which show that his tires are the best of all competitive brands. It is worthy of note that laboratory abrasion tests do correlate fairly well with service wear when the latter is simple enough to be readily analyzed or capable of being closely duplicated under laboratory conditions.

Improper design of laboratory tests may result also from failure to carry over into the test apparatus a proper balance of the conditions and forces known to exist in the service. This is often caused by the necessity of accelerating the investigation. Performance tests would fall short of their purpose if they required as long a time as the service life of the article. The acceleration of failure is secured usually in one or more of the following ways: (1) by increasing the severity and intensity of forces on the sample (higher pressures or loads, harsher abrasive surfaces, etc.); (2) by increasing the temperature; and (3) by increasing speeds. Through emphasizing certain of these individual factors, the normal balance of service conditions may be upset, both directly and, as is often not realized, indirectly, since change in one condition may cause resultant changes in others. Obviously, without such emphasis the test would not be accelerated. If the emphasized conditions are those which are principally responsible for the ultimate failure of the article and if the other factors which are involved are not important in contributing to the cause of failure even though they may be indirectly affected, reasonable success may be anticipated with respect to correlation of such tests with

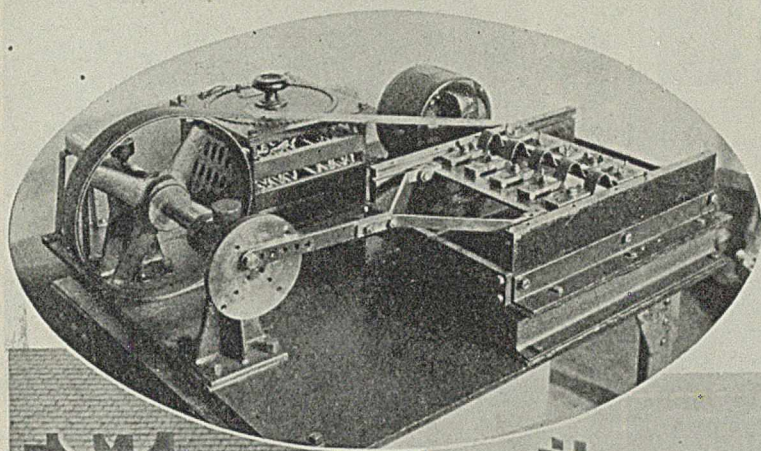


FIGURE 10 (LEFT). FATIGUE TESTING IN FLEXURE

FIGURE 11 (BELOW). FLEXING TEST FOR SOLING

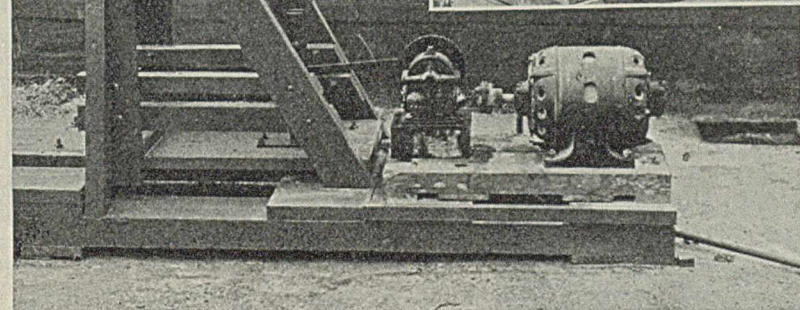
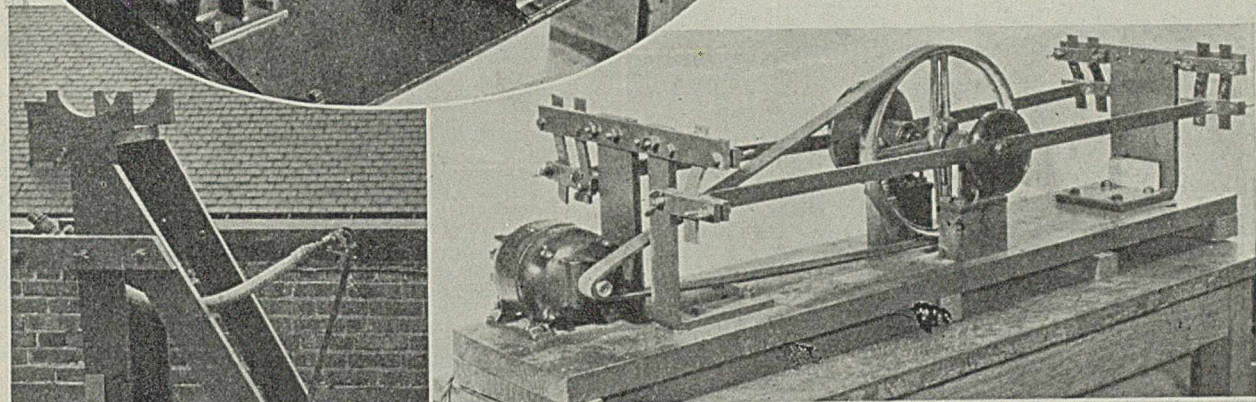


FIGURE 12 (LEFT CENTER). FLEXING TEST OF GASOLINE HOSE WHILE CONTAINING LIQUID

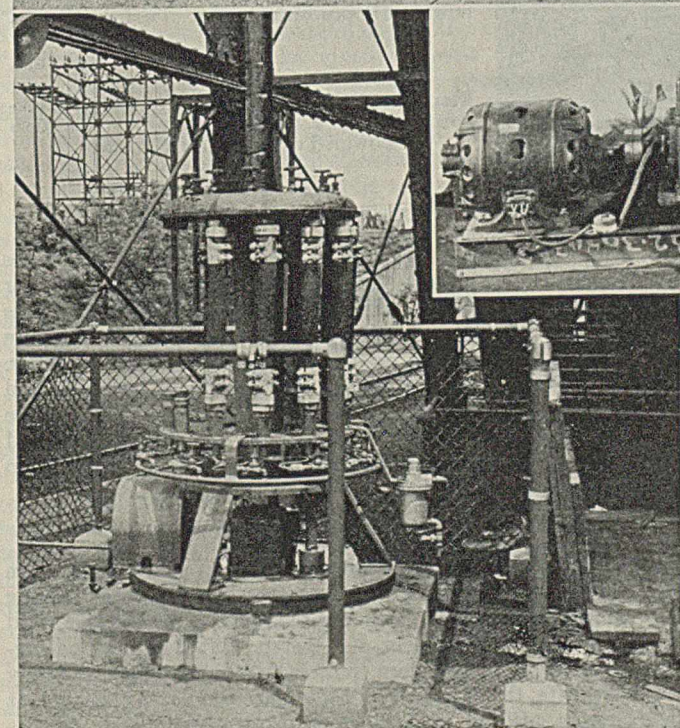


FIGURE 13 (ABOVE). FLEXING TEST OF GREASE-GUN HOSE UNDER 2500 POUNDS PER SQUARE INCH GREASE PRESSURE

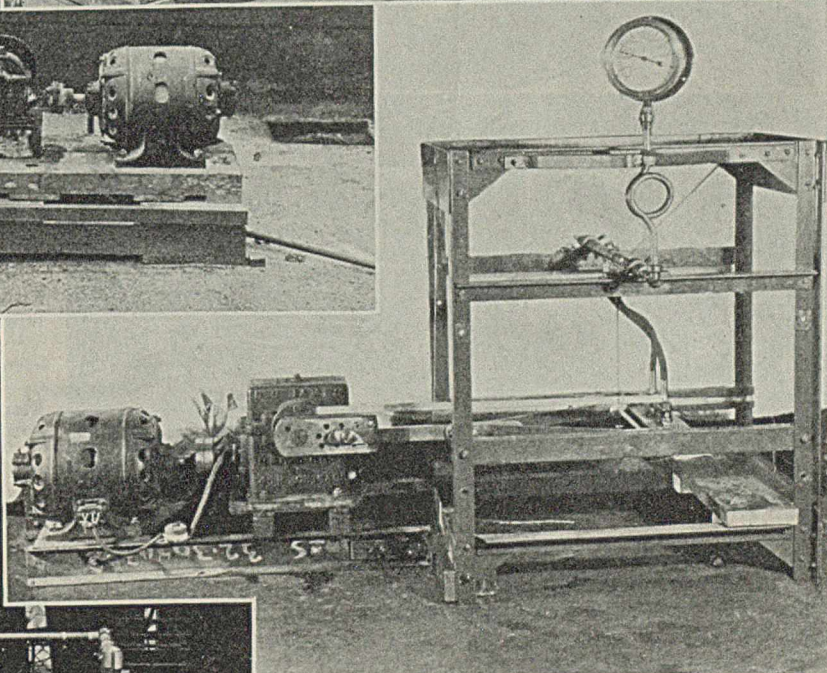


FIGURE 14 (LEFT). PERFORMANCE TESTING OF STEAM-HOSE TORSIONAL FLEXING UNDER 250 POUNDS PER SQUARE INCH STEAM PRESSURE

FIGURE 15 (RIGHT). COMPARATIVE PERFORMANCE TEST OF PNEUMATIC TOOL HOSE

FIGURE 16 (BELOW). PERFORMANCE TEST OF STEAM VALVE DISKS

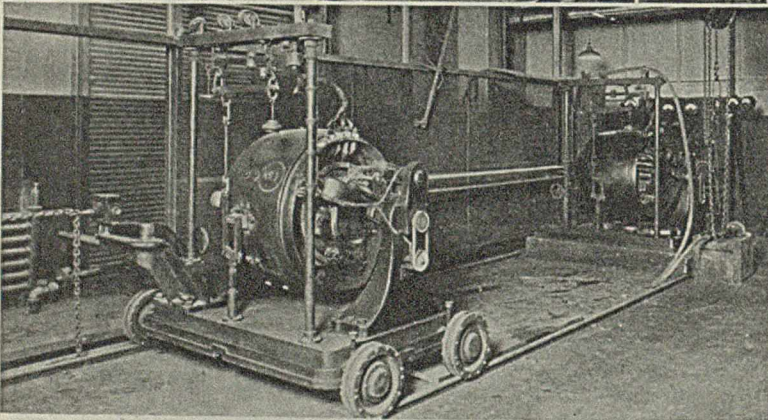
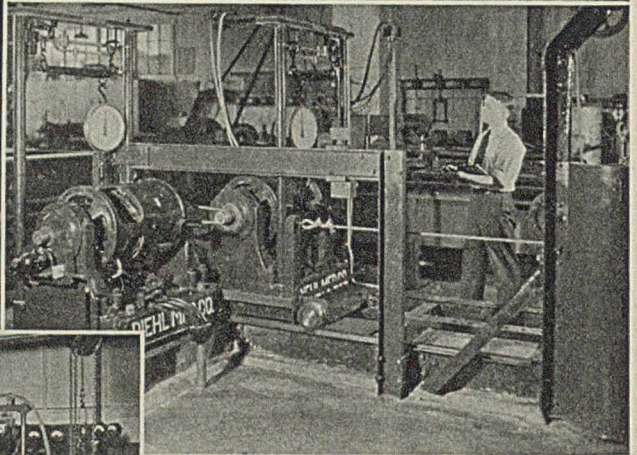
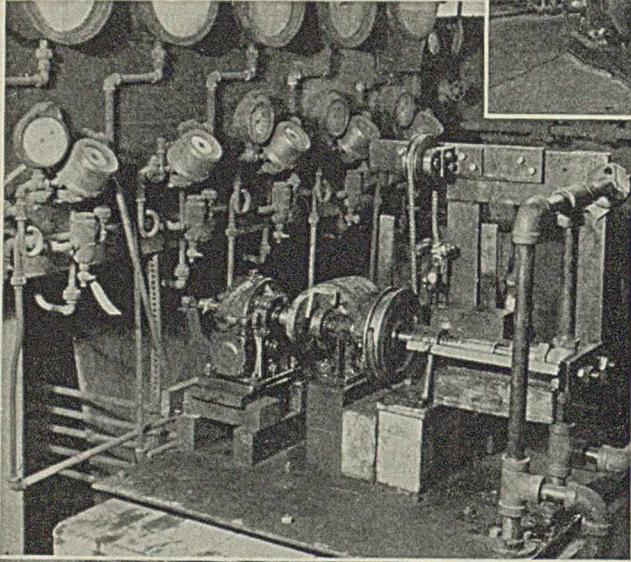
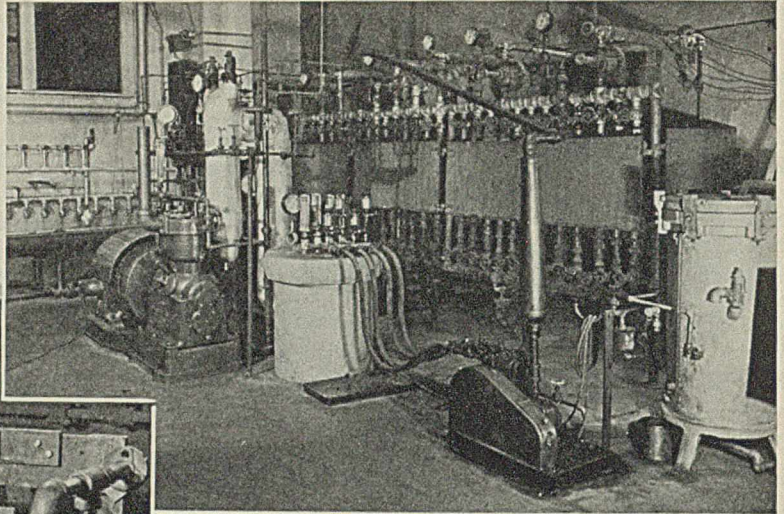


FIGURE 17 (ABOVE). HIGH-SPEED, 25-HORSE-POWER DYNAMOMETER FOR TESTING SMALL BELTS

FIGURE 18 (LEFT). ONE-HUNDRED-HORSE-POWER SPRAGUE DYNAMOMETER FOR TESTING POWER-TRANSMISSION BELTING

service. On the other hand, when the balance of the service factors is seriously disturbed in the test conditions, it is unlikely that good correlation can be obtained. The only alternative which remains then is to analyze the service completely and emphasize all factors in the same proportion.

In regard to interpretation of laboratory tests, it is not infrequent that attempts are made to apply test data to services that involve differences in conditions which are significant but not fully appreciated. Here, again, the solution of the difficulties which arise must reside in more careful analysis of both the test and the service. It is also quite usual to encounter lack of understanding of the limits in precision of engineering data secured by test. Almost any of the performance tests serves to eliminate products which are radically unfit for the intended services. It is only when finer distinctions are involved that serious reversals are encountered. For instance, several of the better abrasion resistance tests will distinguish between first grade

and second grade treads when the actual service differences in the treads are fairly wide and when the treads have similar degrees of hardness. It is only when close comparisons between treads of dissimilar hardness characteristics are required that serious reversals occur. While such accurate measurement and correlation are extremely desirable and may some day be possible when we have learned to analyze all of the conditions closely enough, it must be admitted that as yet we are somewhat in the position of trying to weigh a dust particle with ordinary counter scales.

LABORATORY TESTS

Some pictures of laboratory testing which follow are shown, not with any idea that they may serve as shining examples of perfect mechanical analysis or as the last word in quality measurement, but merely that they may be suggestive as to the modern trend of test development and may illustrate the simplicity of the mechanical movements at present utilized in developing performance tests. As has

already been suggested, the details of such tests are extremely varied but the fundamental mechanical principles are not nearly so diverse as appears at first glance. Figure 4 shows a machine test for adhesion or "friction pull." The specimen in this case is a strip of transmission belting one inch in width. This test involves simply the measurement, by means of a pendulum dynamometer head, of the force required to separate plies of the specimen under standardized conditions. As has been frequently pointed out in the literature, the correlation of such tests as this with service performance is extremely unsatisfactory. Figure 5, however, shows a test in which the service correlation is very positive. In this case the deflection of a rubber bearing is being measured under various compressive loads applied to a shaft by means of a universal testing machine.

As has been suggested, performance tests which appear to be very good imitations of service conditions often fail to give satisfactory service correlation, probably because of failure to include in the test the essential characteristics of the actual service. Figure 6 illustrates such a case. This machine was designed to test tread wear, using as test specimen a small pneumatic tire which is run on a rotating track made of standard road concrete. The test is of the angle-slip type and provision is made for control of the angle. The speed can be varied as well as the dead-weight load supported by the tire. The road wheel is the driven member and in turn, through contact, rotates the tire wheel which is mounted as an idler on ball bearings. The amount of tread wear is measured by accurately calipering the depth of the nonskid grooves. For a time it appeared that this test would correlate very reliably with actual road service, but, as often happens, it was necessary only to continue testing on a sufficient number of tires to encounter serious reversals.

In Figure 7 is shown a view of tire testing on Sprague dynamometers. In such tests a generator is driven by a motor through controlled contact of tire and road wheel. The actual horsepower expended on the road wheel is measured by weighing the generator torque and measuring the speed, using the Prony brake formula for the calculation. These tests have been quite reliably correlated with actual service for the evaluation of tire carcass performance. Figure 8 shows a rather obvious but useful impact test known as the "guillotine test." This has given valuable information concerning the ability of tires to withstand service conditions. In this case the impact member is dropped between guides from controlled heights in an elevator shaft, striking a blow of known force on an inflated full-sized tire, properly mounted.

Another device for impact testing, as shown in Figure 9, has been successfully used for the testing of rubber-covered metal plates, such as are used in lining chutes, grinding mills, etc. In this device a chain elevator raises a 50-pound weight carrying a hemispherical impact surface to a predetermined height at which the weight is tripped from the elevator. The heavy body falling freely between nearly frictionless guides strikes a blow of known force on the specimen placed below on a suitable solid support. A very interesting result was observed with this apparatus while testing sheets of rubber which had been bonded firmly to metal backing (3). Certain specimens, when tested dry, required approximately one hundred blows before complete failure, which was taken as the number of impacts necessary to cause the rubber to tear apart sufficiently to expose the metal base. In appearance the failed sample showed a very roughened surface over a circular area of diameter about equal to that of the impact ball. At the center of this area a circular hole of small diameter extended down through the rubber to the metal. When the experiment was repeated, with the difference that the surface of the rubber was kept wet with water, failure took place after three or four blows.

Irregular radial cracks extended from the center of percussion outward, and there was no appreciable roughening of the surface. Apparently the water acted as a lubricant, concentrating the full force of the blow at the center of percussion rather than permitting the energy of the blow to be dissipated through a larger volume of rubber by means of friction.

Figures 10 to 14 show applications of flexing tests to various rubber products. Such tests can seldom be correlated directly with service performance, but they are extremely useful for comparative purposes. The machine illustrated in Figure 10 is used with rubber strips or dumb-bell specimens and is similar to the DeMattia flexing machine (4). A crosshead is driven by an eccentric at controlled variable speed. By using suitable settings of the clamps, it is possible to flex the rubber samples in bending only, as shown, or in extension. In either case the first sign of failure will be the development of small cracks which finally lead to a complete rupture of the specimen. Figure 11 shows a bending fatigue test on soling stock. This differs from the previous test in that the specimens are under slight tension produced by the weight of the driving arms which are supported by the specimens. In Figure 12 the performance relationship is more clearly defined, for in this case a specimen of gasoline hose full of the liquid is bent back and forth until the tube fails and the gasoline penetrates into the body of the hose. Figure 13 shows specimens of grease-gun hose filled with grease under high pressure, which are flexed with a reciprocating motion until failure and consequent release of the pressure take place. Figure 14 shows a recent performance test for steam hose. In this case the lower platform moves with an eccentric motion, causing the lower end of the hose specimen to be rotated in a circle about 4 inches in diameter. During test the hose is subjected to internal steam pressure of 250 pounds per square inch and external action of the weather. It is thus quite typically a performance test imitating actual service conditions as encountered by railway steam hose.

Another performance test, in which a rather elaborate attempt is made to duplicate on a laboratory scale, a complicated set of service conditions, is shown in Figure 15. In this case, service life of four samples of pneumatic tool hose is being compared. The apparatus consists of an air compressor which discharges into a receiver through equipment arranged to give constant temperature and pressure in the receiver. The compressed air from the receiver flows through the hose specimens after having received a known addition of lubricating oil at the receiver outlet. The compressed air is released from the hose through a valve mechanism which duplicates the impulse action of a pneumatic hammer. The test may be accelerated by raising the temperature and pressure of the compressed air. Figure 15 also shows a steam rack and a digester which are used for heat deterioration tests of hose specimens. In Figure 16 equipment for testing steam valve disks is shown. A valve installed in a high-pressure steam line contains the disk under test, and mechanical arrangements are provided whereby the valve is opened by a motor which raises a weight at the same time. The mechanism then trips and the falling weight closes the valve, assuring duplicate force conditions at each closure.

Figures 17 and 18 show dynamometer equipment for testing belts. Both of these sets are so arranged that very complete information can be secured. In each case one dynamo is mounted on a track which permits control and measurement of the total tension on the test belt. In each set both dynamos are cradled and equipped for torque and speed measurement so that the actual pulley horsepowers can be calculated excluding the dynamo losses. In each case one

dynamo operated as a motor drives the other dynamo as a generator through the belt. Knowing the pulley horsepower in each case, the power transmission efficiency is determined. The effective power load can be regulated by means of adjusting known resistances in the generator discharge circuit. With a given total tension on the belt, it is possible to use so much resistance that slippage of the belt occurs as would be evidenced by the readings of the revolution counters on the units. The set shown in Figure 17 was recently designed for testing small V-belts at high speeds. It is capable of being operated continuously at speeds up to 5000 r. p. m. with power loads of 25 horsepower. The set shown in Figure 18, similar to that previously described by Sturtevant (?), is capable of handling 100 horsepower at speeds up to 1800 r. p. m. It is suitable for use with full-size power-transmission belting of either flat or V-type.

It is hoped that this discussion and the illustrations may

serve to stimulate ideas and work which will lead to progress in development of well-designed laboratory performance tests and their correlation with service.

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Chemical Studies of Wood Preservation

I. The Problem and Plan of Attack

ROBERT R. WILLIAMS, Bell Telephone Laboratories, New York, N. Y.

PRESERVED timber has been used in industry for about a hundred years with results so satisfactory as to leave no question as to the economic value of preservative treatment. However, a quantitative measure of this economic advantage and the relative merits of the several kinds of treatment which are available still remain doubtful in many particulars. A constant stream of unanswerable questions is still arising with regard to the quality of creosote oil for preservative purposes and the methods of application of such oils to various kinds of timber, so that a systematic continuing study of the subject is necessary.

Such a study has been under way for many years in the Bell Telephone System and in recent years the volume of useful information on the chemical aspects of the subject has attained considerable proportions. Much of this information is available for publication. In presenting it, however, the authors wish to emphasize that it should be construed as an account of experimental work, the significance of which is left to the judgment of the reader. Although the study has naturally shaped itself around Bell System problems, the experimental methods and results described are not to be regarded as a statement or a forecast of the engineering practices or preferences of the system. These practices are based on a variety of considerations, many of which involve nothing of chemical interest and are accordingly omitted from the present discussion.

It is the purpose of this paper to outline the chemical problem and to state the plan of attack which has been followed. Later papers will deal more in detail with the methods used and with some of the results of the study.

The authors have limited themselves at the outset to a cer-

The chemical problems involved in wood preservation are discussed with special reference to pressure-treated pine poles. Preservation of wood is achieved by the use of poisons which in reasonable concentration are destructive to a variety of wood-destroying organisms and which must be permanent in the weather. Variability of penetration of preservatives and inequality of their distribution in wood, partly due to Nature's infinite variety, make significant sampling and analysis difficult. Accordingly little quantitative information has been available about the distribution of preservatives and the depletion of toxic value by sun, wind, rain, and soil moisture. Some of the devices and methods which promise to accelerate testing and to supply quantitative data are outlined.

tain well-defined but important area of the field of wood preservation. Because of the preponderating importance of the telephone pole to the industry, attention has been largely confined to it in the present papers. To a great extent the discussion is further limited by excluding from extended consideration those sorts of poles, such as chestnut and cedar, which are not usually economically susceptible to pressure treatment. The depth of sapwood in these species is small; the penetration of preservative beyond the sapwood into the heartwood is very slight; and the heartwood has a greater natural durability than the sapwood. Chestnut and cedar poles are accordingly commonly

treated only in the butt section by an open-tank treatment at atmospheric pressure. Such treatments protect the underground section of the pole very materially and are economically valuable. Poles so treated are, however, less well adapted to reveal the full possibilities of wood preservatives than poles of the cheaper, less durable, and more treatable species which have been subjected to full-length pressure treatment.

The principal object of the authors' concern has therefore been pressure-treated Southern pine, a type of timber which has been extending its field of use more and more into areas in the North, East, and Southwest. Other species of treatable timber which come in for incidental consideration in these studies are Douglas fir and lodge-pole pine which have intermediate depths of sapwood. The former is usually subjected to full-length pressure treatment, the latter to open-tank butt treatment.

For similar practical reasons the data to be published largely concern creosote oil as a preservative, although the authors have examined, to a limited extent at least, most other

preservatives which are in use or have been proposed. Creosote oil is the middle cut from the distillation of coal tar, a by-product of the coking of bituminous coal. The processes of coking are and have been for many years undergoing an evolution which reflects itself in the nature of the coal tar produced. Likewise the processes of distillation of the resulting tar have undergone changes from year to year, making for changes in the character of the creosote oil. In general, however, it may be said that creosote oil represents from one-fourth to one-half of the original tar and has a boiling range from about 200° to 360° C. The portions of the tar which are rejected consist of light oils of low boiling point and residual pitches. The creosote oil is a mixture of two or three hundred chemical substances in varying proportions and displaying a variety of physical and physiological properties.

For present purposes, one may think of the process of applying creosote oil to timber as essentially one of driving the oil into the wood by external application of hydraulic pressure, either with or without previous evacuation of the air in the cells of the wood. Numerous variants of the process are in use.

PENETRATION OF PRESERVATIVE

Even a casual examination of poles treated in this manner reveals facts of fundamental importance in a consideration of the problem of wood preservation, most important of which is that the heartwood is rarely penetrated to any extent. This means that during service we must depend upon the natural durability of the heartwood or upon the continuity of the envelope of treated wood with which it is surrounded.

According to the practice of some years ago, perhaps the majority of the poles in a given cylinder charge were penetrated to the extent of 90 per cent or more of the depth of the sapwood. Some might be penetrated to the extent of only 50 per cent or even less, especially if the sapwood was very deep; some pieces, particularly of shallow sapwood, might be penetrated to the surface of the heart. Substantial progress has been made in recent years in many plants toward securing complete and uniform penetration, but the danger of incomplete penetration is still present and must be constantly combated. In addition, while it often happens that the depth of penetration is approximately uniform on all sides of the pole, not infrequently the penetration is much deeper at some points than others, leaving an untreated core of wood of very irregular cross section.

It is also found that the oil is not evenly distributed throughout the treated portion of the wood. Cases of decay have been discovered which were due to a deficiency in quantity of oil retained in portions of the wood which the oil had actually reached. Often the oil concentration is greater in the outer layers of sapwood, sometimes in the inner; rarely is it uniform within the limits of experimental error of analysis.

The causes of the uncertain and uneven distribution of creosote in wood are somewhat obscure, but are known to involve among other things the moisture content, the thickness of growth rings, the over-all density of the wood, the characteristics of the oil, and the nature of the impregnating process. It is sufficient for present purposes to point out that the creosoter has to deal with a raw material of far more variable character than fabricated material with which manufacturers are commonly concerned and that this variability tends to be reflected in the finished product. The examination of old creosoted poles also reveals that variability of penetration is a factor of prime importance in determining the excellence of the finished material. In the great majority of cases decay occurs sooner or later in the untreated part of the wood.

From the laboratory man's point of view this variability

results in an extremely difficult problem of sampling. Indeed, a primary need of the industry today is a simple quantitative measure of the amount and excellence of distribution of preservative in a train load of timber. Accordingly, the problem of sampling poles for analysis will constitute the subject of a later paper.

SERVICE CONDITIONS

In considering the quality of the preservative treatment one must take into account the peculiarities of service conditions. Proper creosoting of ties, piles, cross-arms, or poles calls for adaptation of the treatment to the kind of use to which the timber is to be put. In the case of the pole, the upper part is exposed to sun and wind and the lower part to more or less moist and close-packed earth, at more nearly constant temperature and with little ventilation. Just above the ground line there is a region which is kept continuously moist by capillary flow of water from the earth and is also exposed to the sun and to winds laden with spores of wood-destroying fungi. In general, at least in untreated poles, this region is most subject to decay. Obviously one cannot ignore differences of climate, including rainfall, sunshine, and air temperature as affected by latitude and general topography. Thus a degree of preservation which is quite adequate for the high latitudes of Central Europe may be wholly insufficient for subtropical conditions.

This observation immediately points to the necessity of some means of measuring the permanence of preservatives introduced into the wood and of determining the loss of preservative value. In this connection some quantitative measure of the toxicity of the residual preservative is essential and for this purpose resort must be had to the use of cultures of wood-destroying fungi. These cultures, for the sake of constancy of performance, had best be pure cultures of single organisms and, in order to avoid overlooking specific toxic effects, preservatives need to be tested with several representative organisms. Such tests are subject to the influence of a great many factors and the whole matter will be dealt with at length in later papers.

The merits of a preservative treatment naturally depend not only upon the distribution of the preservative and the influences which tend to deplete the supply of preservative, but also upon the quality of the material which is introduced. Contrary to wide-spread opinion, it is possible to find creosoted timber which has undergone decay within the penetrated part of the wood. With the radical innovations that have taken place in recent years in the processes of creosote oil production, this fact should be recognized as one of outstanding importance. Indeed, the reputation of creosote oil is based principally on the behavior of a product distinctly different (whether better or worse) from that which tends to prevail in the treatment of new timber at the present time in America. The older types of oil are naturally more generally represented in timber which has withstood the test of decades of service.

INTERPRETATION OF TEST DATA

Assuming that one has devised means of sampling and analyzing a lot of timber and of determining the distribution and toxic effectiveness of the preservative in it, there remains the question of how to forecast permanence without waiting many years to observe the behavior of new experimental material. The Bell System is fortunate in having available for examination several millions of poles in all parts of the United States. Information is on record about a considerable number of these poles concerning the kind and quality of oil originally used, the method of treatment, and the age of the specimens. These poles are affording a rich fund of information as the examination of them is extended from year to year.

Particular attention is being paid to poles which have behaved conspicuously well or conspicuously badly in service and a great deal of insight has been gained thereby into the nature of the depletion processes and causes of decay.

The examination of old poles furnishes information primarily with regard to the behavior of poles in the latter part of their life. The known facts about the treatment of these timbers are often insufficient to define their original condition with exactitude. In order to complete the picture, one must know about the behavior of poles in infancy and youth. For this purpose, in common with many other investigators of wood preservatives, the authors have resorted to the use of posts specially treated for the purpose. These are exposed in convenient plots located in different parts of the country in order to observe the effects of climatic influences. The value of this method has been greatly enhanced by analytical examination of the condition of the posts at the outset and from year to year. The trouble with most of the published work about this type of experiment in the past has been that it consisted largely in counting the number of specimens which showed decay after various intervals of time and that the total time elapsed has been insufficient to put the material to a crucial test. By periodic sampling and analysis of such posts the authors have been able for the first time to plot depletion curves which show clearly that the loss of creosote from wood proceeds at an astoundingly large rate during its early years. It dies away later to a slow depletion which may be only roughly extrapolated into the far distant future. However, by piecing together the information secured from old poles in service with that obtained from young ones in test plots the whole process of senescence can now be pictured much more adequately.

After all, we are interested in post-mortem findings primarily in order to protect material which is yet to be manufactured and installed. Still more rapid methods are necessary to secure adequate information about new preservatives or new varieties of creosote if this information is to be of value within the lifetime of the present generation. For this purpose the authors have resorted to small-size specimens, depending on the principle that the ratio of surface to volume must determine in large measure the rate of weathering, and in order to imitate poles, have used sections cut from pine saplings about 15 to 20 mm. in diameter and of length in proportion to that of standard poles. The sapling has a great advantage over a turned stick of wood in that the grain runs parallel to the surface and the structure is otherwise imitative of the full-size pole. Allowance must be made for the fact that the sapling contains little or no heart and therefore is impregnated throughout. Roughly speaking, such saplings

have a ratio of surface to volume ten times that of normal size poles and will lose preservatives at correspondingly greater rates.

The authors have considered and to a limited extent experimented with artificial weathering machines for hastening the depletion process in such specimens. However, such devices are somewhat cumbersome and expensive and a considerable uncertainty always remains as to whether the several depletion factors have been accentuated in proper proportion to one another. For this reason this type of device has not been extensively used. It has been found that saplings treated with standard preservatives when exposed to the weather, especially in southern climates, will within a year or two give comparative results which are in harmony with industrial experience in full-size material. The process of treating such small saplings is so expeditious and inexpensive that it has been possible to carry on simultaneously experiments with scores of new preservatives or variations of preservative treatment. With relatively little expenditure of labor, the specimens can be inspected from time to time and first approximations to a reliable prediction of behavior can be made by comparison of the behavior of unknowns with standard materials of well established industrial history.

When one contemplates the necessity for some sort of specification test for the purchase of a complex preservative such as creosote oil, he realizes that a practical test must be completed within a few hours or at most a few days. Such a test cannot be expected to have the finality of an actual exposure test and requires much correlative information for its interpretation. However, it may be briefly stated that the principal cause of depletion of preservative value in creosote oil is evaporation. Accordingly, a useful tool has been developed which measures the rate of evaporation of an oily preservative under conditions which are imitative of those which prevail within the wood structure. The data so obtained about a variety of oils have been correlated in some detail with tests of the identical materials in actual exposure to the weather. The evaporimeter which has been devised also furnishes material for estimation of residual toxicity at various stages of evaporation. An account of this device will constitute the subject matter of an early publication.

The papers which are to appear within the next few months must be regarded as progress reports, since knowledge is not complete at the present time upon any phase of the subject. They are to be published to supplement the experimental work of others and to secure the benefit of critical comment.

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II. Sampling Poles for Chemical Analysis

ROBERT E. WATERMAN AND CHARLES O. WELLS, Bell Telephone Laboratories, New York, N. Y.

IN THE study of the changes in quantity and quality of preservatives in poles over a period of years, an accurate, convenient, and nondestructive sampling method is required. It should provide a sample suitable for extraction, giving extracts ample for toxicity tests; should leave the pole uninjured with respect to its future behavior as a test specimen or as a pole in service; and should, preferably, permit observation of wood structure, penetration of preservative, etc. Above all, the sample should be accurately representative of the pole as a whole.

The normal distribution of preservative in poles treated by even the most thorough pressure processes is far from ideal. Most timbers used for poles have a well developed

heart, or inner wood, which is functionally inactive in the growing tree. It results from a gradual conversion of sapwood during the growth of the tree and is more rot-resisting, more resinous and impenetrable than the sapwood. The latter which forms a shell around the heartwood varies from a comparatively thin layer, as in the case of cedar or chestnut, to such a thickness that it constitutes practically the whole volume of the wood, as in the case of younger specimens of the fast-growing varieties of pines. With present methods preservatives can economically be introduced in round timbers only into the sapwood; in practically every case, there is a much higher concentration of preservative in the outer layers than in the inner layers of freshly treated sapwood (Table I).

TABLE I. RADIAL DISTRIBUTION OF CREOSOTE IN TYPICAL FRESHLY TREATED SOUTHERN PINE POLES

SAPWOOD LAYER ^a	SPECIMEN NUMBER							AVERAGE
	1	2	3	4	5	6	7	
Outer	16.3	19.1	18.7	17.0	25.2	20.5	14.4	18.7
Intermediate	8.2	12.6	6.1	6.1	13.9	22.0	11.1	11.5
Inner	6.9	5.4	3.7	4.0	4.3	7.4	7.7	5.6

^a Each layer 1 inch (2.54 cm.) thick.

Other forms of maldistribution of preservative are often present. For example, conditions of growth may effect an asymmetric development of the trunk of the tree. This circumferential variation in the development of the annual rings of the wood may be reflected in the distribution of preservative in the pole, so that there may be substantially more oil in one quadrant or sector than in another. Probably in most cases variations in the treatability of different sectors are caused by nonuniformity of moisture content or inherent deviations of structure. At all events the circumferential distribution is somewhat irregular in almost every observed case of pole treatment (Figure 1).

A true sample must not only represent each layer in the same proportion as it exists in the pole—that is, in a quantity directly proportional to the distance from the center—but also, at least approximately, represent each sector in the proportion that it exists in the pole. A cross-sectional slab of uniform thickness cut from approximately the mid-point of a pole closely approximates a true sample, in that it represents each concentric layer and each sector in the proper proportion. Such a sample is often too large for convenience. It may be cut into sectors by splitting repeatedly through its center. Providing these sectors, or wedge-shaped pieces, are chosen from each quadrant so that they approximately represent circumferential distribution, they may be used collectively as a sample.

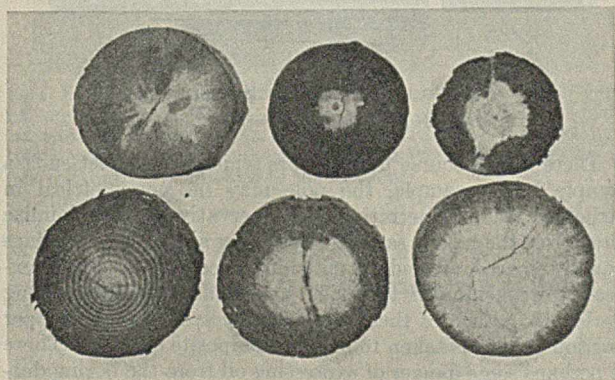


FIGURE 1. DISTRIBUTION PATTERNS ENCOUNTERED IN PRESSURE CREOSOTED SOUTHERN PINE POLES

This collective sample or the slab from which it is derived constitutes a satisfactorily representative sample, but such a method of sampling obviously cannot be used for repeated examinations of a pole at intervals of service or experimental exposure. In view of the idiosyncrasies of each pole, it is impossible to examine a lot of poles reliably by choice of a few poles at random. It therefore becomes essential to be able to reexamine each pole or at least a substantial proportion of each lot of poles individually if one is to learn anything quantitative about changes of condition with time.

CORRECTIONS OF SAMPLING ERRORS

The increment borer, designed for studying the growth of living trees, removes a small, solid cylindrical core which may be so taken as to extend from the surface to the center of the tree. This sample lends itself readily to the study of wood structure and penetration. Sampling a pole with this instrument (Figure 2), provided a reasonable number of borings are taken and the holes are filled with preserved wooden plugs, does not seriously injure a pole for service purposes nor greatly alter the weathering process in nearby wood. Although this sampling method has a number of advantages, it does not give a representative sample. It takes equal quantities of wood from each layer of the pole and thus incorporates in the sample too large a proportion of the inner layers.

However, if the penetration can be measured accurately and if it could be safely assumed that the concentration of the preservative is substantially constant in all portions penetrated, the results obtained from the analysis of cylindrical (increment) borings could be corrected by applying a suitable mathematical factor. This expedient has been of some value in many instances in which borings had been analyzed prior

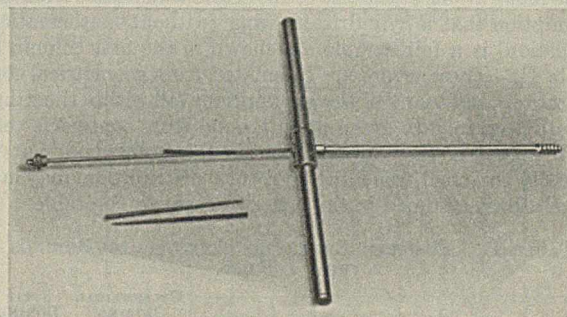


FIGURE 2. INCREMENT BORER

A split boring in lower left

to the development of newer and more accurate methods of sampling. This correction factor may be derived as follows:

Assume a sector of a cylinder and a boring taken from the same pole of unit radius.

In the boring (Figure 3)

$$\begin{aligned} a &= \text{volume of impregnated wood} \\ b &= \text{volume of unimpregnated wood} \\ R &= \text{radius} = 1 \\ p &= \text{fraction of radius penetrated} \end{aligned}$$

The volume of the impregnated cylinder is to the volume of the entire cylinder as the altitudes of the cylinders—i. e., $\frac{a}{a+b} = \frac{p}{R} = p = \text{fraction of the volume of wood which is impregnated according to the cylinder sample.}$

In the sector (Figure 3)

$$\begin{aligned} a_1 &= \text{volume of impregnated wood} \\ b_1 &= \text{volume of unimpregnated wood} \end{aligned}$$

The volume of the whole sector ($a_1 + b_1$) is proportional to R^2 ; that of the small sector (b_1) is proportional to the square of its radius ($R - p$); that of a_1 is proportional to the difference of the squares of the two radii—i. e., to $R^2 - (R - p)^2$ or

$$\frac{a_1}{a_1 + b_1} = \frac{R^2 - (R - p)^2}{R^2} = \frac{R^2 - (R^2 - 2Rp + p^2)}{R^2} = p(2 - p) =$$

the true fraction of the pole which is impregnated as shown by the sector.

$$\frac{\text{True fraction}}{\text{Fraction shown by cylinder}} = \frac{p(2-p)}{p} = 2-p$$

$$\text{True fraction} = (2-p) \times \text{cylinder fraction}$$

To correct cylinder analyses merely multiply the weight of preservative found per unit volume by $2-p$.

Accurate analyses cannot be obtained in all cases by correcting in this manner, both because of the difficulty of determining with sufficient accuracy the value of p , and because of the nonuniform distribution radially of the preservative in the impregnated portions of the pole. The error from this latter source applies to an analysis regardless of the substance in question. Preservatives in general are more or less concentrated near the surface in freshly treated poles but, depending on their solubility, volatility, and viscosity, may redistribute themselves on standing. Test posts analyzed

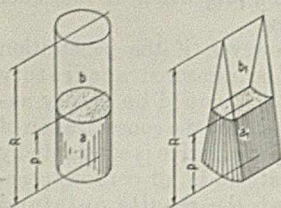


FIGURE 3. COMPARISON OF BORING AND CYLINDER SECTOR

by sampling in this fashion have shown, paradoxically, an increase in creosote oil content after one year's exposure, due to a redistribution of oil from circumference toward the center. In moisture determinations where, depending on circumstances of seasoning, almost any distribution of moisture is possible, errors of a magnitude equal to that of the true moisture content may occur. Some illustrations of the size of the errors which arise from the assumption that a cylindrical boring (without mathematical correction) is a fair sample are shown in the first column of Table II. These errors are calculated from geometrical considerations, but many of the assumptions fall within the range of actual cases. In green wood the moisture content is very much higher in the sapwood than in the heartwood, but in partially seasoned wood the moisture distribution may approach those assumed in the last two cases in the table.

TABLE II. POSSIBLE ERRORS BY ANALYSIS OF BORINGS FROM A POLE

	PENETRATION	CYLINDRICAL BORING ERROR	SPLIT BORING ERROR ^a
		%	%
Oil concentration varying linearly from maximum at surface to zero at limit of penetration	0.1 radius	- 48.3	+ 3.1
	0.2 radius	- 46.4	+ 3.5
	0.3 radius	- 44.4	+ 4.3
	0.5 radius	- 40.0	+ 5.1
	Entire radius	- 25.0	+ 3.1
MOISTURE LIMITED TO			
Moisture in inner part of pole and uniformly distributed therein	Inner 0.2 radius	+400.0	-41.5
	Inner 0.5 radius	+100.0	-15.3

^a See later discussion.

In Table II, an assumption is made that the oil is distributed so that the concentration is a maximum at the outside and declines linearly to zero at the limit of penetration. This is the most reasonable assumption with regard to freshly treated poles and it is obvious that a mathematical correction could be applied on the basis of this assumption. However, such a correction would be somewhat complicated. Moreover, the same assumption is unjustified for old poles. In weathering there is a marked tendency for depletion to occur at the surface by evaporation, so that in extremely old poles the fairest simple assumption might be that the concentration is at a minimum at the surface and increases linearly to a maximum at the limit of penetration. Accordingly, it would be necessary to modify the basis of correction progressively with the age of the pole.

In view of these facts, a method was sought which would

directly provide an approximately representative sample. A tapered twist drill was designed which would remove a sample having the mathematical properties of a wedge. This method gives an approximately true sample from symmetrical poles of any diameter by drilling just to the center of the

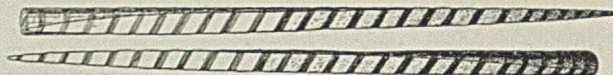


FIGURE 4. DIAGRAM OF A BORING SPLIT DIAGONALLY

pole and catching the shavings as they are expelled. The practical difficulties of such a method, especially loss of shavings in a breeze, make it objectionable in sampling telephone poles.

A practical and approximately accurate sample is secured by taking an increment boring and discarding an appropriate part of the cylinder. For this purpose, a boring whose length is equal to the radius of the pole is sliced diagonally with a knife blade in such a way that the plane of the cut is tangential to the basal cross section of the boring at its outer end and tangential to the opposite side of the boring at its inner end, as illustrated in Figure 4. A guillotine for doing this rapidly has been developed and is illustrated in Figure 5. The part of the boring having its small end at the center of the pole is used as the sample for analysis; the remainder is discarded. In the appendix by Peek it is shown that, if such a sample is geometrically perfect, the maximum error introduced will be 7.0 per cent provided the greater portion of the oil lies outside the half radius of the pole. In general the error will be substantially less than 7.0 per cent. By means of the equations given in the appendix, the errors resulting for the illustrative cases of Table II have been computed.

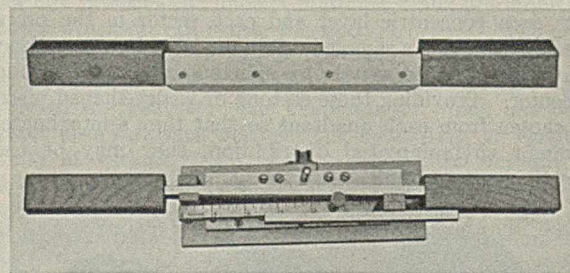


FIGURE 5. BORING SPLITTER

Top view, and above, disassembled knife

There are of course other errors which may affect such a sample. For example, the pole may be asymmetrical in structure or in penetration of preservative. To minimize this error, the pole is sampled by taking a number of borings equally spaced around its circumference and to avoid excessive weakening of the pole, somewhat distributed along its length. Each of these is diagonally split and the proper portion of each is taken to make a composite sample. There is perhaps some danger of expressing oil from the boring during the process of boring, but evidence of this has not been detected. Observation shows that the pressure is exerted outward rather than inward. There is also some error due to deviation of the dimensions of the split boring from the nominal ones on account of mechanical inaccuracy of implements. For this reason, the actual diameters of borings should be checked occasionally. Still another difficulty that is inherent in all extraction methods of analyzing for creosote oil is due to the extraction of a variable amount of resin from the wood; the weight of this resin is counted as creosote. This error is considerably lessened by discarding all the untreated portions of the borings before extracting.

Table III gives a comparison of the results obtained by the three methods of sampling. Mathematically corrected values for the cylindrical sample are included. They serve on the average to bring the results in fair agreement with the correct value, but involve an assumption as to distribution.

TABLE III. ANALYSIS OF SEVEN CREOSOTED POSTS BY THREE METHODS

(Grams per 100 cc. of total wood)

WEDGE SAMPLE	P/R	2-P	OIL CONTENT BY CYLINDRICAL BORING		MATHEMATICALLY CORRECTED OIL CONTENT		OIL CONTENT BY SPLIT BORING		
			ER-ROR ^a %	ER-ROR ^a %	ER-ROR ^a %	ER-ROR ^a %			
1	8.89	0.895	1.105	7.73	-13.1	8.54	-3.96	9.73	+9.35
2	9.82	0.455	1.545	5.06	-48.3	7.84	-20.1	9.36	-4.56
3	8.57	0.573	1.427	4.80	-44.0	6.85	-20.0	9.20	+7.46
4	6.54	0.545	1.455	4.77	-26.9	6.95	+6.36	6.51	-0.50
5	11.00	0.494	1.506	7.42	-32.4	11.18	+1.75	11.81	+7.42
6	12.82	0.489	1.511	9.12	-28.9	13.77	+7.36	13.96	+8.85
7	10.81	0.677	1.323	7.47	-29.6	9.89	-6.79	11.28	+6.33
Av.	9.76	6.63	-32.1	9.30	-4.75	10.27	+5.24

^a In all cases the wedge sample is assumed to give the true result and the "error" represents the deviation from this value. The correction involves the assumption that the concentration is uniform throughout the treated portion.

In certain cases this assumption is very faulty and the correction fails badly. The uncorrected values for the split cylinder are so near the true values that the corrections are omitted. Imperfect as they are, the uncorrected values obtained with the split boring are apparently within 10 per cent of the truth and have the great merit of involving no arbitrary assumption about the concentration gradient. They are sufficiently reproducible to afford valuable data about the progressive loss of creosote and changes in its toxicity with the lapse of years. The method is being applied both to service pole lines and experimental material in test plots. It has also been of great value in measuring uniformity and the level of quality of product from commercial treating plants.

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Appendix

R. L. PEEK, JR.

IT IS desired to compare two samples of equal length l and equal volume V , one being a wedge of height d and width at the base b , the other a cylinder of radius r bisected by a plane passing through a diagonal of a longitudinal section through the axis and perpendicular to the section.¹

For the wedge

$$V = \frac{bdl}{2}$$

and as both samples have the same volume, and as that of the cylinder is $\frac{\pi r^2 l}{2}$, evidently

$$bd = \pi r^2$$

Area A of cross section of wedge at any point distant x from the base is given by

$$A = \frac{l-x}{l} bd = (1-m) \pi r^2 \tag{1}$$

where $m = \frac{x}{l}$ (fraction of length).

¹ Strictly speaking, neither the ideal (wedge) sample nor the actual (split cylinder) sample has a plane base as assumed in this formulation, as the base surface is that of the tree, which is approximately cylindrical. As in both samples the dimensions of the base are small compared with the radius of the tree, the distinction between a plane and cylindrical base has been ignored as trivial.

Typical sections of the split cylinder are shown in Figure 6. Let the perpendicular distance from the center to the boundary be ρ , as shown, positive if to the right and negative if to the left. From inspection of Figure 6

$$\rho = r - \frac{x}{l} \cdot 2r = r \left(1 - \frac{2x}{l}\right) \tag{2}$$

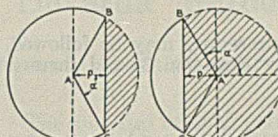


FIGURE 6. TYPICAL SECTIONS OF SPLIT CYLINDER

To obtain the area of any section there must be subtracted from the area of the circle the section cut off, shown shaded in the drawing. This shaded area is given by the area of the sector $r^2\alpha = r^2\cos^{-1}\frac{\rho}{r}$, less the area of the triangle ABC , and hence

$$A' = \pi r^2 - \left(r^2 \cos^{-1} \frac{\rho}{r} - \rho \sqrt{r^2 - \rho^2} \right) \\ = \pi r^2 - r^2 \cos^{-1} (1 - 2m) + r^2 (1 - 2m) \sqrt{1 - (1 - 2m)^2} \tag{3}$$

Here $m = \frac{x}{l}$ as before. The ratio A'/A for any value of m is the ratio of the cross-sectional areas of the two samples (half-cylinder and wedge) at the fraction of the sample length given by m . Values of this ratio, computed by means of Equations 1 and 3, have been plotted in Figure 7 against corresponding values of m .

In the wedge sample the quantity of creosote (or other material) contained in a portion of the sample bounded by the planes $m = a$ and $m = b$ will be given by

$$Y = \int_a^b Q A' dm \tag{4}$$

where A is the cross-sectional area of the sample and Q the amount of creosote or other material per unit volume at the point m . If A' is substituted for A in Equation 4, the resulting expression gives Y' , the quantity of creosote lying between $m = a$ and $m = b$ in the split cylinder sample.

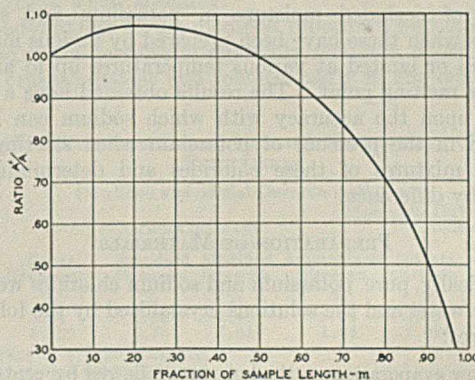


FIGURE 7. RATIO OF CROSS-SECTIONAL AREA OF SPLIT CYLINDER AND WEDGE AT SUCCESSIVE DEPTHS

The two samples have, as shown by Figure 7, the same cross-sectional area at $m = 0.5$. For values of m between 0.0 and 0.5, the ratio A'/A varies from 1.0 to a maximum of 1.07 and then back to unity. For values of m greater than 0.5, A' is always less than A . From this it at once follows that if, as is in general the case, the greater portion of the creosote is in the outer portion of the pole (between the cylinders $m = 0$ and $m = 0.5$), Y' will be greater than Y —i. e., the value for the creosote content obtained from the split cylinder sample will be greater than the correct value as given by the wedge sample. It is also evident that the greatest possible error in this case will be that corresponding to the maximum ratio of A'/A (1.07), or 7 per cent, and that the error will in general be less than this.

To determine the error for any given distribution of creosote or moisture it is necessary to integrate Equation 4 with Q given the values as a function of m that express this distribution. As any curve can be approximated by a series of straight lines, approximations to any concentration gradient [$Q = f(M)$] can be made by a series of straight lines, and therefore it will be sufficient to integrate Equation 4 for the case

$$Q = cm + k \quad (5)$$

Substituting in Equation 4 the value of Q given by Equation 5 and the value of A given by Equation 1, integration yields

$$Y = \pi r^2 l \left[\frac{cm^2}{2} - \frac{cm^3}{3} + km - \frac{km^2}{2} \right] \quad (6)$$

the value of Y for the wedge.

For the split cylinder the same procedure may be followed, taking the value of $A(A')$ given by Equation 3, and there is obtained

$$Y' = r^2 l c \left[\frac{\pi m^2}{2} - \left(\frac{1}{16} [2(1-2m)^2 - 1] - \frac{1}{4}(1-2m) \right) \cos^{-1}(1-2m) + \left(\frac{3}{32}(1-2m) - \frac{1}{4} + \frac{m}{6}(1-(1-2m)^2) + \frac{1}{48}(1-2m)[1-(1-2m)^2] \right) \right]$$

$$\sqrt{1-(1-2m)^2} + \frac{1}{32} \sin^{-1}(1-2m) \left] + r^2 l c \left[\pi m + \frac{1}{2}(1-2m) \cos^{-1}(1-2m) - \frac{1}{2} \sqrt{1-(1-2m)^2} + \frac{1}{6}(1-(1-2m)^2)^{\frac{3}{2}} \right] \quad (7)$$

Having found Y and Y' by means of Equations 6 and 7 for any given distribution, the error caused by using the split cylinder is given (in per cent of the true value) by the expression $100 \frac{Y' - Y}{Y}$. Similarly, the apparent creosote content obtained from a split cylinder sample may be corrected by multiplying by the ratio $\frac{Y}{Y'}$, if Y and Y' are evaluated for some assumed distribution, such as that in which the concentration is constant from $m = 0$ to $m = p$, and zero for $m > p$.

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Occlusion of Water by Potassium and Sodium Chlorides

The Influence on Indirect Determination of Sodium

G. FREDERICK SMITH, F. M. STUBBLEFIELD, AND E. B. MIDDLETON, University of Illinois, Urbana, Ill.

THE mixed salts of potassium and sodium in the form of their chlorides are often weighed after ignition at approximately 500° C. in preparation for the determination of sodium by difference after the determination of potassium. Ignition to the fusion temperature is not advisable, since these salts are appreciably volatile at their melting point. Heating to 500° C. is usual, since it is recognized that prohibitive amounts of water are occluded at lower temperatures.

The present investigation was carried out to establish the amount of occluded moisture in potassium and sodium chlorides when these have been prepared by various methods and dried or ignited at various temperatures up to and beyond the melting point. The results obtained have a direct bearing upon the accuracy with which sodium can be determined in the presence of potassium when starting with weighed mixtures of these chlorides and determining the sodium by difference.

PREPARATION OF MATERIALS

Chemically pure potassium and sodium chlorides were dissolved in water and the solutions crystallized by the following procedures:

1. Slow evaporation on the hot plate followed by centrifugalizing and drying at 140° C. Samples 1 and 2.
2. Precipitation of the saturated solution using a stream of gaseous hydrochloric acid. Crystals centrifugalized and dried at 140° C. Samples 3 and 4.
3. Per-crystallization¹ using collodion sack as semi-permeable membrane. The crystals thus obtained were dried at 140° C. These crystals were in the form of needles and were of low bulk density. Samples 5 and 6.

The odd-numbered samples were sodium chloride and the even numbers potassium chloride.

APPARATUS AND METHOD OF TESTING

Small samples of the salts prepared by the three methods described were weighed into covered crucibles and dried for 1 hour at the temperatures noted below the fusion point in an electrically heated crucible furnace, cooled, and weighed. The loss in weight determined the moisture liberated at the temperature employed. Loss by decrepitation was prevented by a crucible cover. A J. Lawrence Smith crucible was generally employed and the samples were placed in the bottom half. The top half and the cover were

shielded by a piece of transite board drilled to receive the crucible and allow the upper third and cover to project above. The crucible cover was kept cool by a porcelain crucible filled with water which was replaced as it boiled away. Temperatures were measured by a platinum-platinum rhodium thermocouple and potentiometer or by a quartz, nitrogen-filled mercury thermometer. The time of heating for determinations above the melting point was 20 minutes only.

TABLE I. DEHYDRATION OF POTASSIUM AND SODIUM CHLORIDES AT 550° AND 900° C.

SAMPLE	SAMPLE WEIGHT RANGE Grams	Loss at 550° C. ^a		Loss at 900° C. ^a		TOTAL Loss %	RATIO OF Loss 550°/900°
		Mg.	%	Mg.	%		
NaCl 1	0.7555-0.9770	1.75	0.196	0.62	0.069	0.264	2.9/1
NaCl 3	0.6822-0.9978	2.18	0.248	0.97	0.110	0.358	2.25/1
NaCl 5	0.8783-1.1560	3.85	0.393	0.79	0.081	0.475	4.9/1
KCl 2	0.7096-1.2272	1.53	0.156	0.63	0.064	0.217	2.4/1
KCl 4	0.8350-1.3131	4.84	0.487	0.78	0.079	0.566	6.2/1
KCl 6	0.6493-1.1812	1.69	0.200	0.58	0.069	0.269	2.9/1

^a Average of six determinations.

The total occlusion of water by sodium chloride increases when precipitated from hydrochloric acid as compared to crystallization from water. This result would not be predicted, since in the hydrochloric acid precipitation the crystals are very finely divided as compared to those obtained from evaporation of an aqueous sodium chloride solution. The total occluded water in per-crystallized sodium chloride is roughly twice that found in crystals obtained from aqueous solutions. The ratio of water liberated at 550° C. as compared to the water liberated at 900° C. follows closely values which would be predicted by comparison of crystal magnitudes. The ratio increases as the particles diminish in size.

The same relationships are found using potassium chloride, except that occlusion of water in the per-crystallization process is roughly half as great as that for sodium chloride similarly prepared. The ratio of water liberated at 550° compared to that at 900° C. is correspondingly low.

From an analytical point of view it may be said that mixed crystals of sodium and potassium chlorides occlude too much water after drying at 550° C. to be negligible and weighing after fusion with precautions to prevent volatilization, which at 900° C. would be prohibitive, is recommended. The residual moisture after drying at 550° C. averages 0.08 per cent in the three types of crystallization employed,

¹ Kober, P. A., *J. Am. Chem. Soc.*, **39**, 944 (1917).

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Determination of Nitrates

Modification of the Devarda Method

JEHIEL DAVIDSON AND ALEXANDER KRASNITZ, Bureau of Chemistry and Soils, Washington, D. C.

THE Devarda method for the determination of nitrates is coming more and more into use for the determination of nitrates in fertilizer mixtures (1) and in plant materials (2). The reduction is accomplished in a sodium hydroxide solution and in the case of inorganic salt mixtures the distillation is generally carried out in large Kjeldahl flasks with a Davison (3) scrubber with precautions to minimize frothing.

Magnesium oxide is used for the determination of ammonia in both organic and inorganic materials, primarily because of its slight effect, if any, upon nitrogenous organic materials. The object of the present investigation was to determine whether magnesium oxide could be used instead of sodium hydroxide in the Devarda method for the determination of nitrates. Such a modification would offer many advantages.

EXPERIMENTAL

The first step was to try the modification on solutions of known concentrations. Solutions of sodium nitrate and of ammonium chloride (0.02 N) were made from c. p. chemicals and analyzed—the ammonium chloride solution for ammonia by distillation with magnesium oxide and the sodium nitrate solution for nitrates by the official Devarda method. The results, given in Table I, are averages of triplicate determinations. In view of the small weights of nitrogen used, the variations between the quantities used and those found were considered as being within the limits of experimental error. The percentages of recovery given in Tables II and III were therefore based on the theoretical values of the solutions used.

TABLE I. ANALYSIS OF 0.02 N SOLUTIONS OF AMMONIUM CHLORIDE AND SODIUM NITRATE

CHEMICAL	SOLUTION	NITROGEN		PERCENTAGE RECOVERY
		Found	Theoretical	
	Cc.	Mg.	Mg.	
Ammonium chloride	15	4.31	4.20	102.6
Ammonium chloride	20	5.71	5.60	102.0
Sodium nitrate	15	4.31	4.20	102.6
Sodium nitrate	20	5.74	5.60	102.5

The distillation in the modified procedure was carried out in small Kjeldahl flasks (500 cc.) and without scrubbing bulbs for 1.5 hours, as in the standard Devarda method using 2 grams of magnesium oxide and 3 grams of Devarda alloy. The boiling proceeded quietly without foaming or frothing and required no precautions. It was difficult to account for the low recovery indicated by Table II, in view of the fact that the nitrate was being reduced with magnesium oxide, as registered by the 61 to 88 per cent recoveries obtained.

TABLE II. NITROGEN RECOVERED FROM SODIUM NITRATE (Distillation for 90 minutes specified by official Devarda method)

SODIUM NITRATE Concentration	Found	NITROGEN		PERCENTAGE RECOVERY
		Found	Theoretical	
	Cc.	Mg.	Mg.	
0.02 N	15	3.7	4.2	88.1
0.02 N	20	4.8	5.6	85.7
0.1 N	15	13.0	21.0	61.9
0.1 N	20	19.8	28.0	70.7

After a study of several factors, such as quantities of the Devarda alloy and of magnesium oxide, rate of boiling, and volume of distillate, it was found that the proposed modification required distillation for about 2.5 hours instead of the usual 1.5 hours. When 300 cc. of water were added to the Kjeldahl flasks and the boiling was regulated to require 2.5 hours, the results obtained were close to theoretical.

The modified method permits determination of ammoniacal and nitrate nitrogen in the same solution. A mixed solution containing equivalent quantities of ammonium chloride and sodium nitrate was first distilled with magnesium oxide and the ammonia determined. Enough water to give a total volume of 300 cc. and 3 grams of Devarda alloy were then added to the residues in the Kjeldahl flasks and the nitrate nitrogen was determined, with the results given in Table III.

TABLE III. AMMONIACAL AND NITRATE NITROGEN IN A SINGLE ALIQUOT (Modified Devarda method)

Portion of each	AMMONIUM CHLORIDE AND SODIUM NITRATE Concentration	Taken	THEORETICAL NITROGEN IN EACH FORM		AMMONIACAL NITROGEN FOUND		NITRATE NITROGEN FOUND	
			Cc.	Mg.	Mg.	%	Mg.	%
1	0.02 N	15	4.20	4.21	100.2	4.28	101.9	
2	0.02 N	20	5.60	5.66	101.0	5.71	101.9	
3	0.1 N	10	14.0	14.06	100.4	13.99	100.0	

The standard and modified procedures were then tried on a commercial fertilizer mixture, A, and on fertilizer B, obtained from the Soil Fertility Laboratory, Department of Agriculture. As fertilizer A contained organic matter, large Kjeldahl flasks were used as in the official procedure. The results, given in Table IV, are averages of three determinations except when specified.

The advantages of the modified procedure were marked in the case of the fertilizers, especially fertilizer A, which contained organic matter and foamed badly in the official procedure.

TABLE IV. AMMONIACAL AND NITRATE NITROGEN IN COMPLETE FERTILIZERS (Modified and official Devarda methods)

FERTILIZER	TOTAL NITROGEN	AMMONIACAL AND NITRATE NITROGEN		MODIFIED DEVARDA		
		Standard Devarda	Modified Devarda	Ammoniacal nitrogen	Nitrate nitrogen	Ammoniacal and nitrate nitrogen (calc.)
	%	%	%	%	%	%
A	3.44	2.55	2.48	2.29	0.26	2.55
B	3.72 ^a	3.76	3.64 ^b	1.64	2.09 ^c	3.73

^a Average of 4 determinations.

^b Average of 5 determinations.

^c Average of 6 determinations.

It was found that the sulfates of magnesium, copper, zinc, and aluminum interfered with the recovery of nitrate nitrogen by the proposed modification. The interference varied with the quantity of the sulfates present and with the size of the particles of the Devarda alloy. For example, 1 gram of magnesium sulfate caused interference when 3 grams of 20-mesh Devarda alloy and 2 grams of magnesium oxide were used. On the other hand, 0.3 gram of magnesium sulfate caused no interference under the same conditions, but interference developed when a coarser Devarda alloy was used. When 1 gram of the chloride of any of the above elements was present, no interference was noted when 20-mesh Devarda alloy was used. Interference did occur when coarser alloy was used.

The interference of the sulfates and chlorides of magnesium, copper, zinc, and aluminum is probably due to the lowering of the active alkalinity of the saturated magnesium hydroxide solution. The pH value of a saturated solution of magnesium hydroxide is relatively low—about 9.8—and anything that tends to lower it still further would probably reduce the

alkalinity of the solution below the minimum required for the proper functioning of the Devarda alloy.

The use of barium chloride to overcome the interference of the above-mentioned sulfates was not entirely successful. Nevertheless, it was found that a 1-gram addition of barium chloride materially shortened the distillation period required by the modified method for the complete recovery of nitrate nitrogen from solutions that contained no interfering substances. When barium chloride was added, distillation for 1.5 to 2 hours was sufficient for complete recovery of the nitrate nitrogen. It has not been determined whether this time-shortening effect was due to the rise in boiling point or to some other cause. The same effect can be obtained by the use of 5 instead of 2 grams of magnesium oxide but, if the determination of organic nitrogen in the residue from the ammoniacal and nitrate nitrogen determinations is desired, the use of 1 gram of barium chloride rather than the additional 3 grams of magnesium oxide would be more convenient.

The interference of the sulfates is not considered a serious drawback in the use of the proposed modification, as these are seldom found in nitrate-containing materials, in proportions large enough to cause interference. It has been determined, however, that a 5-gram charge of the 20-mesh or a 3-gram charge of a 40-mesh Devarda alloy overcomes completely the interference caused by quantities of as much as 1 gram of the sulfates mentioned.

It was found advisable, with both the official and the modified Devarda methods, to test the residue for nitrates in case of doubt as to complete recovery of the nitrate nitrogen.

The modified method is also being adapted for the determination of nitrates in plant materials.

PROCEDURE

The modified procedure is as follows:

Introduce a charge of mixed salt, equivalent to not more than 0.1 gram of nitrogen, into a 500-cc. Kjeldahl flask; add 200 cc. of water and 5 grams of magnesium oxide. Collect

about 100 cc. of distillate in a measured quantity of standard acid for the determination of ammoniacal nitrogen. Then disconnect the Kjeldahl flask and add 200 cc. of distilled water; add 3 grams of 20-mesh Devarda alloy and distill for 1.5 to 2 hours into a measured quantity of standard acid for the determination of nitrate nitrogen. If the sulfates of magnesium, copper, zinc, or aluminum are present in quantities above 0.3 gram, use 5 instead of 3 grams of Devarda alloy.

If no ammoniacal salts are present, add the magnesium oxide and Devarda alloy simultaneously and proceed as above.

SUMMARY

Magnesium oxide was substituted for sodium hydroxide in the Devarda method.

The modified method admits determination of ammonia and of nitrate nitrogen in the same solution, prevents frothing, and obviates precautions against passage of spray into the standard acid.

The distillation period stipulated is longer than that required by the official method. Addition of either barium chloride or larger quantities of magnesium oxide shortened the distillation period required for complete recovery of the nitrate nitrogen.

When present in relatively large quantities, the sulfates and, in a lesser degree, the chlorides of magnesium, zinc, copper, and aluminum interfered with the complete recovery of nitrate nitrogen by the modified procedure when coarse Devarda alloy was used. This difficulty was overcome by using more finely divided Devarda alloy or by increasing the commonly used quantities of the 20-mesh Devarda alloy.

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Rapid Potentiometric Method for Quantitative Determination of Copper in Alloys

HENRY B. HOPE AND MADELINE ROSS, Cooper Union Institute of Technology, New York, N. Y.

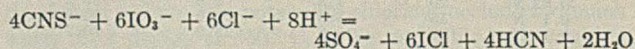
THE industrial importance of copper has led to the investigation of many methods of determination, of which the electrolytic is the most accurate. However, the time required, the technic, and the use of considerable platinum have made desirable a more rapid and easy method of analysis. The large potential break shown in the titration curve of potassium thiocyanate with potassium iodate using a bimetallic electrode system, as noted by Fenwick (2), has led to the suggestion by Kolthoff (5) that a similar break might occur with a monometallic system. The method herein described involves the precipitation of copper as cuprous thiocyanate, with an excess of standard thiocyanate solution, filtering off the precipitate formed, and titrating potentiometrically the excess thiocyanate with potassium iodate.

Among the methods for the determination of copper as cuprous thiocyanate, the following three are now in general use: (1) igniting to the oxide and weighing; (2) titrating with potassium permanganate; (3) adding an excess of potassium iodate and potassium iodide and titrating the liberated iodine with sodium thiosulfate. A less frequently used method is

that of Jamieson, Levy, and Wells (4), involving the direct titration of copper as cuprous thiocyanate, using chloroform. The present method avoids the large ignition errors of the first, the necessity of empirical factors of the second, and the tedious chloroform titration of the last. Another factor in its favor is the short time required for analysis, a complete determination requiring about 30 minutes.

DISCUSSION

According to Kolthoff (5), the reaction involved in the titration of the thiocyanate ion with the iodate ion is:



Experience has shown, however, that the thiocyanate must be standardized against the iodate and also against pure copper, whereby the method is rendered quantitative. The amount of hydrogen cyanide generated during the reaction is almost unnoticeable.

The platinum electrode used in this investigation was a

small coiled wire type, and was balanced against a saturated calomel electrode. The stirrer and electrode set-up of the Kelly electrometric titration apparatus was found to be the most convenient for the titration. A Leeds & Northrup Type K potentiometer was employed.

The authors have found that for a concentration of hydrochloric acid of less than 25 per cent an incomplete reaction

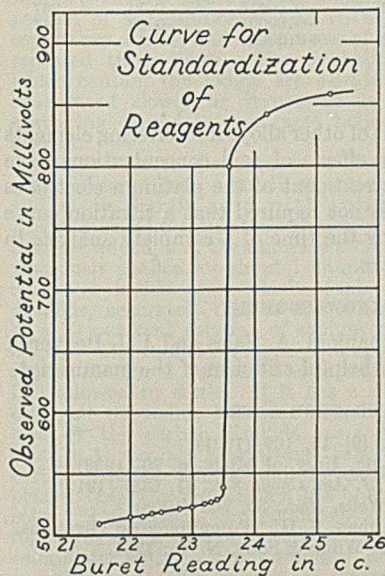


FIGURE 1

upon boiling. However, since the solubility of the precipitate in hot water is appreciable, it is necessary to cool the liquid before filtration. Since the cuprous thiocyanate is not completely insoluble in cold water, it was found desirable to use the same quantity of wash water in both standardization and determinations, limiting the quantity to about 40 cc.

In the method to be described, the potential break is very sharp, and shows a rise of from 200 to 350 millivolts upon the addition of one drop of potassium iodate at the end point. There is ample warning of the approach of the end point, due to a definite color change in the solution, the change being nearly though not altogether sharp enough to enable visual titration.

In determining the inflection point of the titration curve the method given by Hostetter and Roberts (3) has been found both simple and reliable, although the break in the curve is so sharp that for routine work no special method is required to find the end point. The plotting of a curve is therefore not essential. Two typical titration curves are shown in Figures 1 and 2.

In general, any substance which precipitates as a thiocyanate will interfere. The most commonly encountered of these is lead, and it should be removed as the sulfate. Tin should be filtered off as metastannic acid. Nickel, zinc, and small quantities of iron do not interfere with the titration, thus making the method especially applicable to the analysis of German silver.

PROCEDURE

Dissolve the sample, containing 0.1 to 0.2 gram of copper, in 3 to 4 cc. of nitric acid (sp. gr. 1.42) contained in a 150-cc. Erlenmeyer flask. Heat gently until there are no more brown fumes evolved. Add 3 cc. of concentrated sulfuric acid (sp. gr. 1.84), and heat until about 3 minutes after the first appearance of the dense sulfur trioxide fumes, keeping the flask in constant motion during this process. Cool and dilute with water to

about 15 cc., carefully neutralize with concentrated ammonium hydroxide until the appearance of a deep blue color, then pour in 10 cc. of a saturated solution of sulfurous acid. Add from a buret a measured volume of standard potassium thiocyanate solution, making sure that an excess is present. Heat the solution containing the flocculent white precipitate over a free flame, with constant rotation of the flask, until there can be detected no more evolution of sulfur dioxide. Where the sample is such that the amount of copper exceeds 0.1 gram, care should be taken in boiling off the excess sulfurous acid, since the large amount of precipitate has a tendency to cause bumping. This is easily avoided, however, by swirling the precipitate about in the flask during heating. The heating causes the precipitate to become granular. Cool to room temperature, and filter through a Gooch crucible with an asbestos pad of medium thickness. Wash with two 20-cc. portions of cold water.

Transfer the filtrate to a beaker suitable for titration, and rinse the filter flask with two 50-cc. portions of hydrochloric acid (sp. gr. 1.19), which must be added to the solution in the beaker. Dilute with water to a volume of 250 cc. Titrate potentiometrically with potassium iodate, which has been standardized against the potassium thiocyanate used. The addition of potassium iodate may be quite rapid until the yellow-brown color, which appears at first, begins to assume a green tone. Then titrate drop by drop until the point of maximum inflection, which is the end point. In the titration set-up, the platinum electrode is positive. If a curve of potential readings is to be plotted, it is essential that the readings of the potenti-

After frequent use, the electrode loses its sensitivity. Billmann's (1) suggestion that the electrode be heated to white heat in an alcohol flame is satisfactory.

The cuprous thiocyanate precipitate

becomes granular

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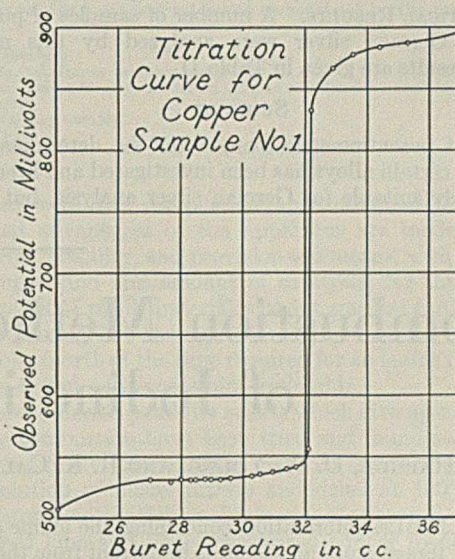


FIGURE 2

ometer be obtained directly after the addition of each portion of the potassium iodate, otherwise polarization results. The stirrer used with the apparatus should be kept in constant motion during the titration, especially when potentiometric adjustments are being made.

In their work the authors have found the use of 0.02 M potassium iodate and 0.05 M potassium thiocyanate to give a very satisfactory ratio. It is not necessary to weigh either of these reagents accurately, as they are standardized by titration.

TABLE I. STANDARDIZATION OF POTASSIUM IODATE AGAINST THIOCYANATE

POTASSIUM THIOCYANATE	POTASSIUM IODATE	RATIO	RISE IN POTENTIAL
Cc.	Cc.		Ms.
5.00	20.05	4.010	260
5.00	20.05	4.010	259
5.03	20.15	4.006	278

STANDARDIZATION OF POTASSIUM IODATE. The potassium iodate to be standardized is titrated against a 5-cc. portion of the potassium thiocyanate, first adding 50 cc. of concentrated hydrochloric acid, and diluting to 100 cc. The end point is obtained exactly as in the case of the actual copper deter-

TABLE II. TITRATION OF COPPER SAMPLES

WEIGHT OF SAMPLE Gram	COPPER PRESENT		TOTAL KCNS USED Cc.	KIO ₃ USED Cc.	KIO ₃ /KCNS Cc.	KCNS/Cu	COPPER FOUND Gram	ERROR		Rise Mv.
	%	Gram						Gram	%	
0.1064	...	0.1064 ^a	32.00	13.18	3.800	0.003745	0.1068	+0.0004	+0.37	276
0.1078	64.96 ^b	0.07003	23.60	18.77	3.800	0.003745	0.06988	-0.00015	-0.21	208
0.1472	60.57 ^b	0.08916	27.00	12.36	3.800	0.003745	0.08894	-0.00022	-0.24	303
0.1105	...	0.1105 ^a	32.00	11.95	4.010	0.003823	0.1109	+0.0004	+0.36	274
0.0999	...	0.0999 ^a	30.00	15.40	4.010	0.003823	0.1000	+0.0001	+0.10	310
0.1059	64.96 ^b	0.06879	20.10	8.37	4.010	0.003823	0.06885	+0.00006	+0.09	300
0.1274	64.96 ^b	0.08276	26.10	17.88	4.010	0.003823	0.08273	-0.00003	-0.04	202
0.2248	60.57 ^b	0.13616	38.36	15.37	4.010	0.003939	0.13601	-0.00015	-0.11	267
0.2150	60.57 ^b	0.13023	37.17	16.54	4.010	0.003939	0.13019	-0.00004	-0.03	247
0.2814	60.57 ^b	0.17044	47.20	15.55	4.010	0.003939	0.17064	+0.00020	+0.11	355

^a Nichols Copper Co., special sample (99.993 per cent copper).

^b V. L. Logo, analyst, Fales Chemical Co.

mination. The titer obtained gives the potassium iodate-potassium thiocyanate ratio. Table I shows typical results for a standardization.

STANDARDIZATION OF POTASSIUM THIOCYANATE. The potassium thiocyanate need not be accurately weighed, but must be standardized by titration against a sample of known copper content, or against a sample of pure copper. For this standardization, the method should be carried out exactly as described above, and a titer obtained of grams of copper per cubic centimeter of potassium thiocyanate.

ANALYTICAL RESULTS. A number of samples of pure copper and German silver were analyzed by this method. Typical results are given in Table II.

SUMMARY

A rapid potentiometric method for the determination of copper in certain alloys has been investigated and been found particularly suitable for German silver analysis, but is also

applicable to the analysis of other alloys if interfering elements are first removed. The effects of acid concentrations have been investigated. Pretreatment of the platinum electrodes may be necessary. It is not required that a titration curve be plotted, thus reducing the time of a complete analysis to approximately 30 minutes.

ACKNOWLEDGMENT

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Combustion Method for the Determination of Iodine in Plant Material

J. S. MCHARGUE, D. W. YOUNG, AND R. K. CALFEE, Kentucky Agricultural Experiment Station, Lexington, Ky.

RELIABLE information concerning the iodine content of forage crops and foods is important from the standpoint of nutrition and good health.

Iodine usually occurs in minute quantities in plant material grown under normal conditions in a fertile soil, and has an extremely important function in the metabolism of animals. The Kentucky Agricultural Experiment Station is now investigating the iodine content of forage crops and foods produced in the principal soil areas of the state. The authors have previously reported on the iodine content of soil and waters in Kentucky (5, 6). New methods for the determination of iodine in various kinds of organic matter by combustion with pure oxygen gas in closed systems have been published in recent years (1-4). A study of these methods reveals some points to be desired in the way of less complicated apparatus and technic. The attainment most desired is complete combustion of rather large samples of plant material at a uniform rate and at a moderate temperature, together with as complete recovery of iodine as is possible. After a considerable number of check determinations (duplicate determinations being made on all samples) with the apparatus described in this paper, the authors feel that substantial progress has been attained in devising a method whereby considerable quantities of plant material can be completely burned in a closed system, without the customary white fumes mentioned by previous authors, and iodine and

other elements which occur in small amounts determined quantitatively.

The set-up of the apparatus as used in the authors' laboratory is shown in Figure 1.

PROCEDURE

A sample of 50 grams of finely ground, air-dry, plant material is weighed, transferred into a porcelain dish, and thoroughly mixed with 10 grams of finely pulverized calcium oxide and 10 grams of finely pulverized copper oxide. The sample is then distributed in 3 alundum boats which are put end to end, in the large combustion tube. The right end of the large combustion tube is closed tight with a rubber stopper which carries a glass tube connecting with the wash bottle. The wash bottle on the left is connected to a suction pump. The current is connected to the electric furnace and when tube 3 attains a red heat air is drawn through the system and the first burner on the left of the gas furnace is lighted. After a short time the heat from this burner sets the plant material in the first boat on fire and a moderately rapid current of air drawn through the tubes and the turning on of other burners of the gas furnace at the proper time keeps the sample burning at a slow and uniform rate, somewhat in the manner of a lighted cigar. Any unburned vapors from the sample are drawn over the red-hot platinized asbestos catalyst where they are completely burned and the iodine vapors are carried into the gas wash bottles and absorbed.

After the combustion of the sample is completed the sources of heat are turned off and the apparatus is cooled by continuing to draw the current of air through the system. The suction pump is turned off, the boats are carefully removed, and the ash is digested and leached with hot distilled water. The filtrate

from the ash is combined with the potassium carbonate solutions from the absorption flasks and evaporated to dryness. (The authors have tried a solution of sodium bisulfite as suggested by McClendon but were unable to recover the iodine quantitatively. Accordingly a solution of potassium carbonate has been used in these experiments.) Just enough distilled water is added to dissolve the residue and the solution is transferred to a separatory funnel of the proper size. Enough 95 per cent ethyl alcohol is added to form two immiscible layers and the funnel is shaken vigorously for about 10 minutes. The aqueous portion of the solution is run into another separatory funnel and the process of extraction repeated three times. The alcoholic extracts which contain the iodine are combined and evaporated slowly to dryness so as to avoid spattering caused by too rapid boiling of the alcohol.

The residue is dissolved in a few drops of water, filtered into a small separatory funnel, and made slightly acid with sulfuric acid. About 3 cc. of a saturated solution of sulfurous acid are added, and the funnel is stoppered and vigorously shaken for about 1 minute to reduce iodate to iodide, after which 1 ml. of carbon disulfide, accurately measured, and about 2 ml. of a 10 per cent solution of sodium nitrite are added. The funnel is stoppered and vigorously shaken for about 1 minute and the carbon disulfide allowed to settle. If it has a slight pink color, all the iodine has been absorbed. However, if the carbon disulfide has a deep pink color, it is run into a centrifuge tube, 1 ml. of carbon disulfide added, and the extraction repeated until the last portion has only a faint color. The extracts are combined and centrifugalized, and a portion is compared in a microcolorimeter with an iodine standard prepared in a similar way. The results are reported in parts per million if high, or parts per billion if low.

A number of duplicate determinations were made on several different plant materials, using different catalysts alone and in combination. The results obtained are contained in Table I.

DISCUSSION OF RESULTS

From Table I it is apparent that fairly consistent results for iodine in several different kinds of plant material can be

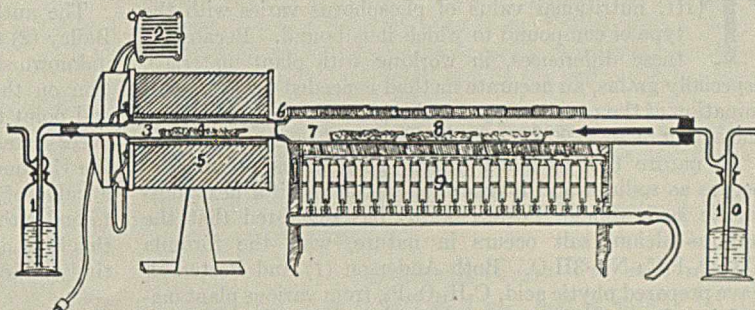


FIGURE 1. DIAGRAM OF APPARATUS

1. Absorption bottle containing 5 per cent potassium carbonate (2 bottles used)
2. Rheostat
3. Silica catalyst tube
4. Platinized asbestos catalyst
5. Electric tube furnace, maximum temperature 1100° C.
6. Asbestos cement seal, sealing large combustion tube to smaller tube containing catalyst
7. Silica combustion tube
8. Aluminum boats containing sample
9. Gas combustion furnace
10. Wash bottle containing 10 per cent potassium hydroxide

TABLE I. EXPERIMENTS TO TEST METHOD

PLANT MATERIAL USED	AMOUNT (AIR-DRY)		CATALYST USED	IODINE RECOVERED	
	Grams	Gram		Fusion Gram	Combustion in quartz tubes Gram
Sawdust (pine)	25	0.0000	None	0.0000	Trace
	25	0.000764	None	0.000760	...
	25	0.00190	10 (CaO) 10 (CuO)	...	0.001847
Persimmon leaves	50	Ni(NO ₃) ₂ 3	P. p. b. 160	P. p. b. 180
	50	3	175	183
Forest leaves	50	3	127	120
	50	3	147	133
Pine needles	50	3	476	470
	50	3	510	470
Beet tops	50	3	540	590
Lespedeza	50	3	535	600
	50	3*	521	600
Tobacco (dark)	50	3	1400	1520
Tobacco, Burley	50	3	1600	1680
Hay, soy bean, C-608a	50	3	...	80
Hay, timothy, No. 97955	50	3	...	600
Hay, red clover, No. 97972	50	3	...	500
Hay, orchard grass	50	3	...	1,200
Hay, bluegrass, No. 99494	50	3	...	588
Mixed grain ration (corn, wheat, oats, linseed oil meal, alfalfa leaf meal)	50	3	...	356
Hay, soy bean, C-1172, 1933 crop	50	5	...	390
	50	8 [Ce(NO ₃) ₄]	...	395
	50	20 (CuO)	...	420
	50	10 (CuO) 10 (CaO)	...	388
Hay, (mixed) timothy, red clover, crabgrass, 2nd cutting, 1933	50	10 (CaO) 10 (CuO)	...	324
	50	5 [Ni(NO ₃) ₂]	...	77
Corn, grain, yellow, C-1064, 1933	50	10 (CaO)	...	90
	50	20 (CuO)
Broom sedge	50	[Ni(NO ₃) ₂]	...	85
	50	10 (CuO)	...	104

obtained with the combustion apparatus described. The principal advantages of the apparatus are moderate cost, simplicity, stability, and provision of a means, with the use of the proper kind and amount of catalysts, for the complete combustion of plant material without smoke or other visible vapors passing out through the exit end of the system, in about one-fourth of the time required for an iodine determination by fusion with potassium hydroxide.

Several different catalytic agents which give up oxygen during the combustion have been tried and found satisfactory. When the finely ground plant material is wet with a 10 per cent solution of nickel nitrate and dried at 100° C., very satisfactory combustion is obtained. However, a mixture of powdered lime and finely pulverized copper oxide is as effective and more easily prepared and mixed with the plant material than the nickel nitrate. The copper oxide dust adheres and forms a film around the particles of plant material and furnishes oxygen for the combustion. The lime absorbs carbon dioxide to form calcium carbonate and apparently assists in the combustion without furnishing any oxygen.

Some samples of plant material were found to contain considerably more iodine than others, indicating either that different species of plants vary in their capacity to absorb iodine or that the soil in which they grew contained different amounts of this element.

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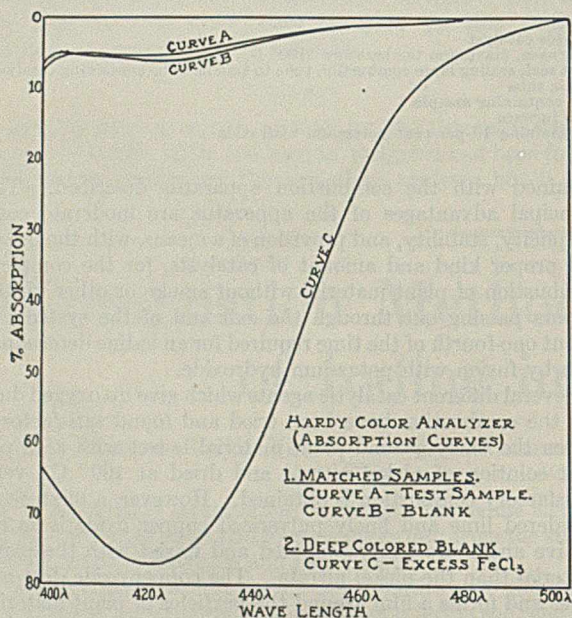
Estimation of Phytin Phosphorus

ROBERT S. HARRIS AND L. MALCOLM MOSHER

Department of Biology and Public Health, Massachusetts Institute of Technology, Cambridge, Mass.

THE nutritional value of phosphorus varies with the type of compound to which it is bound. Because of these differences, in working with plant materials, especially grains, an accurate method is needed for the determination of the peculiar type of phosphorus which prevails to the extent of 70 to 90 per cent in grains and seeds.

In nature this so-called phytin phosphorus presumably occurs as sodium and magnesium salt of inositol hexaphosphoric acid, though Posternak (6) has suggested that the sodium-calcium salt occurs in nature, with the formula $C_6H_8O_{24}P_6Ca_2Na_3 \cdot 3H_2O$. Both Anderson (1) and Posternak have prepared phytic acid, $C_6H_{13}O_{24}P_6$, from various plant materials. It seems likely, therefore, that phytin phosphorus occurs as some salt of inositol hexaphosphoric acid (phytic acid).



The best method which has been offered is that of Heubner and Stadler (4). Phytin phosphorus is extracted from pulverized plant material with 2 per cent hydrochloric acid for 3 hours, filtered by gravity through hardened filter paper, and precipitated from the filtrate with ferric chloride in acid solution with the formation of insoluble ferric phytate. Ammonium thiocyanate is used as indicator of the ferric thiocyanate which forms after all of the ferric phytate has been precipitated.

This method has been modified several times. Rather (7) has used a 1.2 per cent acid solution for the extraction of the grain. Averill and King (3) have used a strong ferric chloride solution (the upper limit suggested by Heubner) for titration. Knowles and Watkin (5) have used sodium salicylate rather than ammonium thiocyanate as indicator, on the basis that the pink end point is easier to read than the yellow-brown end point given by the ammonium thiocyanate. In the authors' hands these modifications have been inconsequential and have not removed the chief difficulty of the Heubner determination: titration of a solution containing a slow-settling colloidal precipitate. Check titrations are extremely difficult because the end point is uncertain.

The authors have tested the suggestion of Andrews and Bailey (2) that this difficulty can be removed by titrating the unknown short of the end point and then completing the titration on the filtrate. Unless one titrates very close to the end point the ferric phytate still interferes somewhat. This necessitates a preliminary determination of the end point by the Heubner (4) method. Even so, the determinations give a value of phytin phosphorus which is lower than that obtained with the Heubner method. The authors have modified this Heubner procedure in such a way that this difficulty is entirely removed.

PROCEDURE

Extract an 8-gram sample with 200 cc. of 2.0 per cent hydrochloric acid for 3 hours with occasional shaking and filter through a double layer of hardened filter paper. To a 50-cc. aliquot of this filtrate in a 400-cc. beaker add 10 cc. of a 0.3 per cent ammonium thiocyanate solution and 107 cc. of distilled water (resultant acidity is therefore 0.6 per cent). Add standardized ferric chloride solution (0.001 gram of iron per cc.) from a buret until the typical brown color of ferric thiocyanate no longer appears to be fading, then add 0.25 to 0.50 cc. more. Allow to stand until the precipitate flocculates (10 to 20 minutes) and filter through two layers of hardened filter paper. The flocculation may be induced by occasional stirring. Wash the precipitate with three 11-cc. portions of distilled water.

Make up a blank by adding 10 cc. of 0.3 per cent ammonium thiocyanate and 3.16 cc. of hydrochloric acid (sp. gr. 1.19) to 187 cc. of distilled water. Add ferric chloride solution to the blank until the color matches that of the unknown. Calculate the percentage of phytin phosphorus by the following formula:

$$\text{Per cent of phytin phosphorus} = \frac{\text{cc. of ferric chloride (sample - blank)} \times \text{grams of iron per cc.} \times 1.19 \times 100}{\text{weight of sample}}$$

The authors are not yet convinced that this 1.19 factor is correct. Tests have shown that the gravity filtration, taking perhaps 1 hour, causes no perceptible diminution of the color.

The advantage of the proposed modification in terms of reduced variability as compared with the original Heubner method is shown by the data in Table I.

TABLE I. COMPARISON OF METHODS

INVESTIGATOR	(Corn extract)		PHYTIN PHOSPHORUS	
	FERRIC CHLORIDE ^a Heubner Cc.	HARRIS-MOSHER Cc.	Heubner Gram per 100 grams	HARRIS-MOSHER
B. P.	3.59	3.89	0.209	0.227
	3.85	3.88	0.225	0.227
P. K. B.	3.95	3.92	0.230	0.229
	3.55	3.91	0.207	0.228
S. J.	4.03	3.93	0.236	0.229
	3.17	3.91	0.185	0.228
J. M. B.	4.24	3.92	0.248	0.229
	3.61	3.92	0.211	0.229
G. B. A.	3.82	3.87	0.223	0.226
	3.83	3.89	0.224	0.227
	3.94	3.90	0.230	0.227
J. F.	3.91	3.89	0.229	0.227
	3.81	3.88	0.223	0.227
	3.70	3.87	0.217	0.226
	Average		0.221	0.228
		Average deviation	0.011	0.001
		Maximum deviation	0.036	0.002

^a 0.000965 gram of iron per cc.

Table II demonstrates that this modification is equally applicable to determinations of phytin phosphorus in grains other than corn.

The phytin phosphorus content of pure calcium phytate is 19.7 grams per 100 grams (calculated). The crude sample

included in the determinations in Table II is about 50 per cent pure.

TABLE II. HARRIS-MOSHER METHOD

	FERRIC CHLORIDE ^a	PHYTIN PHOSPHORUS	SAMPLE USED
	Cc.	Grams/100 grams	
Oats	3.94	0.228	2.0000
	3.95	0.229	
Barley	3.73	0.216	2.0000
	3.75	0.217	
Corn	3.80	0.222	2.0000
	3.79	0.222	
Wheat gluten	3.24	0.186	2.0000
	3.23	0.185	
Calcium phytate (crude)	4.38	10.07	0.05
	4.40	10.11	

^a 0.000965 gram of iron per cc.

There is always a possibility, in colorimetric titrations of plant extracts, that a substance may be present which contributes a color which either masks the true end point or produces a false one. To check this possibility the authors subjected three solutions to the Hardy color analyzer.¹ The results are shown in the figure. Curve A was made by an extract of corn which had been matched with a blank (curve B). The two curves show that the matching of the color with the eye is quite accurate. They also show that the only color which was visible (and therefore used in matching the solutions) was that produced by the ferric thiocyanate. Therefore false end points are absent from the titration.

¹ Description of an early model, *J. Optical Soc. Am.*, **18**, 98 (1928). Description of instrument used for these determinations will appear in the same journal.

A third solution containing a large excess of ferric chloride was also tested (curve C). This curve indicates that at about 420 λ the absorption produced by ferric thiocyanate reached a maximum.

CONCLUSIONS

The Heubner-Stadler method for the determination of phytin phosphorus has been modified by titrating the unknown solution with ferric chloride beyond the end point, filtering, and matching the color of the filtrate with a blank. Determinations are much more accurate because the insoluble colloidal ferric phytate which clouds the end point has been removed.

Color analyses have shown that there is no color of plant origin which interferes with the end point in the titration of corn extracts with this method.

The color produced by ferric thiocyanate reaches a maximum absorption at 420 λ .

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RECEIVED May 25, 1934. Presented before the Division of Biological Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934. This paper is Contribution 31 of the Department of Biology and Public Health, Massachusetts Institute of Technology.

Improved Method for Determination of Percentage Acetyl in Organic Compounds

MAX PHILLIPS, Bureau of Chemistry and Soils, Washington, D. C.

A NUMBER of methods have been described in the literature for the quantitative estimation of the percentage acetyl in organic compounds. All these methods consist essentially in first splitting off the acetyl group and then determining quantitatively the acetic acid produced. The various methods described in the literature have been adequately reviewed by Meyer (2). Of the more commonly employed methods, mention need only be made in this connection of the method of Wenzel (6) and of Perkin (3). Wenzel hydrolyzes the substance with slightly diluted sulfuric acid, primary sodium phosphate and metaphosphoric acid being then added and the acetic acid distilled off under reduced pressure. Such a procedure, however, involves as a rule long and tedious operations, and the results are not

always reliable, particularly with small quantities of substance. Perkin hydrolyzes the substance with alcohol and concentrated sulfuric acid, distills off the ethyl acetate

formed into an excess of 0.5 N alkali, saponifies the ethyl acetate, and then determines the excess of alkali. The Perkin method, although relatively simple to carry out, suffers from the disadvantage that charring of the sample by the sulfuric acid may take place with the production of sulfur dioxide which, of course, interferes with the determination. With the technic recommended by Perkin it is difficult to obtain quantitative results, particularly with smaller quantities of material. Sudborough and Thomas (5) have used aromatic sulfonic acids such as benzene sulfonic acid or α - and β -naphthalene sulfonic acids. Freudenberg and Harder (1) have

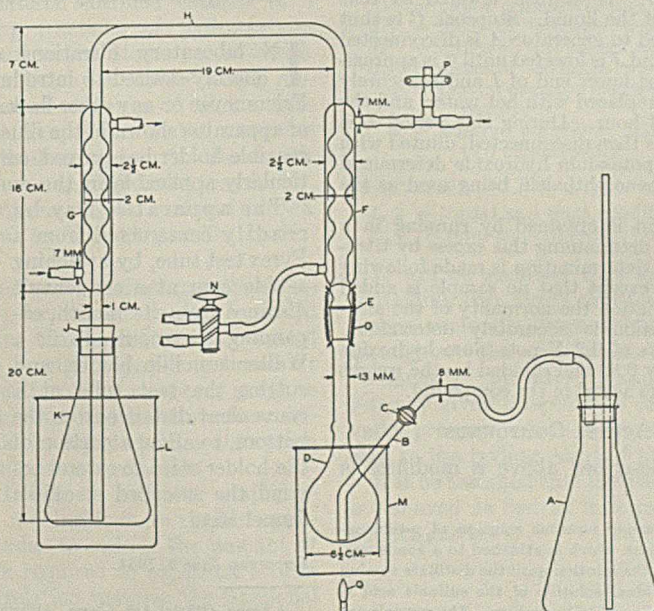


FIGURE 1. DIAGRAM OF APPARATUS

employed *p*-toluene sulfonic acid for breaking up the acetylated compound.

The method described in this paper is a modification of the Perkin method. It has none of the disadvantages of the original method, and is an improvement over the modified procedure employed by Freudenberg and Harder. Using the technic described it has been possible to obtain quantitative results not only with -O-acetyl but also with -N-acetyl compounds.

APPARATUS

The apparatus used is illustrated in Figure 1. It is constructed of Pyrex glass and consists of a reaction flask, *D*, which is provided with an inlet tube, *B*, and stopcock, *C*. *D* is placed in water bath *M*, which is heated with microburner *Q*. Connection between *D* and condenser *F* is made through interchangeable ground-glass joint *E* (No. 11) and is held fast by means of springs *O*. Condenser *F* is connected through glass tube *H* to condenser *G*. *K* is a 300-cc. Erlenmeyer flask upon which two marks have been placed indicating a volume of 100 and 150 cc., respectively. During the distillation *L* serves as an ice bath, and during the hydrolysis of the ethyl acetate, as a water bath. *J* is a rubber stopper, the opening of which has been lubricated with glycerol so that it can readily slide up and down tube *I*. *N* is a two-way stopcock through which cold water for condenser *F* is passed. By turning *N* and opening pinchcock *P* it is possible to drain the water immediately from *F*. *A* is a 500-cc. Erlenmeyer flask, partly filled with aldehyde-free 95 per cent ethanol and used for generating alcohol vapor. It is heated by means of an electric hot plate, not shown on the drawing.

PROCEDURE FOR -O-ACETYL COMPOUNDS

The weighed sample (0.3 to 0.4 gram) is placed in reaction flask *D* to which are also added 5 grams of *p*-toluenesulfonic acid,¹ a small piece of unglazed tile, and 25 cc. of 95 per cent aldehyde-free ethanol (prepared by the method of Stout and Schuette, 4). Into receiver *K*, 25 cc. (accurately measured with a pipet) of an alcoholic potassium hydroxide solution (approximately 0.2 *N*) and a small piece of unglazed porcelain are put. *J* is moved up close to the inner seal of *G*, leaving *K* open to the atmosphere. *K* is surrounded with crushed ice contained in *L*, which is supported by means of a ring and stand. The height of the ring is so adjusted that *I* reaches close to the bottom of *K*. *E* is lubricated with stopcock grease and is attached to *F* with springs, *O*. Cold water is circulated through both condensers, and *D* is placed in water bath *M*, and the reaction mixture is refluxed for 15 minutes. The water in condenser *F* is then drained, stopcock *C* is opened, and a slow stream of alcohol vapor is allowed to pass into *D* from generator *A*. This operation is continued until the total volume in *K* measures 150 cc.

During the distillation, *M* is heated with microburner *Q* at such a rate that at the end of the distillation the volume in *D* is reduced approximately one-half. *K* is then lowered so that the end of *I* is above the level of the liquid. Stopcock *C* is shut off, and the rubber tube attached to generator *A* is disconnected from *B*. *D* is detached from *F*, and *J* is lowered until it is approximately 2 inches (5 cm.) from the lower end of *I* and is securely attached to *K*. The ice in *L* is replaced with hot water, and the distillate is refluxed for one-half hour. During this period *L* is heated with a microburner. *K* is then disconnected, diluted with distilled water, and the unused potassium hydroxide determined by titration with 0.1 *N* acid, phenolphthalein being used as the indicator.

A somewhat sharper end point is obtained by running in a known excess of 0.1 *N* acid and determining this excess by titration with 0.1 *N* alkali. A blank determination is made following the procedure above described, except that no sample is added to *D*. From the blank determination the normality of the alcoholic potassium hydroxide solution is accurately determined. The number of cubic centimeters of 0.2 *N* potassium hydroxide solution used when multiplied by 0.86 and divided by the weight of the sample gives the percentage acetyl in the compound.

PROCEDURE FOR -N-ACETYL COMPOUNDS

The analytical procedure described above is modified as follows:

¹ This is purified as follows: A strong aqueous solution of *p*-toluenesulfonic acid is placed in a distilling flask which is attached to a condenser, and a current of steam passed through the solution until the distillate coming over no longer reacts acid. The residual solution of the sulfonic acid is concentrated on the steam bath and allowed to crystallize. The crystals are filtered off and dried in a vacuum desiccator over sulfuric acid.

Instead of refluxing the solution in *D* for 15 minutes, it is refluxed for 2 hours. The water in condenser *F* is then drained, and alcohol vapor from generator *A* is allowed to pass through the solution contained in reaction flask *D*. This operation is continued until the volume of the solution in *K* measures 100 cc. During this distillation the heating of *M* is so regulated that the volume of the reaction mixture in *D* is reduced one-half. *C* is then shut off, and cold water is again circulated through *F*. The solution in *D* is then refluxed for 30 minutes, after which the cold water circulating through *F* is shut off, the jacket of the condenser *F* is drained, and a current of alcohol vapor from *A* again passed through the solution in *D*. This operation is continued until the volume of the liquid in *K* measures 150 cc. The refluxing of the solution in *K* and the determination of the excess of potassium hydroxide solution are carried out exactly as described above for -O-acetyl compounds.

The results obtained with several -O-acetyl compounds and with acetanilide are given in Table I.

TABLE I. DETERMINATION OF ACETYL

COMPOUND	WEIGHT OF SAMPLE Gram	0.2 N KOH USED Cc.	ACETYL	
			Found %	Calculated %
β -Naphthyl acetate	0.4000	10.87	23.3	23.1
β -Naphthyl acetate	0.4000	10.88	23.3	23.1
β -Naphthyl acetate	0.2000	5.35	23.0	23.1
Diacetyl toxicarol	0.3000	5.95	17.05	17.4
Acetyl dehydrotoxicarol	0.3500	3.90	9.58	9.56
Cellobiose octaacetate	0.2000	23.9	51.3	50.74
Acetanilide	0.3500	13.1	32.1	31.8
Acetanilide	0.3500	13.08	32.1	31.8

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RECEIVED May 8, 1934. 238th Contribution from the Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

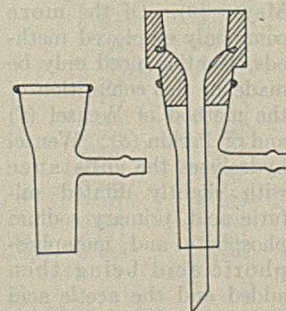
Suction Device

LOUIS COHEN

College of the City of New York, New York, N. Y.

IN laboratory filtrations employing suction, it is frequently desired to introduce the filtrate directly into the Erlenmeyer or any other flask. For such a purpose, the piece of apparatus shown in the illustration as used with a Walter crucible holder has proved convenient. This device is particularly applicable in the analysis of reducing sugars.¹

The apparatus may be readily constructed from a Pyrex test tube, by attaching a side arm at a convenient distance from its mouth, expanding the mouth to fit a Walter crucible holder, and cutting the test tube at a convenient distance from the bottom, to allow a portion of the holder stem to extend beyond the so-called suction funnel stem.



RECEIVED June 9, 1934.

¹ Assoc. Official Agr. Chem., Official and Tentative Methods, pp. 379-80 (1930).

Analysis of Dry Refinery Gases below Pentane by Simple Batch Distillation

J. HAPPEL AND D. W. ROBERTSON, Socony-Vacuum Corporation, New York, N. Y.

THE use of fractionation for analysis of gases and gasolines has come into extensive use in the oil industry during recent years. The most widely used type of apparatus utilizes the principle of rectification in a packed column with controlled countercurrent contact between vapor and reflux. Apparatus of this type has been described by Podbielniak (5), Oberfell and Alden (4), Schaufelberger (7), and Davis and Daugherty (2). This method gives very accurate results, but requires the services of a skillful operator. Furthermore, the apparatus is expensive and its operation requires considerable time. The advantage of a method which would not present these difficulties is obvious.

Simple batch distillation of a condensed gaseous mixture without fractionation has been used for refinery gas analysis in a method described by Robertson and Rosen (6). Before the distillation of the condensed sample, methane and "fixed gases" are pumped off. A good separation between methane and the heavier components at the temperature of liquid air is possible under conditions described in the above-mentioned article, without fractionation. The gas sample remaining, which must be free of pentanes and heavier, is distilled at atmospheric pressure and a curve is obtained analogous to the ordinary A. S. T. M. distillation curve for petroleum products. The material distilled consists of a mixture of three close-boiling fractions of hydrocarbons containing two, three, and four carbon atoms per molecule. From the distillation curve, aided by a master graph previously prepared by distillation of mixtures of ethane, propane, and normal butane, the composition of the sample is obtained. In applying the distillation data to the master graph it is necessary to use an empirical correction factor, since ordinary refinery gas contains unsaturated and branch chain compounds in addition to normal paraffin hydrocarbons.

This short-cut method of analysis possesses numerous features which make it valuable for routine work. A skilled operator is unnecessary to run the apparatus, the method is simple and rapid, and only a small quantity of liquid air is required. Its use in connection with a master graph is limited to four-component mixtures, and therefore to analysis of dry gases, such as would be rejected from absorption plants and high-pressure stabilizers at refineries.

The object of this paper is to present a further simplification of the short-cut method, making it more readily applicable to refinery work. In order to reduce the amount of preliminary experimental work required to construct a master graph, a mathematical correlation between the fractional

A method of calculating a master graph, whereby the composition of a refinery gas may be determined from an ordinary simple distillation of the condensed gas, has been developed. A computed graph is presented for the range commonly encountered, but limited to dry gases containing no compounds of higher boiling point than butanes. The method can be applied, if desirable, to more complex mixtures.

The preparation of a master graph in the manner outlined is believed to be as satisfactory for routine work as the correlation obtained by experimental distillation curves of synthetic mixtures according to the procedure presented by Robertson and Rosen (6). Moreover, since the calculated graph may be based on the particular close-boiling hydrocarbons actually present in the gas, instead of synthetic mixtures of pure paraffin hydrocarbons, the application of the graph is greatly facilitated. For approximate analysis, no correction factor is necessary.

distillation of hydrocarbon mixtures and the short-cut method of simple distillation has been developed, by means of which it is possible to construct a master graph based on the data furnished from a single Podbielniak analysis of a typical gas in the desired range.

METHOD OF COMPUTATION

The computation of the separation possible in any given case of simple distillation without fractionation was first made by Lord Rayleigh. Walker, Lewis, and McAdams (8) present a special form of the Rayleigh equation which applies to any two components of a multicomponent mixture if these two follow Raoult's law. The assumptions involved in arriving at this equation parallel very closely the conditions which exist during the

operation of the short-cut apparatus designed by Robertson and Rosen (6). The mathematical derivation, as applied to the case in hand, follows:

NOMENCLATURE

- E = moles of "ethanes" present in the liquid residue at any time
- P = moles of "propanes" present in the liquid residue at any time
- B = moles of "butanes" present in the liquid residue at any time
- V = vapor pressure of any constituent
- dE = moles of "ethanes" evaporated at any instant
- dP = moles of "propanes" evaporated at any instant
- dB = moles of "butanes" evaporated at any instant
- p = partial pressure exerted by any constituent in the liquid residue
- α = relative volatility, ratio of the vapor pressures of any two constituents

SUBSCRIPTS

- 1, 2 = initial and final conditions
- E, P, B refer to "ethanes," "propanes," and "butanes"

It will be assumed that the three close-boiling fractions, containing two, three, and four carbon atoms in each hydrocarbon molecule, respectively, behave as pure components throughout the distillation. They will be designated as "ethanes," "propanes," and "butanes" for convenience. For any given temperature each fraction will have a definite vapor pressure, which will vary with temperature in the same way as the boiling point of the nearest pure hydrocarbon.

If it be assumed that the vapor evaporated from the sample is removed as fast as it is produced, and that it obeys the perfect gas laws,

$$\frac{-dE}{-dP} = \frac{p_E}{p_P} \quad (1)$$

The validity of Raoult's law as a good approximation for the behavior of hydrocarbon mixtures at low temperatures is quite generally accepted. If this law holds, the following relationships obtain:

$$\frac{p_E}{p_P} = \frac{V_E E/E + P + B}{V_P P/E + P + B}$$

$$\frac{p_E}{p_P} = \frac{V_E E}{V_P P} = \alpha_{EP} \frac{E}{P}$$

Substituting in Equation 1,

$$\frac{-dE}{-dP} = \alpha_{EP} \frac{E}{P} \quad \frac{-dE}{E} = \alpha_{EP} \frac{-dP}{P}$$

If the deviation from Raoult's law were known, a correction factor could readily be applied to the relative volatility in the above equation. The equation may be integrated directly if the value of α_{EP} does not change,

$$\log \frac{E_1}{E_2} = \alpha_{EP} \log \frac{P_1}{P_2} \quad (2)$$

Similarly,

$$\log \frac{P_1}{P_2} = \alpha_{PB} \log \frac{B_1}{B_2} \quad (3)$$

The value of α will remain constant, strictly speaking, only for a constant-temperature batch distillation. For constant-pressure distillations where the initial and final temperatures vary little, a good approximation may be obtained by using the average temperature.

PREPARATION OF MASTER GRAPH

An inspection of these equations shows that the only information necessary to correlate the fractional analysis of a given mixture with its simple distillation is an accurate vapor pressure-temperature plot. The plot used in this work is the one recently published by Copson and Frolich (1).

The average boiling points of the ethanes, propanes, and butanes fractions were obtained by actual calculation from several Podbielniak analyses of the types of gases under consideration—i. e., cracked refinery gases containing no pentanes or heavier. The boiling points were as follows: ethanes, -90.0°C .; propanes, -44.5°C .; butanes, -5.0°C . It is believed that these boiling points are fairly representative of ordinary refinery gas analysis.

The correlation between the composition of the condensed gas distilled, which is a three-component mixture, and the distillation curve obtained is based on the fact that the determination of any two independent properties of a ternary mixture, in this case two boiling points on a distillation curve, is sufficient to fix the composition of the mixture. The points selected in this case were the 20 and 70 per cent points. Theoretically any other points would do just as well. From a practical standpoint, however, it is difficult to duplicate the first and last 10 per cent of any distillation curve. Furthermore, since the accuracy of this method depends on the determination of two clearly defined residue compositions, it is obvious that the faster the boiling temperature, and therefore the composition, is changing with respect to percentage distilled off at the points selected, the more closely will the two compositions and therefore the desired analysis be fixed. This condition is met by selecting points on the distillation curve which correspond roughly to the average percentage composition of the liquid components (for this case 20 per cent ethanes, 50 per cent propanes, 30 per cent butanes).

Several short-cut analyses indicated that the average boiling temperature from the initial to the 70 per cent point was about -50°C . The relative volatilities of ethanes to propanes ($\alpha_{EP} = 7.44$) and of propanes to butanes ($\alpha_{PB} =$

6.62) used in making computations from Equations 2 and 3, respectively, are calculated for this temperature and used as constants in all computations involved in preparing the master graph. Greater accuracy could, of course, be obtained by varying the relative volatility with the boiling point.

The temperatures calculated at the two chosen percentages off are plotted against each other on ordinary graph paper. Lines are drawn through all points having the same concentration of one component and another set of lines drawn through all points having the same concentration of another component. A graph showing these two sets of lines is sufficient to define any composition of the ternary mixture for the range covered.

The detail of the calculation is facilitated by making use of the fact that the equation relating propanes to ethanes must be a straight line on log-log paper with a slope equal to the relative volatility (α) of these two fractions. The original composition of the sample distilled determines this line. Similarly, a line may be drawn on the same graph for

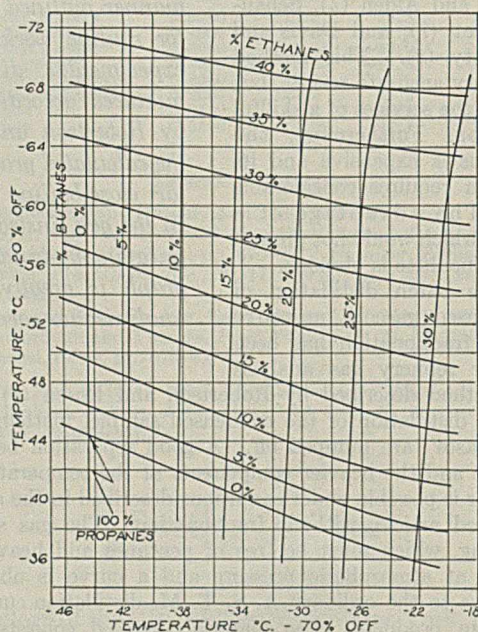


FIGURE 1. MASTER GRAPH FOR REFINERY GASES

propanes and butanes. By means of these two plots the composition of the material remaining in the distilling bulb at any percentage off may be calculated by trial and error, making use of the fact that the sum of the percentages read from the plots must add up to the percentage of residue remaining in the distilling bulb. The boiling point of the liquid residue is obtained by multiplying the mole per cent of each component by the vapor pressure of the pure component at a temperature which is assumed to be near the expected boiling point. The sum of the partial vapor pressures so obtained is divided by 100 to obtain the total vapor pressure of the liquid at the assumed temperature. By several trials the temperature corresponding to one atmosphere, the pressure at which all the analytical distillations are conducted, may be obtained.

The master graph presented (Figure 1) was constructed from 63 calculated points, one for each intersection shown on the plot. The effort involved in the construction of such a plot is much smaller than would be required to make synthetic mixtures and obtain actual data on their distillation characteristics. It is possible to compute the two selected

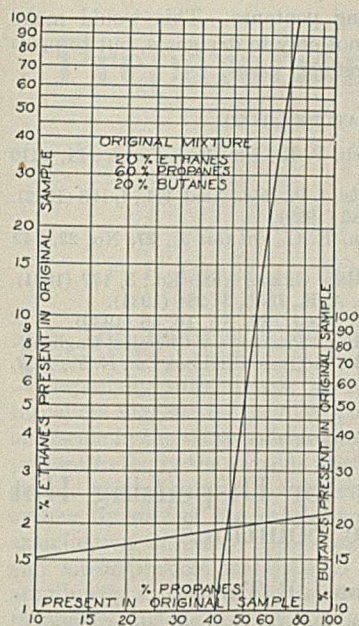


FIGURE 2. CHANGE IN COMPOSITION DURING SIMPLE DISTILLATION

It passes through the point ethanes = 20, propanes = 60. Similarly, the line representing propanes *vs.* butanes has a slope of

$$\frac{1}{\alpha_{PB}} \times \frac{V_B \text{ at } -50^\circ \text{ C.}}{V_P \text{ at } -50^\circ \text{ C.}} = \frac{89.7 \text{ mm.}}{593 \text{ mm.}} = \frac{1}{6.62}$$

This line passes through the point propanes = 60, butanes = 20.

The two lines on Figure 2 numerically represent the percentage at any time of the amount of each component present at the beginning of the distillation. The sum of the percentages of ethanes, propanes, and butanes must add up to the percentage residue remaining at any time during the distillation.

In order to calculate the 20 per cent point, the percentage of any component in the desired residue is guessed. This assumption enables the computation of the percentages of the other two components by means of Figure 2. If the three percentages so determined add to 80.0, the first assumption is correct. By successive approximations, it is possible to arrive rapidly at the following value for the residue composition in terms of 100 parts of original sample:

$$\begin{aligned} C_2 &= 7.6 \\ C_3 &= 52.7 \\ C_4 &= 19.7 \end{aligned}$$

80.0 parts of residue

It is unnecessary to convert this composition to a basis of 100 parts of residue in order to determine its boiling point. The sum of the partial pressures at the assumed temperature must in this case add to 608 mm. (0.8 atmosphere) instead of 760 mm. (1 atmosphere). Since the composition of the sample is always given in volume per cent, which in the case of a gas is interchangeable with mole per cent, no conversion factors are necessary to reduce the composition of the residue to mole per cent before making the boiling point calculation.

	VAPOR PRESSURE At -53° C.		MOLE FRACTION		PARTIAL PRESSURE Mm.
C_2	3960	×	0.076	=	301
C_3	517	×	0.527	=	272
C_4	74	×	0.197	=	15
					588
	At -52° C.				
C_2	4110	×	0.076	=	312
C_3	540	×	0.527	=	285
C_4	80	×	0.197	=	16
					613

By interpolation the value at which the sum of the computed partial pressures is 608 mm. is -52.2° C.

In order to calculate the 70 per cent point on the distillation curve, a similar procedure is followed. Since extrapolation of

boiling points for about twenty theoretical mixtures in a working day.

The following examples show in detail how a typical point on the master graph is calculated and how the graph is used:

ILLUSTRATION 1. It is desired to determine the 20 and 70 per cent points for a gaseous mixture containing 20 per cent ethanes, 60 per cent propanes, and 20 per cent butanes.

The plot, Figure 2, is constructed on log-log paper. The line representing ethanes *vs.* propanes has a slope of

$$\alpha_{EP} = \frac{V_E \text{ at } -50^\circ \text{ C.}}{V_P \text{ at } -50^\circ \text{ C.}} = \frac{4410 \text{ mm.}}{593 \text{ mm.}} = 7.44$$

It passes through the point

the ethanes-propanes line, not shown on the plot, shows the value of ethanes to be less than 0.001 per cent, to obtain the composition of the residue it is only necessary to select such a value for propanes on the propanes-butanes line, that the sum of the propanes and butanes is 30.

$$\begin{aligned} C_3 &= 13.9 \\ C_4 &= 16.1 \\ \hline &30.0 \end{aligned}$$

The boiling point is found by trial and error as before, except that in this case the sum of the partial pressures must add to 228 mm. (0.3 atmosphere).

	VAPOR PRESSURE At -30° C.		MOLE FRACTION		PARTIAL PRESSURE Mm.
C_2	1370	×	0.139	=	191
C_4	262	×	0.161	=	42
					233
	At -31° C.				
C_2	1323	×	0.139	=	184
C_4	251	×	0.161	=	40
					224

The boiling point by interpolation at 70 per cent off is -30.5° C.

ILLUSTRATION 2. A certain dry gas is drawn at barometric pressure into the sampling bulb of the short-cut apparatus. The sample is condensed, and all fixed gases and methane are pumped off at liquid air temperature. The sample is subsequently distilled, according to the Robertson and Rosen (6) method. The analysis of the gas is desired.

DATA (RUN 3)

Pressure in receiver at end of distillation	471.0 mm.
Pressure in receiver after equalization with distilling bulb (P_2)	476.8 mm.
Temperature at 20 per cent point (at $0.20 \times 471 = 94.2 \text{ mm.}$)	-60.5° C.
Temperature at 70 per cent point (at $0.70 \times 471 = 329.7 \text{ mm.}$)	-22.5° C.
Volume of sampling bulb	501 cc.
Volume of distilling bulb + lines + receiver bulb	527 cc.
Barometric pressure	768.6 mm.

The pressure in the apparatus after equalization, if no methane and fixed gases had been removed, would be represented by:

$$P_1 = \frac{\text{volume measured} \times \text{atmospheric pressure}}{\text{volume of distillation bulb} + \text{lines} + \text{expansion bulb}}$$

$$P_1 = \frac{501 \times 768.6}{527} = 731 \text{ mm.}$$

The difference between P_2 and P_1 represents the pressure due to fixed gases and methane pumped off before the distillation is begun. Its fraction of the total pressure, P_1 , gives the percentage of fixed gases and methane in the sample.

$$\begin{aligned} 731 - 476.8 &= 254.2 \text{ mm.} \\ \frac{254.2}{731} \times 100 &= 34.8 \text{ per cent methane} \end{aligned}$$

The composition of ternary mixture distilled is determined by use of the chart, Figure 1.

$$\begin{aligned} C_2 &31.3\% \\ C_3 &27.9\% \\ C_4 &40.8\% \text{ by difference} \\ \hline &100.0 \end{aligned}$$

A mixture of this ternary gas with 34.8 per cent methane and fixed gases gives the analysis of the gas sample.

$$\begin{aligned} C_1 &34.8 \\ C_2 &20.4 \\ C_3 &26.6 \\ C_4 &18.2 \\ \hline &100.0 \end{aligned}$$

DISCUSSION OF PROCEDURE

The apparatus and procedure used are entirely similar to those developed by Robertson and Rosen with several minor modifications. Since the master graph was to be computed from entirely independent vapor pressure data obtained from the literature, it was necessary to calibrate the thermocouple used to measure liquid temperatures very accurately. In order to avoid superheating of the liquid which does not boil rapidly during the removal of methane or the subsequent distillation, it was found advantageous to introduce a small quantity of finely powdered silicon carbide into the distilling

bulb. According to Midgley (3), this material is very effective as a boiling stone.

The fact that the vapors, after boiling from the liquid, immediately come in contact with the relatively hotter walls of the distilling bulb prevents their partial condensation. In consequence, the distillation of condensed gases parallels a simple batch distillation without fractionation much more closely than the ordinary A. S. T. M. distillation, in which the temperature of the walls of the distilling bulb above the boiling liquid is below its dew point. There are, however, certain details in which the experimental procedure does not exactly follow the mechanism assumed in the calculation.

The separation of methane from the ternary mixture involves the loss of a certain amount of ethylene from the ethanes fraction. This would tend to depress the front end of the curve. Moreover, the distillation curve is constructed from readings of the increase in pressure of the overhead gas in a receiving bulb, and therefore represents the percentage of the material finally recovered in the receiver. The graph, however, is constructed on the basis of per cent evaporated from the condensed sample in the distilling bulb. An error is, therefore, introduced by the amount of gas which fills the distilling bulb at atmospheric pressure, before any sample is collected. Furthermore, a lag exists in the thermocouple readings. These conditions, in addition to the approximate nature of the assumptions made in calculation of the master graph will cause discrepancies between the predicted and observed analyses.

APPLICATION OF METHOD

Several typical analyses of dry refinery gases are presented in the accompanying table for comparison with the fractional distillation method. These gases are derived at 25 per cent from crude still operation, 25 per cent from vapor phase cracking in a DeFlorez unit, and 50 per cent from liquid phase cracking in Cross units.

CONSTITUENT	RUN 1		RUN 2		RUN 3	
	Podbielniak	Short cut	Podbielniak	Short cut	Podbielniak	Short cut
Fixed gas and methane	39.4	38.2	1.3	1.1	36.5	34.8
Ethanes	24.0	23.2	10.5	12.0	18.0	20.4
Propanes	25.4	28.1	56.1	57.2	24.8	26.6
Butanes	11.2	10.5	32.1	27.9	20.7	18.2

The reasons for this inconsistency are believed due as much to variations from day to day of the composition of the close-boiling fractions contained in the refinery gases and to errors in experimental observation as to the inadequacy of theoretical treatment.

The data on hand at present indicate that the percentages of ethanes predicted from the master graph are about 2 per cent too high. Likewise, the butanes predicted are about 2 per cent lower than actually obtained in a fractional analysis. Since the accuracy with which the analyses may be performed is not much greater than this deviation, no correction has been incorporated into the master graph. When sufficient data become available to establish definitely this trend of deviation, it may be readily taken into consideration by changing the relative position of the constructed "grid" and the coordinates of Figure 1.

While not as accurate as the best fractional distillation analysis, the short-cut method with the simplification presented is well adapted to routine analysis for plant and laboratory. The method of preparing a master graph indicated above is believed to be quite as satisfactory for this type of work as that based on experimental data for synthetic mixtures of pure paraffin hydrocarbons, and presents the advantage of an appreciable saving of time and expensive chemicals. It is planned to extend the application of the Rayleigh equa-

tion to mixtures containing pentanes. This would make the correlation applicable, not only to dry gases, but to practically all but the heaviest refinery gases.

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Self-Filling Pipet for Dispensing Hot Caustic Solutions

CLIFFORD J. B. THOR

Bureau of Plant Industry, Austin, Texas

AN ORDINARY pipet modified as shown in Figure 1 greatly facilitates manipulation of the hot ferric sulfate-sulfuric acid solution used in the permanganate method for determining copper reduced in the various methods of sugar analysis. For this specific purpose, the lower tube of a 50-cc. pipet was cut off near the bulb and the new outlet fire-polished until the opening was of suitable size (about 3 mm.). The bends in the upper tube were easily made after heating with an ordinary wing-top burner.

The 50-cc. pipet operates satisfactorily when the solution is contained in a 2-liter Pyrex beaker which can conveniently

be heated by means of a small electric hot plate. The pipet is placed in the solution in a position similar to that shown by the dotted lines. It sinks gradually as the bulb fills and eventually assumes the position shown in solid line. The latter position permits removal of a large proportion of the liquid in the beaker before refill-

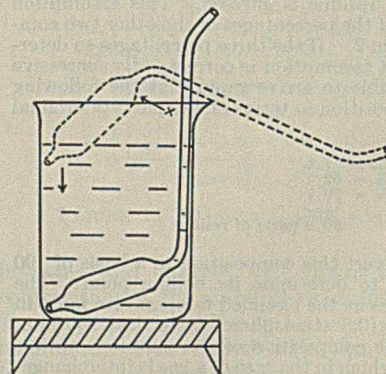


FIGURE 1. SELF-FILLING PIPET

ing is necessary. When the liquid is to be dispensed, the filled pipet is best twisted so the bulb is vertical. When dissolving cuprous oxide which has been collected on an asbestos mat in a Gooch crucible, it is convenient to loosen the mat with a pointed glass rod, transfer the bulk of it to a 250-cc. beaker, and finally wash down the inside of the crucible with the stream of hot acid solution from the pipet.

If such a pipet were to be made specially to deliver a more exact and predetermined volume of liquid, it would undoubtedly be desirable to attach the upper tube near point X since air bubbles tend to collect there when the level of liquid in the beaker becomes low.

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Preparation of Samples for Determination of Arsenic

Oxygen-Bomb Combustion Method

F. P. CAREY, G. BLODGETT, AND H. S. SATTERLEE, 802 Lexington Ave., New York, N. Y.

IN THE course of a clinical investigation of persons observed to be habitually excreting arsenic in their urine, especially with respect to certain cases exhibiting disturbances suggestive of chronic poisoning through the action of arsenic in the tissues of the nervous system, it became important to study the possible existence of sources from which arsenic might gain direct access to the central nervous system by way of the nasal tract. This study led to the examination of many specimens of the finely particulate and air-suspensible materials to which most city dwellers are directly exposed in the course of their daily lives. Such substances include sedimentary house dusts, as represented by the powdery portion of the material ordinarily collected by a household vacuum cleaner, and those finer particles of dust and soot of the inside and outside atmosphere which are obtainable by methods of filtration from the air.

A report on this study will be published elsewhere (16), but we are here concerned only with analytical methods. The quest which led to the development of the method to be described was not directed towards the estimation of arsenic in food materials, but primarily towards the better detection of minute quantities of arsenic in biological specimens as well as in house and atmospheric dusts. For these purposes it became highly desirable to devise an analytical method which would be capable of relatively rapid, simple, and inexpensive performance, and which would give reliable results in the detection of organically bound arsenic in any form. The examination of other materials such as foodstuffs has been included in the series here reported in order to show the general scope of usefulness of the method.

Methods of acid digestion with heat, as usually employed in preparing organic substances for the determination of arsenic in the Marsh or Gutzeit apparatus, are not only slow, laborious, and productive of corrosive fumes, but the results have frequently been questioned (6-13) on the basis of the possible volatilization of at least a portion of the arsenical content in the form of higher molecular arsines. This same objection holds with the well-known chlorate method of Fresenius and Babo, the perchloric acid method of Noyes and Bray (11), or the $MgO \cdot Mg(NO_3)_2$ oxidation of Kohn-Abrest (8), all of which employ digestion in open receptacles at boiling temperature, as well as with air-combustion methods in ignition tubes (12).

Numerous references (5, 7, 10) may be cited, questioning the validity of findings on the ground of contamination of the specimens by reagents employed during preparation or testing, or by exposure to possible contamination from atmospheric dust or laboratory apparatus. It is therefore desirable to employ reagents in which freedom from arsenic is not only generally conceded but readily demonstrable, and still further to avoid criticism on this ground by using relatively small amounts of a few reagents. The proportion, by weight, of reagents to samples ranges high in all acid-digestion methods, especially when supplemented by repeated adsorptions of residues by means of precipitated adsorbents, as ferric ammonium sulfate (5). In such processes lengthy exposure in open vessels of residues and of

adsorbents to atmospheric dust contamination is an important source of error.

The method of bomb combustion using pure oxygen was first devised by Berthelot (1) in 1899. In 1903 Bertrand (2) reported its successful use in the determination of small amounts of arsenic in organic matter. Both of these chemists employed a platinum bomb and ignited the charge by means of a small fuse of gun cotton; they took no cognizance, however, of the loss of arsenic in the form of finely divided oxide dispersed in the combustion gases, and these gases were allowed to escape from the bomb untreated.

Early in their investigation the authors became convinced that the complete extraction of suspended particles of arsenious oxide from combustion gases was an essential requirement in developing an adequate method. Preliminary experiments indicated that the loss assignable to this cause varies widely with the nature of the substance burned and the details of the technic employed in its combustion.

TABLE I. VARIATION IN ARSENIC LOSS

LAB. No.	ARSENIC CONTENT OF SAMPLE	
	Ash only <i>P. p. m.</i>	All products of combustion <i>P. p. m.</i>
117	10	20
99	3	12
102	22	30
120	16	17
467	28	28.6

The arsenical content of the smoke resulting from the explosion of some of the substances examined was found to be present in such a finely divided state that its recovery by ordinary methods was impossible except with a long series of Liebig or Geissler bulbs. The opinion was expressed to one of the authors (H. S. S.) by an authority on electrostatic precipitation¹ that a cloud precipitation would probably be more easily applicable to the problem and quite as effective as an electrostatic precipitation, such as that provided by the apparatus of Drinker and Thomson (3). This was found to be true.

The preparation, by desiccation, of the material to be burned in oxygen under pressure is not difficult, but certain precautions against volatilization losses are necessary. The means of ignition, as provided in oxygen bombs of approved type, involve no difficulty. In the selection of an oxygen bomb it is obviously important to have the surfaces which are exposed to the flame and to the gases of combustion composed of material which is absolutely resistant to the products of combustion. In this respect lined bombs, either of metal or porcelain, have been found less satisfactory than those of solid construction. It is also desirable to have the valve stem and the passages through which the gases of combustion are exhausted to the washing train, not only of noncorrodible material, but of simple design and readily accessible to washing. To meet these qualifications a bomb cover was designed, the details of which are shown in Figure 1, A. Although pressures are safely controlled by a reduction valve on the oxygen line, it is also advisable to place the

¹ The authors are indebted to F. G. Cottrell for his opinion on this subject.

switch which closes the ignition circuit some distance from the bomb, thus eliminating any possible risk to the operator. Although the ordinary fusible nichrome wire of 34 B & S gage has been usually employed by the authors, it was found practicable to use a nonfusing platinum wire to ignite the charge. (While the work here reported has been done with electrical ignition in a rather capacious bomb, it is hoped that an oxygen bomb of smaller capacity can be developed which will be adapted to ignition of the charge by simple conduction of heat.)

biological specimens requires special precautions which are not discussed here.

Where the heat of combustion is small, it has been found advantageous to line the small combustion crucible with arsenic-free cotton gauze. The weighed sample is placed in the bomb and the ignition wires are connected in the usual manner; the bomb is then closed and oxygen is admitted to a pressure between 20 and 30 atmospheres through a pressure-reducing valve connected with the oxygen supply. The charge is then ignited by closing a switch which is preferably situated at some distance from the bomb.

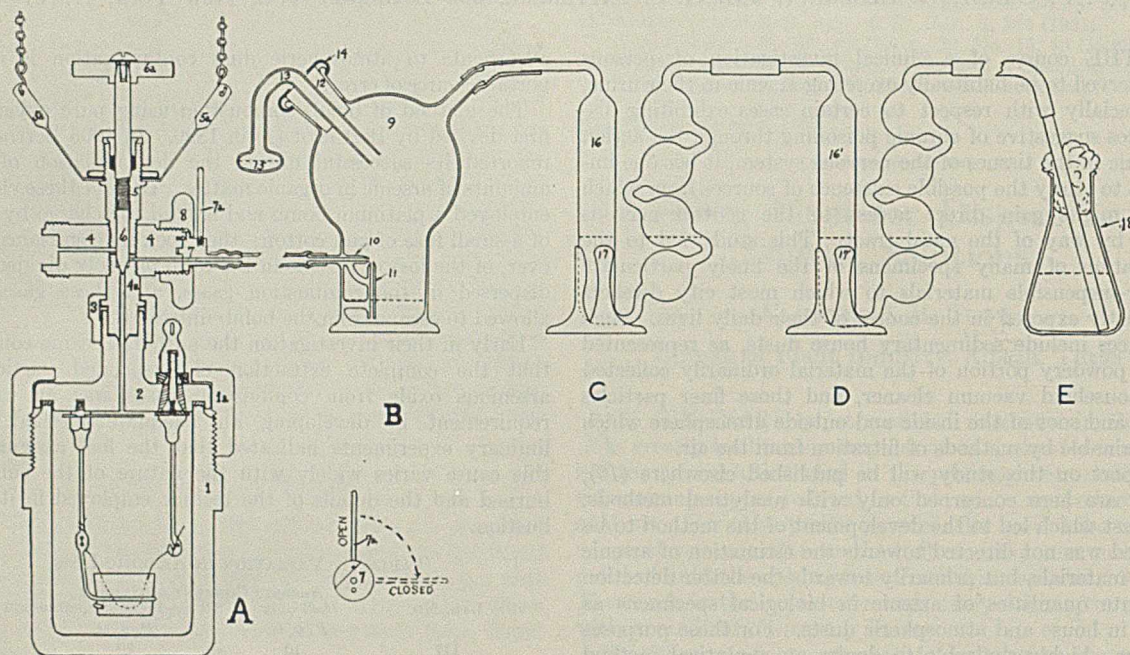


FIGURE 1. CLOUD-PRECIPIATION APPARATUS FOR OXYGEN-BOMB COMBUSTION ANALYSIS

A. Bomb B. Cloud-precipitation chamber and nebulizer C, D. Koeninck bulbs C, D, E. Washing train

The bomb combustion method finally evolved combines a specially designed nebulizing and cloud-precipitating chamber, B, with two or more Koeninck gas-washing tubes in series, C, D. In this nebulizer the combustion gases enter as a fine jet which sprays hydrochloric acid, producing an ammonium chloride cloud within the chamber by reaction with ammonia. This cloud of ammonium chloride vapor acts as a precipitating agent upon the finely particulate combustion products and facilitates extraction by the washing train.

With this arrangement the reagents employed are such as may be easily obtained in a pure state and are few in number—namely, nichrome (or platinum) wire, hydrochloric acid, ammonium hydroxide, sulfuric acid, oxygen, and water, and the quantities of the first four are very small. The sample is heated only while confined in the bomb, so that losses by volatilization during the oxidizing process are most surely prevented. The quantity of acid introduced into the Gutzeit or Marsh apparatus is only that used in the gas-extraction train and is therefore under close control. This avoids the error affecting quantitative determinations ascribed by Lawson and Scott (9) to differences in the rate of evolution of the arsine caused by variations in acid concentration.

METHOD

The sole primary requisite is that the sample be readily combustible. Specimens of high moisture content should be dehydrated, preferably at low temperatures, and for a bomb capacity of 380 ml. as here illustrated, from 0.5 to 1 gram of the dried material is taken. The preparation of certain

The combustion gases are passed into the nebulizing chamber, B, by opening first the cut-off valve, 7, and then the needle valve, 6. The passage of the combustion gases through jet 10 produces a spray of hydrochloric acid (1 to 1), which is controlled by operation of the needle valve. This spray causes a simultaneous precipitation of an ammonium chloride cloud by reaction with the ammonia vapor derived from the ammonium hydroxide reservoir, 15, in the tubulature of the chamber. The resulting vaporous mixture is carried through the train of Koeninck bulbs containing a measured amount of sulfuric acid (1 to 3). The residual gases are then washed out of the bomb into the train by first closing the cut-off valve, 7, on the bomb and repeatedly introducing 2 to 4 atmospheres of oxygen and washing through.

The bomb is next opened, the valve passages and bomb are washed with water, and the ash, washings, and solutions from the absorption train are introduced into the Gutzeit generator.

RESULTS

Over six hundred samples have been examined by this method, but many were not appropriate for use as check samples, principally because of difficulties in obtaining true duplicates. Table II shows the results obtained on a wide variety of specimens by the nitric-sulfuric acid digestion method of Gautier as modified by Sanger and Black (14), in comparison with the method of the authors.

It seems evident that no paralleled series for comparison by recovery of known amounts of arsenious oxide added to organic materials, as used by Sanger and others (5, 9), can be a criterion as to the adequacy of different methods, since the discrepancies between the methods may be attributed to loss of the organically linked arsenical content.

By the method of comparison which the authors have

adopted, employing identical samples of unknown arsenical content, there is always the possibility of nonuniformity of the supposedly identical samples, although an effort has been made to choose for such comparative tests materials which tend to minimize this chance. Conclusions should therefore be drawn only with respect to parities or disparities which show an average consistency or an average tendency in one direction.

TABLE II. COMPARISON OF ARSENICAL CONTENTS

LAB. No.	MATERIAL	METHOD	
		Bomb combustion	Acid digestion
		P. p. m.	P. p. m.
531	Soot from kitchen exhaust fan	46	46
506-7	Atmospheric dust ^a	292	186
547	Atmospheric dust	286	209
552-3	Atmospheric dust	231	208
99	Vacuum cleaner dust ^b	12	5
102	Vacuum cleaner dust	30	12
108	Vacuum cleaner dust	30	12
117	Vacuum cleaner dust	20	10
120	Vacuum cleaner dust	17	8
137	Vacuum cleaner dust	33	20
138	Vacuum cleaner dust	53	53
405	Vacuum cleaner dust	40	20
402	Vacuum cleaner dust	80	25
449	Vacuum cleaner dust	36	15
409	Vacuum cleaner dust	25	10
430	Vacuum cleaner dust	45	20
140	Vacuum cleaner dust	25	27
119	Swept dust from cellar floor	360	200
474	Animal hair	8	1
476	Cotton fiber	4	0.5
495	Animal hair	12.5	2.5
462	Cigar tobacco	12	3
475	Pipe tobacco	1	0.0
479	Pipe tobacco	18	2.5
480	Pipe tobacco	40	6.5
459	Pipe tobacco	14	0.0
157	Cigarette ^c	2.5	0.0
582	Cigarette	10	8
591	Cigarette	17	3.3
592	Cigarette	5.7	6
593	Cigarette	10	5.3
596	Cigarette	3.2	1.3
603	Cigarette	20	2.5
620	Cigarette	9.5	1.5
621	Cigarette	9	3.3
502	Canned vegetable	10.3	0.6
504	Egg yolk	9.2	2.1
574	Cocoa	3.6	3.9
612	Coffee	0.5	0.08
613	Processed coffee	1.3	0.0
626	Milk	0.19	0.05
627	Milk	0.15	0.00
628	Milk	0.15	0.00
629	Milk	0.18	0.00
580	Medicated ointment	2.8	1.6
510	Gasoline	0.7	0.0
511	Gasoline	0.7	0.0
512	Gasoline	0.7	0.03
514	Gasoline	0.4	0.01

^a Samples of atmospheric dust were collected and their weights determined by attaching a dried and tared piece (50 sq. cm.) of specially tested filter cloth to an ordinary domestic air filter and reweighing after exposure and a second drying. Filter and contents were consumed in the analysis.

^b Samples of vacuum cleaner dust were collected by the ordinary household vacuum cleaner, put through an 80-mesh sieve, and the fines taken for analysis.

^c In each case the entire cigarette was taken for analysis.

It has been found advisable to use the smallest crucible that will conveniently hold the samples, and to place it in the bomb in such a position that the flame does not come in contact with the walls of the apparatus. The sudden cooling of the flame by contact with the metal surfaces may result in the deposition of tar. Where the material under examination, such as tobacco, manifests a tendency to form tars, a pressure of 30 atmospheres of oxygen should be used in the combustion.

While the Gutzeit zinc-acid evolution (18) was employed for the ultimate determination of the arsenic, the method here described for preparation of the sample may be combined with any other methods of determination, as with the Marsh-Berzelius generator or with certain electrolytic modifications of the Marsh or Gutzeit method as recommended by Thorpe (17) and Lawson and Scott (9). But where the electrolytic evolution of the arsine involves the use of porous cells, the method cannot be considered reliable because of objections taken by Fink (4), which are based on possible retention of arsenic by the porous cell.

A predetermined constant strength of the acid solutions and combined washings has been found to provide a uniformity of action in the Gutzeit generator which greatly facilitates accurate quantitative estimations in comparison with a standard scale covering a range of low values, and it is desirable to select a suitable aliquot from the combined washings to fall within the optimum range of from 0.5 to 10.0 micrograms.

Where too dense an ammonium chloride cloud is formed, difficulty is experienced in its complete absorption by the washing train, C, D, E. It has been demonstrated, however, that a complete absorption of the ammonium chloride is not essential to the recovery of the arsenical smoke, probably because the particles of arsenious oxide act as nuclei in the cloud formation and are washed out in its coarser particles. Control of the cloud density is, however, desirable, and is effected by adjusting the concentration of the acid in the nebulizer and more particularly by adjusting the surface area of ammonium hydroxide in reservoir 15, by rotation of arm 13 in stopper 12, and by application of gentle heat to this reservoir.

CONCLUSIONS

In the opinion of the authors the disparity in the results shown in Table II, especially with those samples where the arsenic present was presumably in organic linkage, is attributable to loss by volatilization in the acid-digestion treatment. Should the arsenical organic be resistant to oxidation by the mixed acids, or, should the arsenic linkage be of a fugacious type in minute concentration, even an almost inappreciable vapor pressure at the temperature of boiling acid would account for a considerable loss of arsenic due to the relatively large amount of acid boiled off during the digestion. Experimental support for this opinion was given by an apparent decrease in the arsenical content of certain specimens either during desiccation at relatively high temperatures or on long standing at room temperature.

Negative results have repeatedly been obtained throughout the entire series of experiments, and with other samples the arsenical content has frequently been as low as 0.2 p. p. m., conclusively demonstrating that the large disparity in results is not due to contamination by the equipment or the reagents employed.

SUMMARY

The method which has been described for the destruction of organic matter in preparation for the determination of arsenic prevents the loss of arsenic during combustion and is believed effectually to minimize losses in the process of extracting the combustion products. It is particularly applicable to organic substances and to the detection of minute concentrations of arsenic which may be inherent in or adsorbed to such substances.

The advantages claimed for the method are reliability, simplicity, and speed.

Insurance is provided against losses of organically linked arsenic which may be volatilized by the older methods. Because the process of oxidation is practically instantaneous and within an air-tight vessel and the extractions are carried on within closed vessels, there is no exposure to possible contamination of the sample or reagents by arsenical dust as with oxidations involving lengthy digestions, filtrations, and adsorptions. Simplicity is attained through the use of fewer and smaller quantities of reagents in the oxidation process and the avoidance of acid fumes requiring a hood. The actual time required for preparing samples for arsenic determination is from 15 to 25 minutes, in addition to whatever time may be necessary for dehydration, as against the many hours which are required for the proper performance of an acid-digestion process.

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Sulfur Determination in Sulfite Waste Liquor and Organic Compounds

Potassium Permanganate Method

R. N. POLLOCK, Rainier Paper and Pulp Company, Shelton, Wash., AND A. M. PARTANSKY, University of Washington, Seattle, Wash.

THE usual determination of total sulfur in a sample resolves itself into two parts: oxidation of sulfur to sulfate, and determination of the sulfate. For the second part there are a standard method of precipitation with barium chloride and several volumetric methods, but the first step has always presented difficulties to the analytical chemist.

Benson and Benson¹ used five different methods (Schreiber's, Schorger's, fuming nitric acid and potassium chlorate, bromine, and the U. S. Forest Products Laboratory method) for determination of total sulfur content of sulfite liquor, but report considerable difficulty in obtaining check results. The authors had a similar experience with the above methods as well as with the Eschka method and obtained consistently good results only with Parr's sodium peroxide bomb method. Since the bomb is not always available, the following method, which can be used in any modestly equipped laboratory, was developed.

METHOD

A sample containing enough sulfur to give a barium sulfate precipitate of about 0.15 gram is placed in a porcelain crucible of 25-ml. capacity or larger, 0.5 ml. of concentrated sodium hydroxide solution and 5 ml. of saturated potassium permanganate solution (about 1 gram of potassium permanganate) are added, and the contents of the crucible thoroughly mixed with a little stirring rod. The rod is then removed, care being taken to wash off the adhering mixture into the crucible. After evaporation to dryness on a water bath or in a drying oven the crucible is ignited for half an hour in a muffle furnace or on a Meeker burner at approximately 500° C. A thorough ignition is essential; otherwise low results were invariably obtained. The cooled melt is moistened with a little dilute permanganate solution to oxidize any sulfides which may have formed, and hydrochloric acid is then carefully added, care being taken to prevent loss by effervescence. After evolution of the carbon dioxide has ceased, more hydrochloric acid (total of about 5 ml. of 12 N acid or an equivalent amount of dilute acid) is added and the crucible warmed over a steam bath until all manganese dioxide has been converted into soluble manganous chloride. Hot water is then added and the contents of the crucible are filtered through a rapid filter into the precipitating beaker. (Alkali permanganate attacks porcelain crucibles; the amount of silica extracted increases with use of the crucible. On the average, porcelain crucibles can be used only six to eight times, after which results become irregular.) Washing the crucible and the filter is continued until from 200 to 300 ml. of hot water have been used. From this point on analysis proceeds in the usual way: dilution to 400 ml., adjusting the acidity, precipitation with barium chloride, digestion, filtration, ignition, and weighing.

The permanganate method here described has been successfully used by the authors in determination of total sulfur in sulfite waste liquor for a considerable length of time, checks within 0.1 per cent being common, but, as shown by Table II, the method can be used for determination of sulfur in other organic compounds, regardless of its state of oxidation or chemical bonds.

TABLE I. SULFUR CONTENT OF SULFITE WASTE LIQUOR

SULFITE LIQUOR SAMPLE	BY PERMANGANATE METHOD	BY PARR'S BOMB METHOD
	Mg./ml.	Mg./ml.
1	8.57	..
	8.57	..
2	8.83	..
	8.80	..
	8.77	..
	8.77	..
3	8.45	8.27
	8.47	8.32
	8.50	8.37
	8.22	..

TABLE II. DETERMINATION OF SULFUR IN PURE ORGANIC COMPOUNDS

COMPOUND	THEORETICAL PERCENTAGE OF SULFUR	BY PERMANGANATE METHOD		BY PARR'S BOMB METHOD	
		Weight of sample Gram	Sulfur %	Weight of sample Gram	Sulfur %
Sulfanilic acid	18.52	0.1849	18.36
		0.1908	18.48
		0.2300	18.45
Trional	26.47	0.0809	26.35	0.0855	26.25
		0.0995	26.30	0.0898	26.24
		0.1702	26.20
Thiourea	42.13	0.0616	42.02
		0.0740	41.94
		0.0700	42.13

TABLE III. EFFECT OF PRESENCE OF MANGANOUS CHLORIDE ON BARIUM SULFATE PRECIPITATE

Manganous chloride present (KMnO ₄ equivalent)	None	1 gram	2 grams
	Gram	Gram	Gram
Barium sulfate precipitated	0.2010	0.2009	0.2021
	0.2015	0.2017	0.2018
	0.2016	0.2014	0.2020
Av.	0.2014	0.2014	0.2020

DISCUSSION

Table I gives a typical set of checks obtained in sulfur determination of three samples of sulfite waste liquor by the alkali permanganate method and a comparison of one set with results obtained by Parr's method. In the determination by the permanganate method, 2-ml. samples of the liquor were used, while in the determination by bomb method 25 ml. of the liquor were neutralized and evaporated to dryness,

¹ Benson, H. K., and Benson, W. R., *IND. ENG. CHEM., Anal. Ed.*, 4, 220 (1932).

and the weight of the solids was determined. The solids were then ground and samples weighed out, the sulfur content was determined, and the results obtained were recalculated on the volume basis. The slight difference in the results may be due to the difference in methods of taking samples.

Table II gives results of sulfur determination on pure sulfur-containing substances. The values obtained are in sufficiently close agreement with the theoretical.

Table III gives results of precipitating sulfates from 10 ml. of known sodium sulfate solution in the presence of various amounts of manganous chloride. It shows that an amount equivalent to 1 gram of potassium permanganate (the amount used in the authors' procedure) has no effect, and twice that amount gives a variation of only 6 parts in 2000.

The chief advantages of the permanganate method are: It is simple; no special apparatus is required; there is nothing to regulate or watch; and only small quantities of very common inexpensive reagents are used. The method can be used for oxidation of sulfur compounds in water solutions (like sulfite waste liquor) without preliminary evaporation to dryness. The oxidation is rapid and complete in cases tried and the re-

sults agree closely with either those obtained by the peroxide bomb or with the theoretical percentages as shown by Tables I and II. Compounds which will float on the surface of the alkaline permanganate solution cannot be completely oxidized, owing to loss by evaporation or sublimation.

The two filtrations in the procedure are time-consuming. However, if crucibles were made of a material which is resistant to both alkali permanganate and hydrochloric acid, such as acid-resistant alloys, the first filtration would be eliminated and the time necessary for the determination cut to two-thirds of that required at present. The authors did not have such crucibles at hand.

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Colorimetric Determination of Iodine by the Starch-Iodine Reaction

HELEN QUINCY WOODARD, Huntington Fund for Cancer Research, Memorial Hospital, New York, N. Y.

THE use of the starch-iodine reaction for the quantitative determination of iodine has been considered by von Fellenberg (3), Remington et al. (7), and others to be unsatisfactory, and the method has seldom been used, although Turner (10) employs it over a limited concentration range. Examination of the literature of starch-iodine suggests a number of possible sources of error in the use of its formation for the determination of iodine. While Dhar (2) considers that a true but unstable compound between starch and iodine is formed, most authors agree that the union of starch and iodine is by adsorption. Gorbatscheff and Winogradowa (5) claim that molecular iodine is adsorbed. Angelescu and Mirescu (1), Firth and Watson (4), and others consider that the blue color is due to the adsorption of potassium triiodide by starch, while Gramenitski (6) and Staiger (8) present evidence to show that hydriodic acid is the substance adsorbed. It was early pointed out by Treadwell (9) that the starch-iodine compound is readily dissociated at low concentrations.

The present investigation was undertaken in order to develop a rapid method of determining iodine in the presence of 10 per cent of potassium iodide. A study was made of the influence of potassium iodide, acids, and salts on the intensity of the starch-iodine color, and the degree of dissociation of the compound was estimated under a number of different conditions.

METHOD. The method has been described in detail in a previous publication (11). A stock solution of approximately 0.025 per cent iodine in approximately 0.2 per cent potassium iodide was prepared and standardized by titration against sodium thiosulfate. Portions of this were then diluted with starch and potassium iodide solution in 10- or 25-cc. volumetric flasks as required, and read in the colorimeter. For part of the work a solution of iodine in 25 per cent ethyl alcohol instead of 0.2 per cent potassium iodide was used. The stock starch solution was prepared by making a paste of 2 grams of soluble starch with 30 cc. of cold water, adding this slowly to 70 cc. of boiling water, and boiling for 5 minutes. The solution was made fresh every

3 or 4 days. The colorimeter used was a Klett instrument having cups and plungers with black walls, and substage illumination through blue glass.

RESULTS

The effect of potassium iodide on the intensity of the starch-iodine color was studied by adding small quantities of potassium iodide to solutions containing 2.5 per cent alcohol, 0.5 per cent starch, and 1.8 and 5.0 mg. of iodine per 100 cc. It was found that the intensity of color increased rapidly with increasing potassium iodide concentration until the normality ratio of potassium iodide to iodine reached 0.35. This ratio must therefore be equaled or exceeded whenever iodine is to be determined by the starch-iodine reaction. Further additions of potassium iodide caused a slight increase in color intensity until at 1 per cent concentration it became purplish. The color became progressively redder and fainter with increasing concentration of potassium iodide beyond this point. In general it was found that differences in concentration insufficient to change the tint of the starch-iodine color caused no significant change in the intensity of the color, and could be disregarded in analytical work. It is probable that addition of small quantities of potassium iodide to the alcoholic starch-iodine solution increases the intensity of color through the formation of potassium triiodide, which gives the characteristic deep blue compound with starch. Further additions of potassium iodide after all the iodine has been converted to potassium triiodide may then change the tint and intensity of the color by changing the colloidal state of the compound.

Starch-iodine solutions containing sufficient potassium iodide to be definitely reddish do not obey Beer's law with some types of illumination. The deviation is small when the blue filter at present provided with the Klett biocolorimeter is used. In the preparation of the correction curves (Figure 1) the colorimeter plunger was set always at the same depth in the standard solution. The same standard setting was then used for making readings on unknown solutions which were

to be corrected by means of the curve, so that error due to depth effect was avoided.

The effect of concentration of starch on the intensity of color developed in solutions containing 2.4 mg. of iodine plus 20 mg. of potassium iodide per 100 cc. and 5.1 mg. of iodine plus 40 mg. of potassium iodide per 100 cc. was studied. The maximum color was developed when about 40 mg. of starch per mg. of iodine were present. All the correction curves given were obtained with solutions containing 0.5 per cent starch, so that excess was always present beyond the amount necessary to combine with all the iodine. It was found that aging of the starch solution used had no effect on the starch-iodine color so long as the starch remained only faintly opalescent.

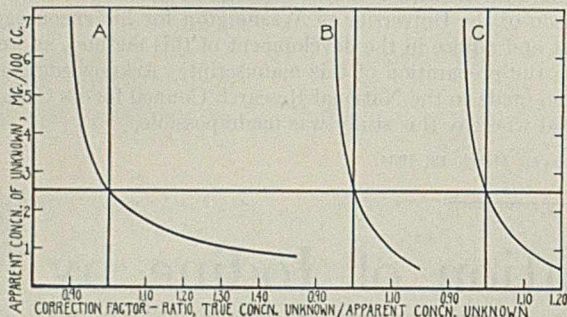


FIGURE 1. CORRECTION CURVES

The dissociation of the starch-iodine compound was found to be the most important source of error in the analytical method. In order to study this, iodine solutions of different concentrations were made up in 0.5 per cent starch with or without potassium iodide in known concentrations. These solutions were then read against a standard containing 2.5 mg. of iodine per 100 cc. The results of this work are given in the form of correction curves in which the apparent concentration of the unknown is plotted against the correction factor to be applied. This method of plotting shows the effect of dissociation of the starch-iodine compound very clearly, but in actual practice it is more convenient to use correction curves in which the apparent concentration of the unknown is plotted against the absolute correction in mg. per 100 cc.

Curve A, Figure 1, shows the correction factors for iodine solutions in 2.5 per cent alcohol and 0.5 per cent starch, when read against a standard containing 2.5 mg. per cent alcohol, 0.5 per cent starch, and 2.5 mg. of iodine per 100 cc. Fifty determinations were made, with an average error of ± 4 per cent. When the unknown is more concentrated than the standard its apparent concentration is too large, and when less concentrated its apparent concentration is too small. This is evidently due to the dissociation of the starch-iodine compound. From the fact that the correction factor becomes nearly constant when the apparent concentration of the unknown is 5 mg. per 100 cc. or more, it seems likely that the dissociation of the compound is small above this concentration. On the other hand, the dissociation is so great in dilute solution that the method is of little use when the iodine concentration is below 1.5 mg. per 100 cc. Furthermore, the intensity of the starch-iodine color in the absence of potassium iodide is so readily affected by contamination with electrolytes that the method is reliable only under very special conditions.

Curve B, Figure 1, shows the corrections for iodine solutions containing 0.5 per cent starch and about 8 mg. of potassium iodide per mg. of iodine, when read against a standard containing 2.5 mg. of iodine and 20 mg. of potassium iodide per 100 cc., and 0.5 per cent starch. Fifty-five determinations were made with an average error of ± 2 per cent. The dissociation in this system is much less than in system A, and the method may be used for iodine concentrations down to 0.5 mg. per 100 cc.

Curve C, Figure 1, shows the corrections for iodine solutions in 10 per cent potassium iodide and 0.5 per cent starch, read against a standard containing 2.5 mg. of potassium iodide per 100 cc., 10 per cent potassium iodide and 0.5 per cent starch.

Eighty determinations were made, with an average error of ± 2.5 per cent. The curve is similar to B, but the corrections are a little larger. This does not necessarily mean that the dissociation of the starch-iodine compound is greater in 10 per cent potassium iodide, but is probably due to the optical peculiarities of the solution. A correction curve was also obtained for solutions in 10 per cent potassium iodide read against a standard containing 1.0 mg. of iodine per 100 cc. When allowance was made for the greater dissociation of the more dilute standard, this curve was practically identical with C.

After correction factors for dissociation had been obtained it was possible to study the effect of acids and salts. This was done for solutions containing 8 mg. of potassium iodide per mg. of iodine, and for solutions in 10 per cent potassium iodide. Unknowns containing 1.1, 2.3, and 4.6 mg. of iodine per 100 cc. and 0.5 per cent starch were made up in 0.1 N solutions of different acids and salts and read against a standard containing 2.5 mg. of iodine per 100 cc., 0.5 per cent starch, and no added acid or salt. The apparent concentration of the unknown was then compared with that of iodine solutions of the same concentration prepared without acids or salts, as shown in the correction curves. The results are shown in Table I, each value being the average of 7 determinations.

TABLE I. ERROR INTRODUCED BY CONTAMINANT

CONTAMINANT 0.1 N	SOLUTIONS CONTAINING 8 MG. OF KI PER MG. OF I True iodine concentration, mg. per 100 cc.			SOLUTIONS IN 10 PER CENT KI True iodine concentration, mg. per 100 cc.		
	1.1	2.3	4.6	1.1	2.3	4.6
Na ₂ SO ₄	+0.11	+0.17	+0.17	-0.04	-0.02	+0.02
NaNO ₃	+0.11	+0.15	+0.19	-0.01	-0.01	0.00
NaCl	+0.10	+0.15	+0.19	-0.02	-0.05	+0.06
CaCl ₂	+0.07	+0.19	+0.26	-0.02	0.00	0.00
H ₂ SO ₄ ^a	+0.11	+0.12	+0.12	+0.12	+0.12	+0.12
HNO ₃ ^a	+0.12	+0.15	+0.14	+0.11	+0.16	+0.25

^a Acid concentration in solutions in 10 per cent potassium iodide, 0.05 N.

The presence of salts in 0.1 N concentration causes appreciable errors in the determination of iodine in solutions containing minimal quantities of potassium iodide, but not in solutions containing 10 per cent potassium iodide. For the former solutions the effect of sulfuric and nitric acids is the same as that of sodium sulfate and sodium nitrate, from which it appears that the adsorption of hydriodic acid by starch is not an important factor in the production of the starch-iodine color. The effect of acids on solutions in 10 per cent potassium iodide is probably due to an increase in the actual concentration of iodine through decomposition of potassium iodide. This takes place rapidly in concentrated potassium iodide solutions, and may have been appreciable in the 2 or 3 minutes which elapsed between addition of acid to the solutions and making the readings.

Investigation of solutions containing 0.1 N disodium phosphate or sodium hydroxide in low concentration showed that large errors were introduced as soon as the pH of the solution rose above 7.

SUMMARY

The most important source of error in the colorimetric determination of iodine by means of the starch-iodine reaction was found to be the dissociation of the starch-iodine compound. Correction factors are given for the determination of iodine in the concentration range from 0.5 to 7.0 mg. of iodine per 100 cc. The effect of the concentration of starch and potassium iodide, and of the presence of contaminating acids and salts has also been investigated.

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Determination of Lead Soap in Oils and Greases

HARRY LEVIN, The Texas Company, Beacon, N. Y.

IT IS FREQUENTLY necessary during the examination of greases, car oils, extreme pressure lubricants, etc., to determine the amount of lead soap present. Various methods have been published for this determination but most of them are inaccurate, difficult, or tedious. The methods generally involve the determination of the combined lead present, from which, by suitable factors, the percentage of lead soap is calculated. The more common methods for the determination of the combined lead are the following:

1. The direct ignition of a weighed portion of sample, the ash being recorded as lead oxide.

This procedure leads to inaccurate results because the ash is practically never pure lead oxide, but contains metallic lead and usually iron oxide.

2. The direct ignition of a weighed portion of sample, followed by digestion with sulfuric acid to convert all the lead present to lead sulfate, which in turn is dissolved in ammonium acetate and subsequently precipitated and determined as the chromate.

This procedure, while sound in principle, is lengthy and offers difficulties in manipulation.

3. The sample is digested with concentrated sulfuric acid followed by ignition of the mass, leaving the lead as sulfate. From this point on, the procedure is the same as the second method.

This method is even more difficult than the second, the oil and sulfuric acid frothing to such an extent as to cause losses.

The procedure which has been developed in the author's laboratory has proved universally satisfactory, even in the hands of comparatively inexperienced operators. It is based on the fact that the sample being analyzed is soluble in a homogeneous mixture of pure benzene and glacial acetic acid, and upon being refluxed the lead compounds are converted to acetate which can subsequently be precipitated as lead chromate. Incidentally, this procedure, if slightly modified, distinguishes between the organic and inorganic lead, the latter resulting either from excess of litharge used in the saponification process or consisting of lead sulfide formed by the interaction of litharge with the sulfur compounds of the mineral oils.

PROCEDURE

The reagents required are a 10 per cent potassium chromate solution, a mixture of glacial acetic acid and pure benzene (1 to 2 by volume), and pure benzene.

Two to ten grams of sample, depending upon the concentration of lead soap, are weighed into a suitable Erlenmeyer flask, 45 cc. of the glacial acetic acid-benzene mixture are added, and the mass is boiled actively under a reflux condenser for 1 hour. It is allowed to cool, and is then transferred to a globe-shaped separatory funnel, the flask being rinsed with two successive 10-cc. portions of the glacial acetic acid-benzene mixture.

To the separatory funnel are added 50 cc. of distilled water, the contents are gently shaken and allowed to settle, and the aqueous layer is withdrawn into another separatory funnel. Experience has shown that when decomposition has been completed the layers separate rather sharply. Emulsions usually indicate incomplete decomposition.

The benzene layer is washed with 50-cc. portions of distilled

water until the aqueous extract is free of acetic acid. Combined aqueous washings are then filtered through wet paper to remove entrained oil, and the lead in the filtrate is precipitated as chromate by the addition of an excess of 10 per cent potassium chromate solution.

When the precipitate is thoroughly settled and the upper layer is perfectly clear, it is filtered on a Gooch, washed thoroughly with hot water, dried at 105° C., and weighed as lead chromate. By a suitable factor the lead chromate is converted to the particular lead soap involved—for example, lead chromate multiplied by 2.381 gives lead oleate; lead chromate multiplied by 2.949 gives lead naphthenate, of a naphthenic acid whose molecular weight is 374.

Tables I and II indicate the reproducibility of results by the different methods in the hands of a competent chemist who had not used any of these methods before. It is apparent that the proposed method was the only one which consistently gave reproducible and accurate results. The solvent used for the solution samples was a pale mineral lubricating oil.

TABLE I. DETERMINATION OF LEAD SOAP AS OLEATE

SAMPLE	METHOD 1		METHOD 2		METHOD 3		PROPOSED METHOD	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
	%	%	%	%	%	%	%	%
Lead oleate, comm.	102.1	97.0	94.5	91.6	96.6	53.3	96.5	96.4
3 per cent lead oleate, solution	4.3	3.1	1.8	0.7	.. ^a	.. ^a	2.79	2.82
10 per cent lead oleate, solution	11.4	11.0	8.8	5.3	.. ^a	.. ^a	9.73	9.59

^a Lost by violent spattering or uncontrollable frothing.

TABLE II. DETERMINATION OF LEAD SOAP AS NAPHTHENATE

SAMPLE	METHOD 1		METHOD 2		METHOD 3		PROPOSED METHOD	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
	%	%	%	%	%	%	%	%
Lead naphthenate, comm.	84.6	84.6	80.1	58.0	86.6	82.1	86.4	86.2
3 per cent lead naphthenate, solution	2.57	2.67	2.25	1.93	1.33	1.20	2.53	2.53
10 per cent lead naphthenate, solution	8.3	9.1	8.1	7.3	8.60	8.37	8.56	8.56

The naphthenic acid component of the lead naphthenate used in these tests had a molecular weight of 374.

When it is desired to distinguish between the organically combined lead present as lead soap and the inorganic lead compounds, the procedure should be modified: The weighed sample is first refluxed with benzene, then filtered as hot as possible through the Gooch crucible, and to the filtrate is then added the required amount of glacial acetic acid to give the proportion indicated above; the rest of the procedure for organically combined lead is identical with that outlined. Experience with a great many commercial lead soap lubricants has shown very few lead soaps, basic or otherwise, which are not soluble in boiling benzene. The inorganic lead compounds which remain insoluble in the benzene can be digested with nitric acid and the lead determination carried out in the usual manner.

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The Microanalysis of Gases

III. Hydrogen, Carbon Monoxide, Hydrogen Chloride, and Ammonia

FRANCIS E. BLACET AND GEORGE D. MACDONALD

University of California at Los Angeles and Stanford University, Calif.

IN THIS article the methods of microanalysis of gases which were described earlier (1, 2) are extended to include a new method for the determination of hydrogen and carbon monoxide, and to include hydrogen chloride and ammonia as gases which may be determined by known procedures.

ADDITIONS TO APPARATUS

In applying the methods of microanalysis, it has not always been possible to collect the gas directly in the analytical apparatus, and it has therefore been necessary to arrange for the transportation of samples. A circular iron pneumatic trough, 2 cm. in diameter and 1 cm. in depth, which can be lowered into the mercury reservoir of the analytical apparatus (2, Figure 1), is welded to an adjustable iron arm of a small ring stand. A second adjustable arm carries a steel spring clamp into which the gas holders can be slipped by a horizontal movement. This device makes it possible to take a small sample of gas to or from the main apparatus without

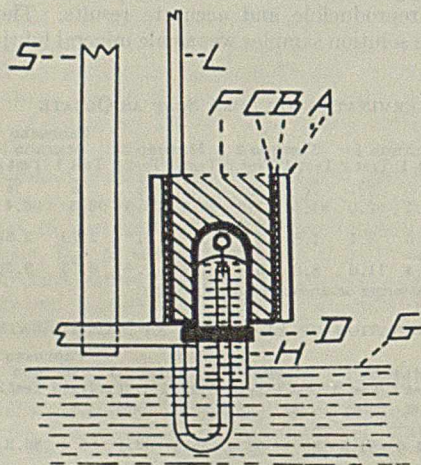


FIGURE 1. DIAGRAM OF GAS HEATER

and Ellis (9) describe a similar apparatus.

In developing the method for the analysis of hydrogen, it was found necessary to elevate and control, within limits, the temperature of the gas sample. The method adopted does not give the true temperature of the reaction system but does give an upper limit above which the temperature cannot go. There are other more exact means of temperature control, but it has been the desire of the authors to attain simplicity of method and construction whenever this could be done without the sacrifice of results. The heater which has been devised is shown in cross section in Figure 1.

The gas holder, *H*, is shown in its normal position over the mercury reservoir of the microanalytical apparatus. *C* is a copper vessel. Projecting up in the center of *C* is a cavity which is shaped to fit snugly around the gas holder. The upper part of *C* is hollowed out forming the space, *F*, which is approximately 1.5 cm. in diameter and 2.5 cm. in depth. This vessel may be machined directly from a solid rod, or made in pieces and then put together by means of silver solder. Around *C* is wrapped a thin

layer of mica, then the electrical heating coil, *B*, and finally asbestos sheet *A*. In *F* are placed about 2.5 cc. of some relatively stable solid substance which has a definite, known melting point.

In operation, the gas sample is introduced in the usual way and the absorbent placed in position. The heater is then slipped over the gas holder and the electrical current applied. When most, but not all, of the substance in *F* has melted the heating is discontinued. Since the thermal conductivity of the mercury reduces the temperature of the gas much below that attained in the heater, a solid substance has to be chosen which has a melting point somewhat higher than that desired in the gaseous system. Potassium dichromate and lead were both found to be satisfactory in the analyses which are described.

SPECIFIC METHODS OF ANALYSIS

HYDROGEN. In certain photochemical studies it has become very important to determine the presence or absence of small amounts of hydrogen in the products of photolysis. The explosion method (1) is only moderately accurate at best and is valueless for the determination of small percentages of hydrogen in the presence of several saturated hydrocarbons.

The problem of selectively absorbing this gas in the presence of other combustible gases has been met in macroanalysis by oxidation with copper oxide in a temperature-controlled dynamic system (3, 5), but application of this method to the authors' problem was not successful. Experiments were made with mixtures of hydrogen and nitrogen of known percentage composition. A bead of cupric oxide was prepared by fusion in a platinum loop with the aid of a blast lamp. The gas sample was heated to a temperature somewhat below the melting point of potassium dichromate by means of the electric heater described above. After sufficient time had been allowed for the oxidation of the hydrogen, the copper oxide and heater were removed and phosphorus pentoxide was introduced to take up the water vapor formed in the reaction. Although considerable oxidation did occur, it was found impossible to remove all the hydrogen in this way. In this static system, it is possible that an equilibrium condition was reached before oxidation was complete. This idea is substantiated by the fact that a second bead of the oxide placed in the same sample removed more, but not all, of the remaining hydrogen.

Assuming that the foregoing explanation is correct, it was reasoned that if the moisture produced could be removed from the gaseous phase as it was formed, complete oxidation of the hydrogen would occur. This involved the simultaneous introduction of the oxidizing agent and a drying agent into the gas sample. A bead made by fusing together cupric oxide and potassium hydroxide accomplishes this purpose and can be used for the rapid and complete absorption of hydrogen.

The reagent is prepared by first fusing the oxide in the platinum loop and then touching the molten mass to an approximately equal amount of the solid hydroxide. The two substances coalesce and, after cooling, a smooth, dark blue bead results. By heating the gas sample in the presence of this solid, hydrogen is readily oxidized and the water formed in the reaction is absorbed at the same time. The decrease in volume represents directly the amount of hydrogen in the sample. Absorption is very rapid and the time required for the complete analysis does not exceed 15 minutes.

Known mixtures of hydrogen with nitrogen, butane, and methane have been analyzed with the success indicated in Table I. Lead was the substance used in the heater. Potassium dichromate is equally satisfactory as far as the separation of hydrogen from other gases is concerned, but because of its high melting point (398° C.) there is danger of vaporizing the mercury and losing the sample of gas. It has been found by one of the authors, while working at relatively high altitudes, that under these conditions lead and not potassium dichromate must be used because of this danger.

TABLE I. RESULTS OF ANALYSES OF HYDROGEN AND METHANE MIXTURES

DETERMINATION	VOLUME OF SAMPLE Cu. mm.	HYDROGEN		DIFFERENCE
		Theoretical %	Determined %	
1	86.51	46.49	46.30	-0.19
2	97.43	38.11	38.00	-0.11
3	83.35	52.00	52.18	+0.18
4	87.98	47.38	47.17	-0.21
5	91.45	44.25	44.20	-0.05
Average difference				0.15
Average deviation from mean				0.11

CARBON MONOXIDE. Carbon monoxide may be selectively oxidized in the presence of methane, and other members of its series, by the same reagent and method as hydrogen and with approximately the same degree of accuracy. Lead was used for temperature control in obtaining the values in Table II.

By lowering the temperature of the reaction system, attempts were made to remove carbon monoxide by this cupric oxide-potassium hydroxide reagent in the presence of hydrogen. These experiments, however, were not successful. Temperatures sufficiently low to leave the hydrogen unoxidized gave incomplete removal of the carbon monoxide.

TABLE II. RESULTS OF ANALYSES OF CARBON MONOXIDE AND METHANE MIXTURES

DETERMINATION	VOLUME OF SAMPLE Cu. mm.	CARBON MONOXIDE		DIFFERENCE
		Theoretical %	Determined %	
1	88.37	50.81	50.81	0.00
2	86.40	47.77	47.59	-0.18
3	87.32	49.05	49.20	+0.15
4	89.41	42.64	42.64	0.00
5	92.34	44.78	44.68	-0.10
Average difference				0.09
Average deviation from mean				0.09

HYDROGEN CHLORIDE. Gaseous hydrogen chloride may be absorbed by the method described for carbon dioxide (1). An alternative method is to use a concentrated potassium hydroxide solution in a sintered glass bead. The procedure in this case is similar to that which is employed for the determination of ethylene (2), except that the concentrated alkali is used instead of sulfuric acid. The water vapor pressure over this absorbent is small and may be neglected in the analysis.

In both methods the absorption process is very rapid, 2 minutes being ample to allow in any case for complete removal of the hydrogen chloride. Because it is slightly more convenient to use, the authors prefer the second method and the results given in Table III were obtained in this way. The samples were mixtures of hydrogen chloride with dry, carbon dioxide-free air.

TABLE III. RESULTS OF ANALYSES FOR HYDROGEN CHLORIDE

DETERMINATION	VOLUME OF SAMPLE Cu. mm.	HYDROGEN CHLORIDE		DIFFERENCE
		Theoretical %	Determined %	
1	154.38	50.81	50.91	+0.10
2	148.79	49.43	49.47	+0.04
3	148.30	48.81	48.81	0.00
4	145.71	48.22	48.26	+0.04
5	138.92	45.39	45.45	+0.06
Average difference				0.05
Average deviation from mean				0.03

AMMONIA. Ammonia has been absorbed by the use of a moistened phosphorus pentoxide bead prepared as previously

described (1) and also by means of concentrated sulfuric acid in sintered glass. There is little choice to be made between these methods. As far as absorption of ammonia is concerned, both reagents will give constant results very rapidly. However, in analyzing prepared samples of ammonia mixed with nitrogen or hydrogen, consistently high percentage values of ammonia were obtained. Since the nitrogen or hydrogen was always treated with phosphorus pentoxide or sulfuric acid before it was mixed with ammonia, these abnormal values were not due to impurities of ammonia or similar gases.

In Table IV are given consecutive results of analyses of mixtures of ammonia and hydrogen, using phosphorus pentoxide as the absorbent. Although the results, which are typical of over fifty separate analyses, are sufficiently accurate for most purposes, they are not as good as results obtained for other gases.

TABLE IV. RESULTS OF ANALYSES FOR AMMONIA

DETERMINATION	VOLUME OF SAMPLE Cu. mm.	AMMONIA		DIFFERENCE
		Theoretical %	Determined %	
1	95.00	48.00	48.40	+0.40
2	104.20	46.26	46.42	+0.16
3	97.20	49.59	49.78	+0.19
4	108.90	46.37	46.57	+0.20
5	104.60	49.04	49.34	+0.30
Average difference				0.25
Average deviation from the mean				0.08

DISCUSSION AND SUMMARY

The apparatus used for the studies herein described was the same as that described before (2), except for the additions indicated. Pierce, Friedenwald, and Freeman (8) have suggested the use of an ivory tip to insure bringing back the mercury in the reservoir to the same level each time before reading the gas volume in the buret. Swearingen, Gerbes, and Ellis describe a similar gas analysis apparatus in which a horizontal buret is used (9).

Although the percentage composition of small gas samples can be determined to the degree of accuracy indicated in the several methods outlined, the absolute volume of samples cannot be ascertained with equal precision by capillary burets. In order to test this point, several relatively large volumes of air, measured by weighing the same volume of mercury, were measured in steps using the microburet. The buret readings gave an average of 1.8 per cent larger total volume than that obtained by weighing the mercury. Using the data given in International Critical Tables (4) for the surface tension of mercury and for the contact angle of mercury and glass, corrected volumes were obtained which were 1.1 per cent smaller than those obtained by weighing mercury. No doubt this correction is too great, because under working laboratory conditions where the walls of the buret may not be perfectly clean, the values for surface tension and contact angle must be somewhat smaller than those given in the literature. Since we cannot know these values, because of constantly changing conditions of cleanliness, adsorbed gases, etc., the absolute volume of small gas samples cannot be determined with great accuracy. Using the authors' data and buret, which has a capillary diameter of 0.52 mm., a negative correction of 1.8 per cent would give the absolute volume of gas to within ± 0.5 per cent.

Burets having diameters up to 0.7 mm. are being used by the authors. In operating all of these, the effect of the surface tension of mercury is pronounced. Capillaries much larger than these would require unduly large samples in order to obtain the highest percentage accuracy in analyses.

The consistently high values obtained for ammonia may be due to the low surface tension of mercury when ammonia is in contact with it (4). It has been suggested (9) that solid

potassium bisulfate may be used to absorb ammonia, but no quantitative results are available.

In using sulfuric acid in sintered glass beads, it has been stated by others using this method that the acid may spread over the surface of the mercury. The authors, using sintered beads made from 100- to 150-mesh soft glass and following the procedure previously outlined (2), have not experienced this difficulty. However, if too much acid is left on the bead and spreads over the mercury, it can be removed by the use of a follow-up bead of potassium hydroxide.

TABLE V. SUMMARY OF GASES ANALYZED AND REAGENTS USED

GASES	REAGENTS
Water vapor	Potassium hydroxide or phosphorus pentoxide (1)
Carbon dioxide, hydrogen chloride, and other acid-producing gases	Potassium hydroxide (1)
Acetaldehyde, and vapors of similar compounds	Potassium hydroxide (6)
Oxygen	Phosphorus (1)
Ammonia and other base-producing gases	Phosphorus pentoxide, or concentrated sulfuric acid in sintered glass
Acetylene	Cuprous chloride and potassium hydroxide (2)
Ethylene and other unsaturated hydrocarbons	Concentrated sulfuric acid (fuming, for ethylene) (2)
Carbon monoxide	Silver oxide (2), cupric oxide and potassium hydroxide, or explosion (1)
Hydrogen	Cupric oxide and potassium hydroxide, or explosion (1)
Methane and ethane, or any two readily combustible gases	Explosion (1)
Nitrogen and other inert gases	By difference

The dark blue bead for the oxidation of hydrogen and carbon monoxide probably consists in part of a solid solution of cupric oxide in potassium hydroxide (7). The color is a good indication of the effectiveness of the bead as an absorbing agent. Care should be taken not to use a large excess of potassium hydroxide and this hydroxide should be relatively pure. The presence of an appreciable amount of potassium carbonate seems to reduce the reactivity of the absorbent.

It is evident that this cupric oxide-potassium hydroxide reagent cannot be used to effect a separation of carbon monoxide and hydrogen. The silver oxide method does this very well with the limitations previously described (2).

The methods for the microanalysis of gases described in this series of articles have been developed to the point where they may be used successfully to determine quantitatively an appreciable number of the more common gases. In Table V may be found summarized the gases which have been studied by the authors in this way, along with the reagents and methods employed. By absorbing the gases in the proper sequence, almost any compatible mixture of these gases may be analyzed. For example, the following nine gases could be systematically separated by removing them in the order named: water, carbon dioxide, ethylene, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen. It should be possible to accomplish this separation, using an original sample of 100 cu. mm., with the same degree of accuracy as by standard macroanalytical methods using an original sample of 100 cc.

ACKNOWLEDGMENT

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Anhydrous Sodium Carbonate for Standardization

LOUIS WALDBAUER, D. C. McCANN, AND LAWRENCE F. TULEEN

The State University of Iowa, Iowa City, Iowa

SODIUM carbonate has been used as a standard for many years in neutralization methods of analysis. Many textbooks quote Lunge (4) and require that, in the preparation of sodium carbonate from sodium bicarbonate, the sample should not be heated over 300° C. Some state that sodium carbonate decomposes above this temperature; some, that it becomes hygroscopic. It was the purpose of the authors to investigate thoroughly the whole matter of preparation, as well as the mass of conflicting statements.

EXPERIMENTAL

REAGENTS. Stock c. p. sodium bicarbonate, such as is available in any laboratory, was used as a starting material for sodium carbonate preparation. In terms of sodium bicarbonate this material analyzed 100.45 per cent.

The hydrochloric acid solution was prepared from re-

distilled hydrochloric acid and water redistilled from alkaline potassium permanganate solution. The acid was standardized against calcite, benzoic acid, and potassium acid phthalate, making suitable corrections for indicators. The error in standardization was 1 part in 2500.

The sodium hydroxide solution was prepared carbonate-free by the method of Cornog (1).

PREPARATION OF SODIUM CARBONATE. Sodium bicarbonate decomposes to sodium carbonate at any temperature above 102° C. A sample heated at this temperature for one week analyzed 100.20 per cent in terms of sodium carbonate. When heated to higher temperatures a well-stirred sample remained at 140° for some time. Samples heated to 150° C. and cooled at once were found to be completely converted. It is obvious therefore that any sample heated above 150° C. is completely converted, regardless of the length of time of heating.

TABLE I. RESULTS OF HEATING SODIUM BICARBONATE

TEMPERATURE OF CONVERSION ° C.	TIME OF HEATING Hours	PER CENT IN TERMS OF Na ₂ CO ₃
102	1 week	100.20
115	1 week	100.04
165	24	100.10
200	24	100.15
260	12	100.07
260	24	100.09
260	48	100.17
300	24	100.09
375	24	100.13
375	48	100.10

It would seem from the analyses in Table I that temperature and time of heating made very little difference. There is no indication of decomposition at temperatures as high as 375° C.

INSTABILITY. Instability in the presence of moist air and moist, carbon dioxide-laden air is rather difficult to measure. The results in Table II should be taken only qualitatively. The samples were those of Table I (of 24 hours' heating) and were in all cases exposed for 6 hours.

TABLE II. INSTABILITY OF SODIUM CARBONATE

TEMPERATURE OF CONVERSION ° C.	EXPOSURE	Na ₂ CO ₃ %
260	Moisture	98.80
375	Moisture	99.86
260	Carbon dioxide and moisture	78.50
375	Carbon dioxide and moisture	97.85

Table III illustrates the results obtained under the same conditions as in Table II, but using pure sodium carbonate, prepared by washing with ethyl alcohol, recrystallizing, and drying at 110° C.

TABLE III. INSTABILITY OF PURE SODIUM CARBONATE

EXPOSURE	Na ₂ CO ₃ %
Carbon dioxide and moisture	91.62
Moisture	98.36

It is obvious that both pure and impure sodium carbonate are subject to change on exposure, regardless of the temperature at which they have been heated. No other conclusions should be drawn from Tables II and III.

IMPURITIES. The nature of the impurities causing high results on the samples of sodium carbonate and bicarbonate was not easily discovered. Carbon dioxide analyses were made on several samples but the results could not be made sufficiently precise to warrant any conclusions. It is significant, however, that a sample of sodium carbonate, washed with ethyl alcohol and dried, analyzed, by neutralization methods, 100.00 per cent within experimental error. This would lead one to suspect sodium oxide or hydroxide, since sodium hydroxide is soluble in ethyl alcohol.

Table IV illustrates some results of washing sodium bicarbonate alcohol before conversion to sodium carbonate, and washing sodium carbonate after its preparation. The temperature of preparation of sodium carbonate was 260° C.

TABLE IV. RESULTS OF WASHING

	Na ₂ CO ₃ %	Av.
Sodium bicarbonate washed before conversion	{ 100.18 } { 100.17 }	100.17
Above sodium carbonate washed after conversion	{ 100.00 } { 100.05 } { 100.03 }	100.03
Sodium carbonate prepared directly from c. p. sodium bicarbonate and washed after conversion	{ 100.02 } { 100.04 }	100.03

It is obvious from Table IV that some sodium oxide or hydroxide is formed in the conversion of sodium bicarbonate

to carbonate regardless of temperature, since all previous samples analyzed high. Further evidence that no other decomposition takes place is given by Table V in which samples of the above purified sodium carbonate were heated.

TABLE V. RESULTS OF HEATING PURIFIED SODIUM CARBONATE

TEMPERATURE OF HEATING ° C.	TIME Hours	Na ₂ CO ₃ %
100	24	100.04
375	24	100.05

VAPOR PRESSURE. Johnson (3) has found that at 940° C. sodium carbonate exerts a pressure of 5 mm. of mercury and at 1100°, 10 mm. of mercury. Measurements were made in this laboratory at temperatures up to 940° C., using an evacuated system and a calibrated McLeod gage. Precautions were taken by prolonged pumping and heating to drive off all adsorbed gases inside the system before a determination was made. These precautions were the result of the work of Hariba and Baba (2) on the vapor pressure of sodium and potassium chloride.

The pumps were sealed from the system and the pressure was checked for 6 hours before heating the sample. Pressures were read at 10° intervals during heating, allowing 20 minutes at constant temperature for each reading. The first observable pressure due to decomposition was shown at 482° C. The average of several trials was 499° C. This eliminates any possibility of decomposition below 450° C., a temperature far above any needed for preparation of sodium carbonate from sodium bicarbonate.

CRYSTAL STRUCTURE. It was thought that a change in crystal structure might be responsible for the previously mentioned theories of decomposition. X-ray photographs of samples at 25°, 260°, 300°, and 375° C. were made by the powder method, using a heater to maintain the sample at the above temperatures. In no case was any change in structure found, other than the expected shift of lines due to expansion. The authors were unable to prepare crystals large enough for a complete crystal analysis, but were able to check the petrographic results of Winchell (5), who states that sodium carbonate crystals from fusion are biaxial, negative, with $2V = 34^\circ \pm 3^\circ$. The authors, using crystals grown from fused sodium hydroxide, also noted that the crystals appear to have three good cleavages and show marked lamellar twinning. Extinction angles with the cleavage were found varying from zero to 30°. From the above evidence, it appears that anhydrous sodium carbonate may be monoclinic.

CONCLUSIONS

Washing so-called c. p. anhydrous sodium carbonate with ethyl alcohol and drying it at 110° C. render it satisfactory as a volumetric standard. Anhydrous sodium carbonate does not decompose below 450°, nor does it change its crystal structure below 375° C. The impurities leading to high results are very probably due to sodium oxide and (or) hydroxide and come from the decomposition of sodium bicarbonate during its conversion to sodium carbonate.

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RECEIVED April 6, 1934. Extract from the thesis submitted by D. C. McCann for the degree of Ph.D., June, 1934. The work on vapor pressure measurements of the decomposition of sodium carbonate is an extract from the M.S. thesis of Lawrence F. Tuleen, submitted in August, 1932.

Precise Method for Determining Ammoniacal Nitrogen in Eggs

ARTHUR W. THOMAS AND MARGUERITE A. VAN HAUWAERT, Columbia University, New York, N. Y.

FOR about 25 years it has been known that hens' eggs will evolve traces of ammonia upon aëration in the cold, after the addition of a small amount of alkali carbonate. The ammonia so liberated has been referred to as ammoniacal or loosely bound nitrogen. The exact measurement of the amount of loosely bound nitrogen recoverable from eggs is accepted as perhaps the best means for grading edible eggs, either as shell eggs direct from the nest or from cold storage, or in the form of frozen egg magmas.

Since distillation of alkalized egg magma cannot be used, owing to the danger of decomposing the complex nitrogenous compounds present, an application of the Folin aëration method (4) for the determination of ammonia in urine has been used for several years in the examination of frozen eggs. It consists essentially in making the sample alkaline, removing the liberated ammonia by aëration, and absorbing it in standardized sulfuric acid solution.

The method as now used is not satisfactory because the operating conditions, chiefly with respect to the volume of air required and the rate of aëration, are not well defined. Until now the nearest approach to a quantitative prescription for the conditions of aëration has been the following:

Hendrickson and Swan (6) advised the use of an air pump delivering a pressure of 14 cm. of water. A water gage is connected with the aëration apparatus, keeping the air pressure constant and thus insuring the passage of an equal volume of air through the aëration cylinder in a given time. Redfield (14, 15) used an air pump furnishing a blast with a pressure of 10 pounds per square inch and discharging into a tank of sufficient size to compensate for pulsations of the pump and deliver a steady flow. He also insisted on running a blank experiment to determine the percentage recovery of ammonia, using a known amount of pure ammonium sulfate (containing about 3 mg. of nitrogen) and 25 cc. of water. The recovery should be over 95 per cent to be deemed satisfactory. In subsequent reports by Marsh (11), Lourie (9), and Hertwig (7) no details were given concerning the volume of air used in the aëration. Lythgoe (10) recommended the use of a pressure sufficient to measure 2 inches (50.8 mm.) of mercury in a manometer attached to the outlet pipe.

Pennington and Greenlee (13) applied Folin's method to the determination of loosely bound nitrogen in meat. A small air pump was used to supply the air and the total volume of air passing through a battery of four flasks which contained the alkaline mixture was recorded on an anemometer. This method of measuring does not give the exact volume passing through each individual aëration flask. Kober and Graves (8) expressed the need for determining the exact volume of air passing through the ammoniacal mixture and gaged the volume of air by the time it takes for the air to draw a certain volume of water from one bottle to another connected by means of a glass tube. This, however, does not measure the volume of air passing through the ammoniacal mixture, since the resistance offered by the aëration apparatus is so different that the volume of air passing through it in a certain time is by no means identical with the volume of

An apparatus which renders possible the precise determination of ammoniacal nitrogen by aëration of alkaline mixtures containing very small amounts of ammonia is described.

It is essential that the volume of air be measured. Twelve hundred liters of air passed at a rate of 240 liters per hour are sufficient to remove quantitatively the loosely bound nitrogen from egg samples containing from 1.3 to 6.1 mg. of loosely bound nitrogen per 100 grams of sample, using the apparatus and procedure developed in this investigation.

In order to remove quantitatively the loosely bound nitrogen from eggs, in a reasonable and analytically feasible time, the initial pH of the alkalized egg mixture should be at least 9.5. At pH values higher than 10.7 a continuous decomposition of nonvolatile nitrogenous matter results, yielding ammoniacal nitrogen.

water which would be displaced from one bottle to another in the same time.

Using these methods, checks might be obtained in parallel measurements using the same air pressure and volume, but results could not be duplicated from day to day. The present investigation was undertaken with the object of developing a precise method for the quantitative determination of loosely bound nitrogen in eggs and in whole egg magma. Operating at room temperature, the variables studied were rate of aëration, volume of air, concentration of the aërated alkaline mixture and influence of amount of alcohol therein, and the pH of the alkaline mixture. The need for such a study has recently been asserted by Alfend (1).

AÉRATION APPARATUS

For the purpose of providing a flow of air under fairly constant pressure, and measuring the volume of air involved in the aëration of each individual alkaline mixture, the apparatus shown in Figure 1 was developed.

It was found necessary to introduce a pressure regulator into the system. This regulator consisted of two concentric cylinders of galvanized iron, each with one end closed. The outside cylinder, with the open end upwards, had a height of 47.5 inches (121 cm.) and a diameter of 8 inches (20 cm.), and was filled with water to such a height that at the required speed of aëration, air was continuously escaping from the pressure regulator. The inside cylinder was 51.5 inches (131 cm.) high and 2 inches (5 cm.) in diameter. Its top was connected to the air line. It was provided with rectangular holes, *B*, on the lower end to allow the excess air above the required pressure to escape through the water contained in the outside cylinder. This system gave very satisfactory results. An increase of more than 3 to 4 mm. in the difference of water level in the flowmeters was seldom noticed over a period of 6 hours of aëration at 240 liters per hour.

Flowmeters placed between the air line and the aëration cylinders made it possible to evaluate the volume of air passing through each individual cylinder in a given time. The inside diameter and the length of the capillaries sealed in the upper part of the flowmeters were such that a passage of 265 liters of air per hour was possible.

Aëration cylinder *K* containing the ammoniacal mixture was 15 inches (38 cm.) high and 1.875 inches (4.8 cm.) in diameter. The glass tube for aëration extended to within 0.25 inch (6 mm.) from the bottom of the cylinder.

The flowmeters were standardized in the following manner by means of the apparatus shown in Figure 2:

Water was allowed to flow into jar *B*, pinch clamp *G* was opened, the suction pump was turned on, and air was allowed to pass through the aëration apparatus.

Pinchclamp *H* was opened. An extra outlet was introduced to prevent the formation of an air space in the neck of the bell jar to enable the bell jar to be completely filled with water, before the air was allowed to displace the water contained in the jar.

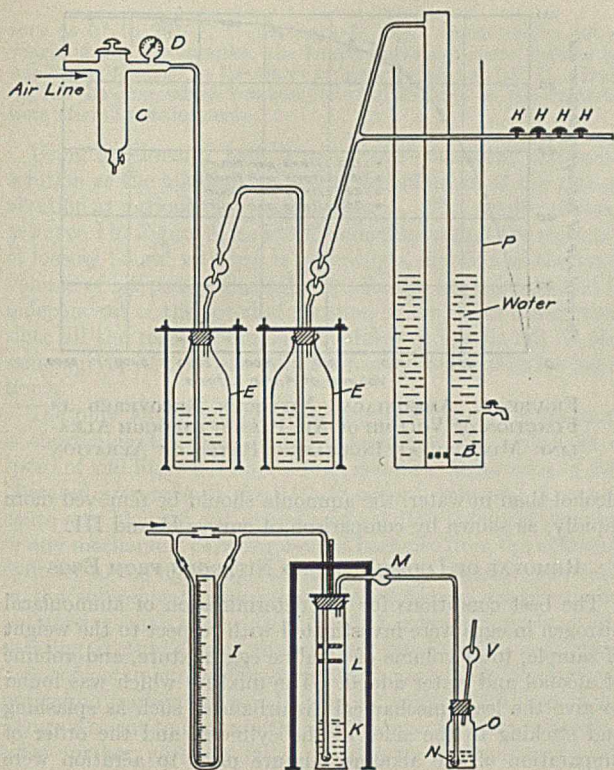


FIGURE 1. AERATION APPARATUS

- A. Air pipe connecting aeration apparatus with air line
- C. Air filter
- D. Reducing valve permitting reduction of line air pressure to that required for work
- E. Wash bottles containing 35 per cent sulfuric acid to remove any ammonia present in air entering apparatus
- H. Valves allowing further adjustment of air flow through flowmeters
- I. Flowmeters
- K. Aeration cylinder
- L. Rubber baffles
- M. Spray trap
- N. Dispersion tube ending with bulb perforated with small holes to allow regular distribution of air through acid solution
- O. Receiver containing 10 cc. of 0.02 *N* sulfuric acid diluted with 50 cc. of distilled water
- P. Pressure regulator
- V. Outlet tube with spray trap

The air was permitted to escape through *H*, thus releasing the pressure at *F*. This permitted the air to flow continuously through the apparatus.

Once the bell jar was filled with water, pinchclamps *G* and *H* were closed and the timing was started by means of a stop watch.

The time necessary to displace the water to the point *F*, corresponding to the atmospheric pressure, was noted. The difference in centimeters was read in the meantime on the flowmeter. Consecutive determinations of time flow were taken at increasing intervals of a 10 cm. difference in water level.

Knowing the volume of the bell jar from the neck to point *F*, it was possible to determine the volume of air passing through the apparatus in a given time and at a given pressure as indicated on the flowmeters.

For each flowmeter the pressure was plotted against the corresponding volume in liters of air passing per hour. In the experiments described, the pressure was observed on the flowmeters and the corresponding volume of air passing per hour through the apparatus was read from the curves.

MATERIAL USED

STANDARD AMMONIUM CHLORIDE SOLUTION. The c. p. salt was recrystallized twice from distilled water, sublimed, and then dried at 105° C. to constant weight. A solution of this salt corresponding to 1.5 mg. of nitrogen per 25 cc. of aqueous solution was prepared and its concentration checked by alkaline distillation into standardized sulfuric acid followed by titration.

POTASSIUM CARBONATE SOLUTION. Fifty grams of potassium carbonate (anhydrous) were made up to 100 cc. with distilled water.

STANDARD SODIUM HYDROXIDE SOLUTION. Using a clear saturated solution of sodium hydroxide, a 0.02 *N* solution was prepared and standardized against Bureau of Standards acid potassium phthalate dried at 105° C. for 2 hours, using phenolphthalein as indicator.

STANDARD SULFURIC ACID SOLUTION. A 0.02 *N* sulfuric acid solution was standardized against the above mentioned sodium hydroxide solution, using methyl red as indicator (0.1 per cent solution in 95 per cent alcohol).

REMOVAL OF AMMONIACAL NITROGEN FROM AMMONIUM CHLORIDE SOLUTION

AS A FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE AMMONIACAL MIXTURE. The percentage of nitrogen recovered as ammonia by aerating alkaline ammoniacal mixtures was carefully investigated first by the use of ammonium chloride solution.

Twenty-five cubic centimeters of 0.02 *N* sulfuric acid were pipetted into the receiver bottle and diluted with 50 cc. of distilled water. Twenty-five cubic centimeters of standard ammonium chloride solution were pipetted into the aeration cylinder and 175 cc. of distilled water added. The cylinders were connected with the receiver bottle and the aeration apparatus.

One cubic centimeter kerosene and 2 cc. potassium carbonate solution were added to the ammoniacal solution. The kerosene was added to prevent foaming. Two cubic centimeters of the potassium carbonate solution were accepted because others found it satisfactory in application to eggs.¹

The aeration cylinders were closed. The rubber stoppers were screwed down by means of metallic plates. Air was blown through the alkaline ammoniacal solution at different speeds and for different lengths of time. The time of the experiment was noted from the moment that aeration was started until the aeration ended.

Pressure was read on the flowmeters; the corresponding volume of air which passed through the ammoniacal mixture per hour was taken from the curves.

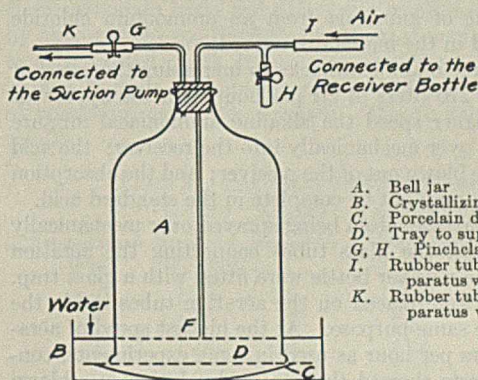


FIGURE 2. APPARATUS FOR STANDARDIZATION OF FLOWMETERS

Once the aeration was stopped, the dispersion tube and the outlet tube were carefully washed with distilled water into the receiver.

The acid solutions were titrated with the standard alkali, using methyl red as the indicator. Two blanks containing 200 cc. of distilled water, 1 cc. of kerosene, and 2 cc. of potassium carbonate solution were run each time.

The difference between the titration of acid solution and of blanks was taken as the measure of the ammoniacal nitrogen carried as a result of the aeration from the alkaline ammoniacal mixture (*K*, Figure 1) into the standard sulfuric acid (*O*, Figure 1).

In all, 119 measurements were made in duplicate at rates of aeration from 124 to 265 liters per hour in the range of 2 to 10

¹ Since the apparatus contained no provision for the removal of carbon dioxide from the air, the following experiment was performed: Eighty cubic centimeters of potassium carbonate solution were added to 520 cc. of distilled water. The pH of this solution was found to be 11.2. Then two portions of 150 cc. each, plus 1 cc. of kerosene, were aerated 5 hours at a rate of 240 liters of air per hour. The pH was then found to be 10.5. Obviously the use of the amount of potassium carbonate specified insures an alkaline reaction.

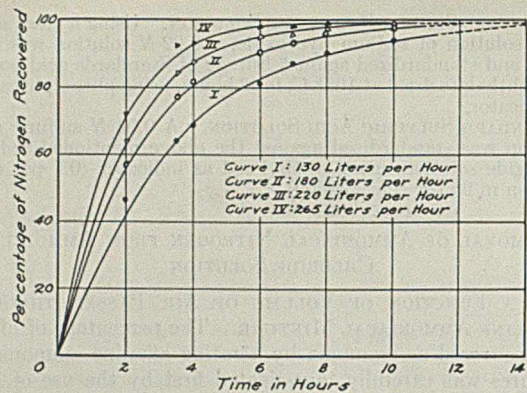


FIGURE 3. AMMONIACAL NITROGEN RECOVERED AS FUNCTION OF LENGTH OF TIME AT INCREASING RATES OF AERATION

hours' aeration. The data obtained in these experiments are summarized in Figures 3 and 4. The curves in Figure 3 show that the percentage of nitrogen recovered is a function of the length of time of aeration, that about half of the ammonia comes over in the first 2 hours, and that a very large volume of air is necessary to remove the last traces of ammonia.

Figure 4 shows conclusively that the percentage of nitrogen recovered is primarily a function of the volume of air which passes through the ammoniacal mixture, since all the results obtained by aeration at different speeds for increasing length of time fall on the same curve. This means that a definite volume of air, regardless of the speed of aeration in the range considered (135 to 265 liters of air per hour), will liberate a definite amount of ammonia from an ammonium chloride solution treated in the manner described.

There are three main drawbacks to increasing the speed of aeration above 270 liters of air per hour with the apparatus used: At a higher speed the alkaline ammoniacal mixture may be carried over mechanically into the receiver; the acid solution may be blown out of the receiver; and the absorption of the ammonia may not be complete in the standard acid.

To prevent particles from being sprayed over mechanically into the receiver, the glass tubes connecting the aeration cylinder and the receiver bottle were fitted with a glass trap. Rubber baffles were placed on the aeration tubes inside the cylinder for the same purpose. At the highest speed of aeration of 270 liters per hour as used in some experiments, controlled blank tests showed that no acid solution was blown out of the receiver.

To investigate the absorption of the liberated ammonia in the receiver containing the acid solution, a second receiver, containing 10 cc. of standard sulfuric acid and 50 cc. of water, was placed in series with the first. The other conditions were the same as above. The titration of the solution in the second receiver in each experiment and of that in the blank checked within the precision of the method. Hence at a rate of aeration of 270 liters per hour the absorption of liberated ammonia is complete in the acid solution contained in the first receiver.

AS A FUNCTION OF VOLUME AND CONCENTRATION OF AMMONIACAL MIXTURES. Folin and Macallum (5) called attention to the fact that the rapidity with which a given air current removes ammonia from solutions depends on the volume of the solution. The extent of the influence of volume is shown by curves I and II in Figure 5.

The conditions represented by the curve I experiment cannot be applied to eggs owing to the high viscosity. Use of alcohol as a diluent has been found necessary in order to inhibit foaming. Since ammonia is five times less soluble in

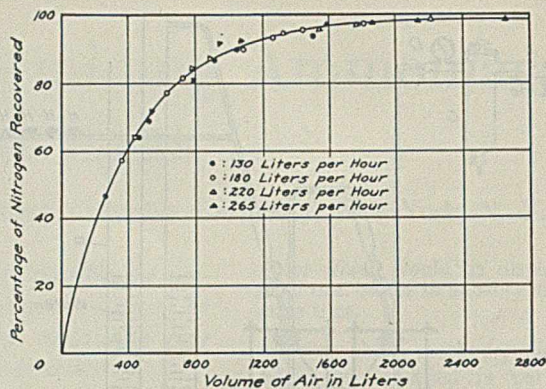


FIGURE 4. AMMONIACAL NITROGEN RECOVERED AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE MIXTURE AT INCREASING RATES OF AERATION

alcohol than in water, the ammonia should be removed more rapidly, as shown by comparison of curves II and III.

REMOVAL OF LOOSELY BOUND NITROGEN FROM EGGS

The best conditions for the determination of ammoniacal nitrogen in eggs were investigated with respect to the weight of sample, total volume of alkaline egg mixture, and volume of alcohol and water added. The mixture which was found to give the least mechanical disturbances, such as splashing and sticking to the sides of the cylinder, and the order of preparation of the alkaline mixture prior to aeration were as follows:

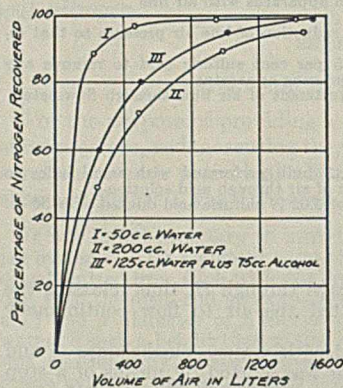


FIGURE 5. INFLUENCE OF VOLUME OF AQUEOUS SOLUTION AND OF SUBSTITUTION OF ALCOHOL FOR WATER ON RECOVERY OF AMMONIA

Ammonium chloride equal to 1.5 mg. of nitrogen present in each case.

One gram of sodium fluoride was put in the aeration cylinder. Twenty-five grams of mixed egg specimen weighed by difference in a weighing bottle were put in the aeration cylinder. The contents of the cylinder were then diluted with distilled water, the volume of added water being 75 cc. minus the number of cubic centimeters of potassium carbonate solution added later.

Fifty cubic centimeters of 95 per cent ethyl alcohol were added and then 1 cc. of kerosene. Kerosene and alcohol are essential as foam breakers. The potassium carbonate solution was added last when the whole apparatus had been connected, and the aeration was immediately started.

AS A FUNCTION OF TOTAL VOLUME OF AIR PASSED THROUGH ALKALINE EGG MIXTURE. The eggs used in these and subsequently described experiments were carefully selected at a storage and egg-breaking plant in Jersey City, N. J.

Specimen I consisted of storage eggs which had been kept at 30° to 32° F. (-1.1° to 0° C.) for 4 months. After removal from the shells, approximately 35 pounds (16 kg.) of the whole egg mixture were passed through a colloid mill to obtain a uniform magma which would not thicken on frozen storage (3). This well-mixed egg magma was poured into half-pint jars which were placed immediately in the storage room at -5° to 0° F. (-21° to -18° C.).

Specimen II consisted of fresh eggs carefully selected and broken out of the shell, then mixed and stored in the same manner as specimen I.

As needed, samples were delivered from Jersey City on the evening prior to their use and were stored overnight in the labora-

tory at 0° to 20° F. (-18° to -7° C.). Immediately before weighing out the samples, the frozen specimens were thawed by immersing the jars in the water of a thermostat at 25° C. During the thawing, which was completed in 20 minutes, the contents were stirred continuously.

Using specimen I with 2 cc. of the potassium carbonate solution as the alkalinizing agent, the influence of the rate of aëration at various times was measured. The results, plotted as curve I in Figure 6, lead to the conclusion that the recovery of loosely bound nitrogen is primarily a function of the total volume of air passed through the alkaline egg mixture and is independent of the speed of aëration in the range considered, since all the results obtained for different speeds fall on the same curve, just as was found for ammonium chloride solutions.

The only advantage of increasing the velocity of aëration is shortening the time of the experiment. Inasmuch as a speed of 240 liters per hour allows complete absorption of the liberated ammonia in the 0.02 *N* sulfuric acid and does not cause any blowing out of the acid solution from the receiver or any mechanical carrying over of particles from the aëration cylinder to the receiving bottle, this rate of aëration was used in the subsequent experiments. Satisfactory precision was obtained, as may be seen from Table I, using egg specimen II, aërating at 240 liters of air per hour for 5 hours, and using 2 cc. of potassium carbonate solution containing 50 grams of potassium carbonate per 100 cc. of solution. Curve I in Figure 6 seems to indicate that 1200 liters of air are sufficient, since further aëration failed to remove more ammoniacal nitrogen.

Experiments were then performed to determine whether this volume of air passing at 240 liters per hour would be sufficient to recover the loosely bound nitrogen from egg samples containing smaller or greater amounts than specimen I.

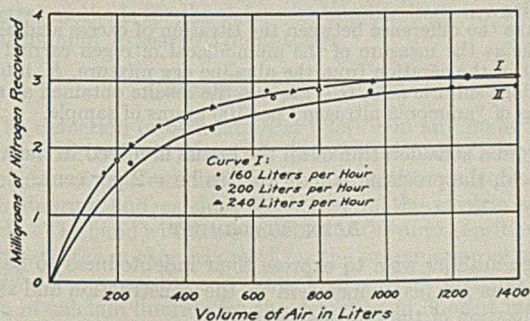


FIGURE 6. REMOVAL OF AMMONIACAL NITROGEN AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE MIXTURE

- I. Ammoniacal nitrogen recovered from egg sample I, expressed in milligrams of nitrogen per 100-gram sample.
- II. Ammoniacal nitrogen recovered from standard ammonium chloride solution, expressed in milligrams of nitrogen per 100 cc. of solution.

Figure 7 gives the results obtained from different samples. Specimens I, II, Ib, and Ic were analyzed under the same conditions, using 2 cc. of potassium carbonate solution as alkaline reagent. Specimens Ib and Ic were prepared by merely keeping specimen I at 45° F. (7° C.) for 39 and 63 hours, respectively, thus permitting slight decomposition to take place. Inspection of Figure 7 shows that additional aëration above 1200 liters failed to remove any more ammoniacal nitrogen, since the curve flattens out; the tangent to the curve at the point corresponding to 1200 liters of aëration is practically parallel to the abscissa. This flattening out of the curve, which in the case of aëration of ammoniacal nitrogen from a standard ammonium chloride solution corresponds to 99.0 ± 0.5 per cent of the actual nitrogen present, has in the case of the determination of loosely bound nitrogen in egg still another significance. It is possible that the presence of the

added potassium carbonate catalyzes the hydrolysis of the egg magma with the consequence that more ammonia is split off, which is then determined as ammoniacal nitrogen. The flattening out of the curve proves that, if there is any such hydrolysis, it is not continuous.

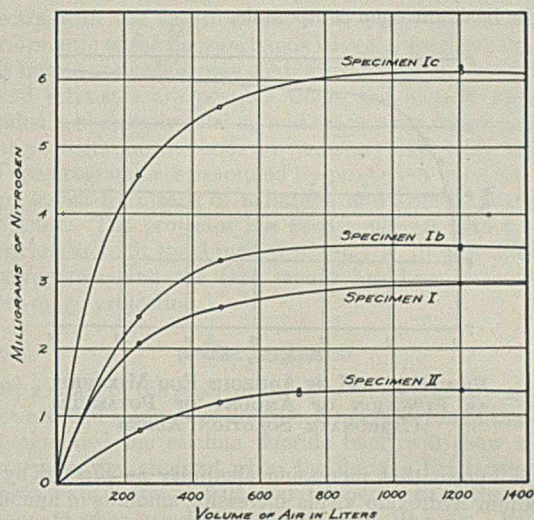


FIGURE 7. REMOVAL OF AMMONIACAL NITROGEN FROM EGGS AS FUNCTION OF VOLUME OF AIR PASSED THROUGH ALKALINE EGG MIXTURE

AS A FUNCTION OF CONCENTRATION OF POTASSIUM CARBONATE. First the influence of different amounts of potassium carbonate upon the pH of the solutions was measured by means of the modified Bailey electrodes (2, 3). The solutions consisted of 25 grams of egg specimen II, 1 gram of sodium fluoride, 75 minus *x* cc. of distilled water, and *x* cc. of potassium carbonate solution. Figure 8 summarizes the results.

TABLE I. PRECISION OF MEASUREMENTS

FROZEN-STORAGE AGE Days ^a	LOOSELY BOUND NITROGEN Mg./100 g.	NUMBER OF EX- PERIMENTS	AVERAGE DEVIATION Single observation ^b	Mean ^c
7	1.34	5	0.04	0.02
8	1.41	6	0.02	0.01
9	1.37	6	0.02	0.01
10	1.25	5	0.04	0.02
11	1.14	6	0.04	0.02
14	1.05	6	0.04	0.02
16	1.32	4	0.02	0.01
17	1.38	4	0.02	0.01
21	1.34	5	0.04	0.02
24	1.33	5	0.02	0.01
25	1.35	2	0.00	0.00
26	1.31	4	0.01	0.006
27	1.34	4	0.01	0.005
30	1.35	5	0.01	0.005
31	1.35	6	0.02	0.01
36	1.38	6	0.01	0.005
48	1.37	3	0.01	0.008

^a Number of days specimen was kept at 0°F. (-18° C.) prior to analysis.

^b Sum of the deviations of each individual measurement from the arithmetical mean divided by the number of experiments.

^c Average deviation divided by the square root of the number of experiments.

Then in order to measure the influence of the concentration of potassium carbonate on the liberation and removal of ammoniacal nitrogen, a series of experiments was performed which are summarized in Figure 9.

From curve 0 it is obvious that an alkaline reagent must be added in order to speed up the recovery of the ammoniacal nitrogen. Curves 0.5 to 12, inclusive, show that upon increasing additions of potassium carbonate solution, increasing quantities of ammoniacal nitrogen are recovered. These curves also indicate that it is necessary to aërate the egg mixture at an initial pH of at least 9.5 in order to obtain a quantitative recovery of ammoniacal nitrogen originally present.

They suggest, too, that more than 4 cc. of potassium carbonate solution should not be used to effect a definite end point for an analytically reasonable expenditure of time and effort. Curves 8 and 12 may be interpreted as showing that the corresponding amounts of potassium carbonate catalyze a hydrolytic decomposition of complex nitrogenous substances into volatile basic nitrogen compounds.

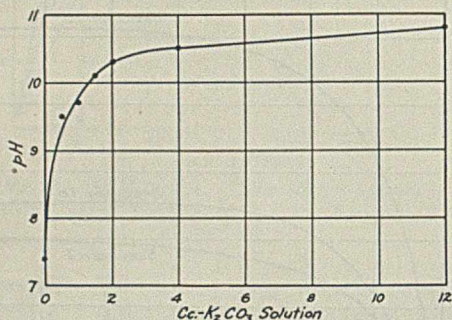


FIGURE 8. pH OF AQUEOUS EGG MIXTURE, AS FUNCTION OF AMOUNT OF POTASSIUM CARBONATE SOLUTION ADDED

It is known that increasing alkalinity as effected by use of sodium hydroxide yields increasing amounts of ammoniacal nitrogen from eggs (6). Also, increasing amounts of sodium carbonate producing pH values over 9.0 have been shown to cause decomposition of amino acids at about 100° C. (12). Results such as those represented by curves 0.5, 2, and 4 in Figure 9 have not been heretofore demonstrated. The selection of any of these three conditions is indicated as proper for the purpose and consequently it is well to adhere to the previous empirical selection of potassium carbonate solution, giving an initial pH of about 10.3.

VALIDITY AND USE OF STANDARD AMMONIA CONTROLS

It has been customary with some workers to run parallel aerations of an ammonium chloride or ammonium sulfate solution to serve as a gage of the efficiency of the analysis of an egg specimen. If over 95 per cent of the actual amount of nitrogen present in the solution was recovered, it was concluded that approximately the same percentage of ammoniacal nitrogen present in the egg sample had been recovered. However, such a conclusion is possible only when the per-

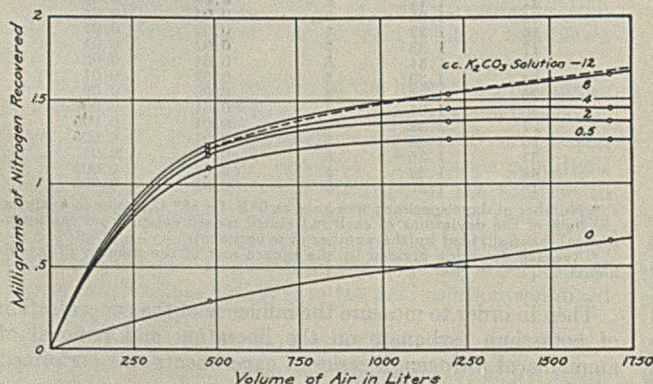


FIGURE 9. REMOVAL OF AMMONIACAL NITROGEN FROM EGG MIXTURES CONTAINING VARYING AMOUNTS OF POTASSIUM CARBONATE

centage of the ammoniacal nitrogen is approximately the same in both egg mixture and ammonium chloride solution and when all other conditions are identical.

Since egg specimen I contained approximately 3 mg. of ammoniacal nitrogen per 100 grams, the ammoniacal nitrogen

was evaluated in a standard ammonium chloride solution containing 2.99 mg. of nitrogen per 100 cc. of solution by blowing air at a rate of 240 liters per hour, using 2 cc. of potassium carbonate solution as alkaline agent. The results obtained are plotted in curve II of Figure 6. Curves II and I are converging; the liberation of ammoniacal nitrogen in eggs is similar to that of standard ammonium salt solutions, when the percentage of ammoniacal nitrogen is approximately the same and when the conditions of the experiment are the same. This investigation shows, however, that when the conditions of rate and time of aeration, pH, and volume of the egg mixture are controlled, it is unnecessary to run ammonium salt controls.

DETAILS OF METHOD

As a result of this investigation, the authors recommend the following method for the precise determination of the loosely bound nitrogen in eggs, using the apparatus described in Figure 1:

Measure accurately 10 cc. of 0.02 *N* sulfuric acid into the receiver, *O*, and dilute with 50 cc. of distilled water. Place 1 gram of sodium fluoride in aeration cylinder *K*. Pour 25 grams of mixed egg magma, weighed by difference from a weighing bottle, into the aeration cylinder. Add 55 cc. of distilled water, 50 cc. of ethyl alcohol (95 per cent by volume), and 1 cc. of kerosene.

Connect the cylinders with the receiver bottle and the aeration apparatus. Add 20 cc. of potassium carbonate solution, containing 5 grams of anhydrous potassium carbonate per 100 cc. of solution. Close the aeration cylinders, and start the aeration, allowing the passage of 1200 liters of air at a rate of 240 liters per hour.

Titrate the excess of acid with 0.02 *N* sodium hydroxide (free from carbon dioxide) by means of a microburet which can be read to 0.01 cc.

Run at the same time two blank experiments, containing 1 gram of sodium fluoride, 80 cc. of distilled water, 50 cc. of 95 per cent alcohol, 1 cc. of kerosene, and 20 cc. of potassium carbonate solution.

Take the difference between the titration of excess acid and of blanks as the measure of the ammoniacal nitrogen carried as a result of the aeration from the alkaline egg mixture, *K*, into the standard sulfuric acid, *O*. Express the results obtained as milligrams of "ammonia nitrogen" per 100 grams of sample.

From a consideration of all the errors involved in the above method, the precision is indicated to be ± 2 per cent.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to Samuel B. Ellis for his coöperation in the construction and standardization of the flowmeters used.

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Spectral Determination of Fluorine in Water

A. W. PETREY, Aluminum Research Laboratories, New Kensington, Pa.

THE occurrence of fluorine in potable waters and the probabilities of its physiological effect have aroused considerable interest in the past few years. Churchill (1), Dean (2, 3), Sebrell, Dean, Elvore, and Breaux (8), Kempf and McKay (4), Smith, Lanz, and Smith (9), and others have made comprehensive investigations on the subject. The general interest has stimulated activity among analytical chemists toward the development of methods for the accurate estimation of fluorine in the quantities which occur in natural waters. The amounts reported have varied from zero to as much as 14 p. p. m. of fluorine. Among the recent developments are the works of Willard and Winter (11), Thompson and Taylor (10), Sanchis (7), and Kolthoff and Stansby (5).

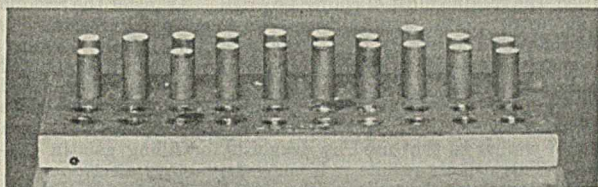


FIGURE 1. ELECTRODE HOLDER PARTIALLY FILLED WITH ELECTRODES

Under certain conditions, difficulties which are not easily obviated, may be encountered in the chemical determination of fluorine in water. For this reason, the possibility of using spectral methods for the determination has been investigated in Aluminum Research Laboratories.

DESCRIPTION OF METHOD

The detection or estimation of fluorine in any material by spectral methods is based on the appearance of the band spectrum of calcium fluoride when a substance containing both fluorine and calcium is excited in the electric arc or spark. The band with head at $\lambda 5291$ is the most sensitive and is the one the author has used for the examination of water. Papish, Hoag, and Snee (6) have made use of the band spectrum of calcium fluoride for the detection of fluorine in gems and other minerals. Fluorine may be detected either by the photographing or visual observation of its spectrum. When the dissolved mineral matter consists essentially of calcium and magnesium compounds, the estimate can usually be made by arcing the dry residue. However, when large amounts of sodium compounds are present, calcium must be supplied externally. The most dependable means found in these laboratories for supplying the calcium is the impregnation of the lower electrode which supports the sample, with calcium chloride. The calcium salt in the electrode eliminates the variable intensities which result from the more or less selective volatilization of the various constituents of saline water residues.

APPARATUS

Aluminum Research Laboratories has available a large Littrow quartz spectrograph and a Hilger constant-deviation spectrometer, either of which may be used for the detection and estimation of fluorine. The spectrometer may be used visually or photographically. In a large part of the experimental work on fluorine both the quartz spectrograph and the glass spectrometer were used simultaneously, recording the

spectra with the spectrograph while observing visually the performance of the fluorine bands with the spectrometer. By this means the author was enabled to reach the decision that visual estimates are possible where the base of the water residue is essentially calcium and magnesium compounds, but that photographic methods are necessary with saline residues. All spectrograms are examined by projection upon an aluminum screen by means of a Bausch and Lomb lantern slide projector. The projector has been equipped with a special plate holder to fit the 3 inch (7.62 cm.) \times 10 inch (25.4 cm.) spectrograms, and the lens mount has been extended for short-range projection.

EXPERIMENTAL

By a study of the spectrum of calcium carbonate containing known added amounts of fluorine, it has been found that when photographed the calcium fluoride band will show a satisfactory density gradient when the fluorine lies between the approximate limits of 0.05 and 1.5 per cent of the calcium carbonate when using a sample weighing 12.5 mg. By varying the amount of material used for the arc, the limits can probably be broadened. For water analysis this range is satisfactory. The series of standards used for this investigation were prepared to contain 0.025, 0.05, 0.10, 0.25, 0.50, 1.00, 1.50, and 2.00 per cent of fluorine. When examined visually during the burning of the sample, the calcium fluoride band was found to disappear after a few seconds, the time varying with the amount of fluorine present. By plotting the time in seconds against the percentage of fluorine in the base material, a satisfactory curve can be drawn. For analysis of water of the same approximate composition as the standards used for plotting the curve, the estimate requires only the observation of the time required for the disappearance of the calcium fluoride band.

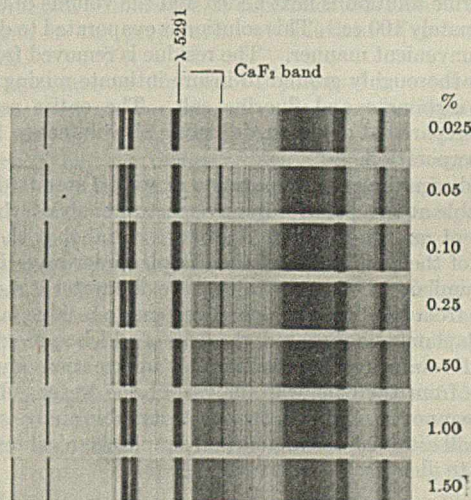


FIGURE 2. SPECTRA OF STANDARDS CONTAINING VARIOUS AMOUNTS OF FLUORINE

Some of the western waters examined contained as much as 2000 p. p. m. of dissolved solids, mainly sodium chloride. With these waters, the best arc performance resulted when specially prepared electrodes were used. The electrodes, 0.25 inch (6.35 mm.) diameter graphite, were prepared by

cutting to 1.25-inch (31.8-mm.) lengths. A shallow cavity, about 0.078 inch (1.98 mm.), was drilled in one end of half the electrodes. The other half, to serve as upper electrodes, were not drilled, nor were they impregnated. The drilled electrodes were placed in a 50 per cent solution of calcium chloride and under a bell jar which was then evacuated in order to fill the voids of the graphite with the solution. When no air

bubbles were observed at the surface of the electrodes, they were removed from the jar and the calcium chloride, dried in an oven at 175° C., and stored in a desiccator.

STANDARDS

For the preparation of standards, c. p. calcium carbonate may be used as the base. Freedom from fluorine is first assured by a spectral analysis of the calcium carbonate. Fluorine in suit-

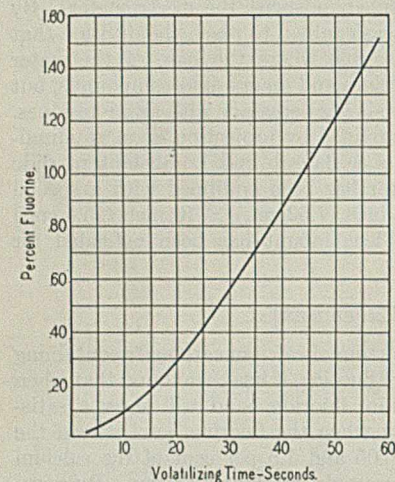


FIGURE 3. CURVE FOR ESTIMATING FLUORINE BY VISUAL OBSERVATION

able amounts is added from an aqueous solution of a fluorine salt. Sodium or calcium fluoride may be used, although sodium fluoride is preferable because of its greater solubility. Both sodium and calcium fluoride have been used in these laboratories, since there is some doubt about the combination of the fluorine as it exists in water. However, the agreement in results of fluorine determined using either salt is such that the choice is considered as optional.

A few grams of calcium carbonate are pulverized to a fine powder in an agate mortar. The desired amount is weighed from the ground material and placed in a platinum dish. The fluorine solution is next added and the volume diluted to approximately 100 cc. This solution is evaporated to dryness in any convenient manner. The residue is removed from the dish and thoroughly ground to insure intimate mixing of the calcium carbonate and fluorine salt. The entire series is usually prepared at one time, adjusting all volumes to 100 cc. before evaporation.

A word regarding the preparation of special standards may be desirable at this point. In any spectral analysis where an estimate of quantity is desired, it is essential that the composition of the standards and the sample under investigation be very similar. If the mineral residue of a water is radically different from the typical calcium carbonate residue, a set of standards should be prepared, the base of which approximates that of the water residue itself. This information is usually available from the chemical analysis of the water. If such analysis cannot be obtained, the spectrographic analysis of the residue will establish the metals and simple chemical tests can be made to identify the acid radicals.

ANALYSIS OF SAMPLES

Since the spectral method for fluorine in water consists of estimating the fluorine in the residue, it becomes apparent that the sensitivity of the test depends largely on the ratio of fluorine to residue. The experimental work has shown that the accurate range for estimating the fluorine extends from 0.05 to 1.5 per cent of the residue. For a great many waters

all that is needed may be evaporation of the water to dryness and immediate examination of the residue. However, there may often be cases where the fluorine is present in too great a quantity to allow direct use of the residue, and dilution will be necessary. For example, assuming that a water contains 200 p. p. m. of "ignited residue," fluorine between 0.1 and 3.0 p. p. m. could be estimated by evaporating the necessary volume to provide the required amount of residue. If such a water contained more than 3.0 p. p. m. of fluorine, the addition of calcium carbonate as a diluent would be necessary to reduce the fluorine to a determinable amount. Electrodes impregnated with calcium chloride are satisfactory for any water and in order to avoid any shortage of calcium are recommended for all analyses.

PROCEDURE: Evaporate enough of the water in a platinum dish to provide 50 mg. of ignited residue. Standard methods of water analysis should be followed in all details except in the quantity of water used for the sample. The ignited residue is merely the mineral matter which is left after the organic matter has been decomposed. A temperature of 500° C. is used for the ignition. Remove the residue from the dish with the aid of a wood spatula, using a little distilled water if necessary. If water is used, the residue must of course be dried. Transfer the residue to an agate mortar and pulverize thoroughly. Pulverizing is essential for a thoroughly homogeneous sample. Place 12.5 mg. of the pulverized residue in the cavity of the calcium impregnated graphite electrode, packing in tightly. A convenient method of filling the electrodes is to deposit the residue on a flat surface and place the electrode over the sample, cavity downward, in a manner similar to that used by druggists for filling gelatin capsules. This usually results in a very satisfactory electrode.

Place the filled electrode in the arc stand, using a solid unimpregnated upper electrode. The lower electrode containing the sample is the anode of the circuit. If the photographic method is being used, burn the residue until it has been completely volatilized. This will require about one minute with a current of 15 amperes. The time will of course vary, depending upon the composition of the residue. If a visual determination is being made, the current is interrupted as soon as the calcium fluoride band disappears. All determinations should be made in duplicate.

Develop the plate if the spectrograph was used, and project the spectrum, matching the intensities of the calcium fluoride bands with those of the standards. Since the difference between adjacent standards is not great, estimation to the nearest standard will usually be sufficiently accurate. Interpolation is possible if greater accuracy is desired.

Because some residues have been found to be slightly hygroscopic, the filled electrodes are placed in an aluminum holder drilled with holes to fit the electrodes. The holder is kept at a temperature of about 200° C. by a gas flame. This precaution often prevents considerable annoyance and delay from the loss of a sample, which is likely to happen if the residues pick up a little moisture. Figure 1 shows the holder filled with electrodes.

Reproduction of the spectra of a series of fluorine standards is shown in Figure 2. The gradation is clearly evident, although considerable detail is lost in the various stages of reproduction. This set was synthesized for determining the fluorine in a certain water containing 200 p. p. m. of residue, principally calcium carbonate. The amounts of fluorine are 0.025, 0.05, 0.10, 0.25, 0.50, 1.0, and 1.5 per cent of the residue, or, respectively, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, and 3.00 p. p. m. of fluorine in the water. This same set of standards would serve for the estimation of fluorine in other waters whose residues are similar, by calculation of the amount of fluorine in the residue to a water basis.

Figure 3 is a curve typical of the results derived from the visual examination of fluorine-bearing waters. When the water residue is such that the visual instrument can be used, this affords the most rapid means of making the determination.

SUMMARY

Spectral methods for estimating fluorine in the mineral residue of water have been found to yield satisfactory results. Photographic methods are suitable for all waters. Visual

methods are satisfactory for waters whose residues consist essentially of calcium and magnesium.

The conditions for most accurate estimation exist when the fluorine is between 0.05 and 1.5 per cent of the residue.

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Analytical Uses of 2-Propanol

G. W. FERNER AND M. G. MELLON, Purdue University, Lafayette, Ind.

In considering 2-propanol as a substitute for ethanol in analytical procedures there are relatively few unfavorable factors. There is very little difference in the physical properties of the two alcohols.

As a solvent for analytical reagents, particularly organic reagents, 2-propanol is a satisfactory substitute for ethanol. For inorganic reagents in rather high concentrations the absolute alcohol must be used, since two liquid phases are formed with the constant-boiling mixture.

As a reagent for the qualitative detection of certain elements or radicals 2-propanol is not effective,

especially where the chemical properties of the alcohol are significant. Thus the flame test for boron and the ester test for acetates fail to work with 2-propanol.

Certain inorganic compounds can be separated with 2-propanol. The advantage of the lower solubility of salts in 2-propanol is canceled by the decreased solubility of the soluble as well as the insoluble salt. However, 2-propanol is a satisfactory substitute for ethanol in this type of separation, and can be used in determinations to decrease the solubility of precipitates, and as a washing medium for precipitates.

THE extent and variety of the uses of ethanol in analytical chemistry, indicated in a preliminary paper (7), include the preparation of materials for analytical work, such as analytical devices, reagents, and samples; and the determination of constituents, involving reactions such as the separation of materials, the reduction of the solubility of precipitates, and the removal of adhering liquids.

In view of the cost of ethanol (including tax) and of the inconvenience of the precautions necessary to prevent its diversion, it would be of advantage to find a suitable substitute. The selection of such a substitute should be made on the basis of low cost and of similarity in properties. Of the lower members of the series of aliphatic alcohols having physical and chemical properties similar to those of ethanol, 2-propanol is most nearly like ethanol. It is completely miscible with water and recent commercial production has brought the price considerably lower than that of taxed ethanol. The data in Table I, obtained from International Critical Tables, indicate the great similarity in the properties of these two compounds.

TABLE I. PHYSICAL PROPERTIES OF ETHANOL AND 2-PROPANOL

PROPERTY	ETHANOL	2-PROPANOL
Boiling points, at 760 mm.	100% C ₂ H ₅ OH, 78.4° C. B. C ₂ H ₅ OH, 78.15°	100% C ₂ H ₅ OH, 82.26° C. B. C ₂ H ₅ OH, 80.37°
Heat of combustion	328 kg.-cal./mole 7.13 kg.-cal./gram	474.8 kg.-cal./mole 7.91 kg.-cal./gram
Heat of vaporization at boiling point	855 joules/gram	667 ± 2% joules/gram
Vapor pressure at 20° C.	43.9 mm. Hg	32.4 mm. Hg
Refractive index. Na D line	1.36242 at 18.35° C.	1.37757 at 20° C.
Surface tension at 20° C.	22.27 ± 0.1	21.7 ± 0.3
Viscosity	1.716 × 10 ⁻²	2.101 × 10 ⁻²

As a laboratory reagent 2-propanol has had some application. Griffin (10) successfully substituted it for ethyl alcohol in histological work, the preparation of reagents, and general laboratory use. Gilson (8) states, "During several years of

biochemical research the writer has found many instances where isopropanol could be substituted for ethanol in laboratory work. It is cheap and there are no restrictions governing its use, nor is it likely to be an object of theft." Schuette and Smith (18), using 2-propanol in the determination of acid numbers, obtained more satisfactory results than with ethanol. Schuette and Harris (17) made the same substitution in the determination of saponification numbers, using 2-propanol in the preparation of solutions of potassium hydroxide.

In references to the use of 2-propanol as a substitute for ethanol, there are few data of value in predicting its applicability as an analytical reagent. Neither International Critical Tables nor Seidell's "Solubilities of Inorganic Compounds" contains any appreciable amount of information regarding the solubility of inorganic salts in isopropyl alcohol, data which would be of importance in predicting the behavior of the reagent in inorganic analysis.

Four articles have recently been published regarding the solubility of compounds in 2-propanol. Kirn and Dunlap (13) studied the solubilities of the alkali chlorides and sulfates in anhydrous alcohols, including isopropyl alcohol. These salts are slightly more soluble in ethanol than in 2-propanol. Ginnings and Chen (9) investigated the ternary systems, water, 2-propanol, and salts, obtaining qualitative results with seventy-five common inorganic salts and quantitative results with ten salts. Hopkins and Quill (12), in a study of the use of nonaqueous solvents in the rare earth group, stated that isopropyl alcohol is a very poor solvent for the rare earth chlorides. In determining the solubility of silver bromate in mixtures of alcohols and water Neuman (15) found that the values in mixtures of isopropyl alcohol and water fall between those in ethanol-water mixtures and those in *n*-propanol-water mixtures.

TABLE II. DETERMINATION OF NICKEL AND COPPER

ELEMENT DETERMINED	AMOUNT PRESENT	ETHANOL SOLUTION OF REAGENT FOUND		2-PROPANOL SOLUTION OF REAGENT FOUND	
Nickel with dimethylglyoxime	0.0564		0.0559		0.0560
			0.0559		0.0560
			0.0559		0.0560
		Av.	0.0559	Av.	0.0560
Copper with 8-hydroxyquinoline	0.1052		0.1054		0.1054
			0.1052		0.1053
			0.1053		0.1054
		Av.	0.1053	Av.	0.1054

TABLE III. SOLUBILITY OF SODIUM AND POTASSIUM CHLORIDES IN ETHANOL

(Grams of salt per 100 grams of solvent)

SALT	TEMP. ° C.	PER CENT ALCOHOL BY WEIGHT			
		86.4	89.6	92.3	96.9
KCl	16	0.1413	0.0865	0.0432	0.0263
		0.2256	0.1415	0.0860	0.0431
KCl	25	0.2777	0.1744	0.1085	0.0502
		0.2780	0.1743	0.1082	0.0499
KCl	35	0.3139	0.1997	0.1203	0.0599
		0.3130	0.1992	0.1212	0.0605
NaCl	16	0.5771	0.3712	0.2369	0.1187
		0.5763	0.3710	0.2346	0.1179
NaCl	25	0.6414	0.4184	0.2671	0.1221
		0.6420	0.4179	0.2669	0.1218
NaCl	35	0.6582	0.4345	0.2708	0.1338
		0.6590	0.4345	0.2705	0.1331

TABLE IV. SOLUBILITY OF SODIUM AND POTASSIUM CHLORIDES IN 2-PROPANOL

(Grams of salt per 100 grams of solvent)

SALT	TEMP. ° C.	PER CENT ALCOHOL BY WEIGHT		
		87.7	92.6	96.5
KCl	16	0.1099	0.0284	0.0078
		0.1092	0.0289	0.0071
KCl	25	0.1279	0.0300	0.0084
		0.1281	0.0296	0.0085
KCl	35	0.1494	0.0362	0.0102
		0.1495	0.0366	0.0107
NaCl	16	0.2647	0.0645	0.0175
		0.2652	0.0649	0.0164
NaCl	25	0.2810	0.0632	0.0157
		0.2813	0.0629	0.0166
NaCl	35	0.2968	0.0697	0.0183
		0.2967	0.0705	0.0184

EXPERIMENTAL WORK

PREPARATION OF MATERIALS. The constant-boiling alcohols were purified by a single distillation of the commercial product through a 40-cm. Vigreux distilling column. The 2-propanol had a density (d_4^{25}) of 0.8120, corresponding to an 87.7 per cent solution by weight; the respective values for the ethanol were 0.8062, and 92.3 per cent. The 98 to 99 per cent commercial alcohols were dehydrated by refluxing for 24 hours over calcium oxide. At the end of this period they were distilled through the 40-cm. column. The density (d_4^{25}) of the 2-propanol was 0.7807 and that of the ethanol 0.7846.

The salts used for the determination of solubilities were purified by double recrystallization. The reagents used were prepared from the usual reagent quality chemicals.

GENERAL USE. The use of alcohol in the preparation of analytical devices depends almost entirely upon its physical properties. No experimental work was done with 2-propanol in this connection; however, there seems to be no reason why it should not be used in cleaning apparatus, in washing crucibles, and in similar ways, since its physical properties are much like those of ethanol.

USE AS A SOLVENT. Quite frequently the organic reagents used in analytical work are insoluble in water. In such cases the most common solvent is ethyl alcohol. Unless the presence of 2-propanol has a detrimental effect in determinations where alcoholic solutions of reagents are used, the only question as to its applicability is its ability to dissolve the reagents.

Solutions of dimethylglyoxime, 8-hydroxyquinoline, and

alpha-benzoinoxime were prepared in 91 per cent 2-propanol and 95 per cent ethanol. The dimethylglyoxime was prepared as a 1 per cent solution and the other two reagents as 2 per cent solutions. No difficulty was encountered in preparing solutions of this concentration, although the reagents dissolved more slowly in the 2-propanol than in ethanol.

In order to determine whether there might be any difference in the effect of 2-propanol and ethanol on the actual determinations, the solutions of dimethylglyoxime were used for the precipitation of nickel and those of 8-hydroxyquinoline for the precipitation of copper, with the results shown in Table II.

In the case of inorganic reagents the application of 2-propanol as a solvent is somewhat limited by the fact that it is salted out by many inorganic compounds. This eliminated the 91 per cent alcohol from consideration except for dilute solutions of reagents. Absolute 2-propanol has been used as a solvent for potassium hydroxide by Schuette and Harris (17) and Schuette and Smith (18) in the determination of acid and saponification numbers. The latter authors state that a yellow color can be avoided by allowing solution to take place without the application of heat. In the present work a yellow color appeared with 2-propanol after a relatively short time in a 0.5 *N* solution of this base, although no heat was applied to hasten solution. The color developed when the solution was stored in the dark as well as in the light. However, a 0.1 *N* solution prepared in a similar manner remained colorless. The hydroxide dissolves more slowly in 2-propanol than in ethanol.

USE IN QUALITATIVE TESTS. In certain qualitative tests for chromates, borates, and acetates, ethanol is used as a reagent or as a solvent for a reagent. In order to test the suitability of 2-propanol for this purpose the tests were carried out in duplicate, using ethanol in one case and 2-propanol in the other.

The test for chromates depends upon the reducing action of alcohol on hexivalent chromium to form green trivalent chromium. For this test 2-propanol was as satisfactory as ethanol, using the procedure recommended by Curtman (3).

Two tests for borates are given by Curtman. One is the common flame test which indicates the presence of borates by a green coloration imparted to the burning alcohol. When 2-propanol is used, a satisfactory coloration is not obtained because of the smokiness of the flame, which obscures the slight green color. The lack of color may also be due to the lower volatility of the isopropyl ester. The turmeric test described by the same author is successful with both ethanol and 2-propanol. However, the test is not as sensitive with the latter alcohol, no color being produced with a 0.01 per cent solution of borax, while ethanolic solutions of turmeric did produce a color at this concentration.

The acetate test as given by the U. S. Pharmacopeia (22) depends upon the formation of the acetic acid ester of the alcohol used. This test is not successful with 2-propanol, presumably because the alcohol is unstable in the presence of concentrated sulfuric acid (20).

QUANTITATIVE USES

In the presentation of the experimental results for the quantitative determinations employing 2-propanol as a reagent the details of the procedures used are not included, because in most cases they are readily available in the literature. In general, the determinations were run in triplicate with each alcohol, six aliquot portions being taken from a solution of a salt of the constituent to be determined. In some cases the strength of the stock solution was determined by an analysis of a third set of triplicates, and in other cases the solution was prepared by direct weighing and dilution to definite volume of a twice recrystallized salt.

TABLE V. SOLUBILITY OF CALCIUM, BARIUM, AND STRONTIUM NITRATES IN ABSOLUTE ETHANOL AND 2-PROPANOL

(Grams of salt per 100 grams of solvent at 25° C.)

SALT	SOLUBILITY	
	Ethanol	2-Propanol
Ba(NO ₃) ₂	0.0020 0.0016	0.0020 0.0016
Sr(NO ₃) ₂	0.0086 0.0062	0.0023 0.0014
Ca(NO ₃) ₂ ^a	85.40	2.65 2.69

^a Values uncertain, presumably because of compound formation. See D'Ans and Siegler, *Z. physik. chem.*, 82, 35 (1913).

TABLE VI. DETERMINATION OF CALCIUM AND STRONTIUM AS SULFATES

(Alcohol used to decrease solubility of precipitates)

CONSTITUENT DETERMINED	AMOUNT PRESENT	ETHANOL	2-PROPANOL
		FOUND	FOUND
		Gram	Gram
Sr	0.4158	0.4062	0.4045
		0.4058	0.4047
		0.4057	0.4050
		Av. 0.4059	Av. 0.4047
Sr	0.1023	0.1021	0.1031
		0.1029	0.1031
		0.1023	0.1023
		Av. 0.1025	Av. 0.1028
Ca	0.06577	0.06546	0.06547
		0.06564	0.06555
		0.06558	0.06552
		Av. 0.0656	Av. 0.0655
Ca	0.0995	0.09960	0.09969
		0.09969	0.09960
		0.09958	0.09975
		Av. 0.0996	Av. 0.0997

SOLUBILITIES. When alcohol is used as a selective solvent in the separation of two or more constituents of a mixture the deciding factor in its application is the solubility of the material in the alcohol. If 2-propanol is to be substituted for ethanol in such procedures it is desirable to know something of the solvent properties of the former as compared with the latter.

In order to compare the variation of solubility in the two alcohols with temperature and concentration of alcohol, a number of solubility determinations were made.

Duplicate determinations were made by placing an excess of the dried salt in each of two glass tubes with a capacity of about 100 ml. The tubes were then nearly filled with alcohol and sealed. One of the tubes was placed in the thermostat immediately after being sealed off and the other was held at a temperature about 10° above that of the thermostat for about an hour and then transferred to the thermostat. The tubes were held in a rack which was arranged in such a manner that it could be rotated, turning the tubes end over end. The tubes were rotated for a period of 12 hours.

At the end of 12 hours the rotation was stopped and the excess salt was allowed to settle to the bottom. The tip of the tube was then broken off and the solution drawn off into a weighing bottle through a tube containing a sintered glass filtering disk. The weighing bottle was stoppered and weighed after standing in the balance case for 15 minutes. The alcohol was then evaporated and the residue dried at 110° C., cooled, and weighed. The results for sodium and potassium chlorides are shown in Tables III and IV.

The solubilities of calcium, barium, and strontium nitrates are shown in Table V. The procedure used for these salts was the same as that for the sodium and potassium chlorides.

TO MAKE SEPARATIONS. In making separations of metallic ions the samples were prepared by making a stock solution of each of the constituents, standardizing each solution, and taking 25 ml. of each solution for a sample.

The separation of calcium from barium by extraction of the calcium nitrate with a mixture of absolute alcohol and ether was carried out according to the procedure given by Hillebrand and Lundell (11). The mixture of nitrates used contained 0.05018 gram of calcium oxide and 0.5015 gram of barium oxide. The calcium was not determined after the extraction.

Separation with ethanol:

BaO: 0.0486; 0.0485; 0.0488; Av. 0.0486

Separation with 2-propanol:

BaO: 0.0487; 0.0490; 0.0491; Av. 0.0489

TABLE VII. ALCOHOLS AS WASHING MEDIA FOR PRECIPITATES

CONSTITUENT DETERMINED	AMOUNT PRESENT	ETHANOL FOUND		2-PROPANOL FOUND	
		Gram	%	Gram	%
Pb as PbSO ₄ (14, p. 523)	0.2051	95	0.2046	91	0.2044
			0.2044		0.2046
			0.2044		0.2046
		Av. 0.2044		Av. 0.2045	
Mg as MgNH ₄ PO ₄ ·6H ₂ O (6, pp. 222, 224)	0.02433	95	0.02426	91	0.02423
			0.02425		0.02425
			0.02424		0.02424
		Av. 0.02425		Av. 0.02424	
CNS as AgCNS (21, p. 303)	0.07686	95	0.07632	91	0.07667
			0.07654		0.07663
			0.07667		0.07667
		Av. 0.0765		Av. 0.07666	
Cr as BaCrO ₄ (21, pp. 106-7)	0.02689	50	0.02662	50	0.02666
			0.02660		0.02670
			0.02656		0.02668
		Av. 0.02659		Av. 0.02668	
Cd as Cd ₂ P ₂ O ₇ (21, p. 192)	0.1028	60	0.1077	60	0.1066
			0.1074		0.1065
			0.1069		0.1071
		Av. 0.1073		Av. 0.1067	
Cu as CuCNS (21, p. 187)	0.1730	20	0.1724	20	0.1719
			0.1717		0.1722
			0.1721		0.1721
		Av. 0.1721		Av. 0.1721	
Cd as CdNH ₄ PO ₄ ·H ₂ O (4, pp. 401-15)	0.1079	95	0.1076	91	0.1077
			0.1078		0.1082
			0.1076		0.1079
		Av. 0.1077		Av. 0.1079	
Na as sodium zinc uranyl acetate (1, p. 1625)	0.00200	95 ^a	0.00197	91 ^a	0.00195
			0.00200		0.00196
			0.00196		0.00192
		Av. 0.00198		Av. 0.00194	
Na as sodium magnesium uranyl acetate (2, p. 1664)	0.0100	95	0.0100	91	0.00987
			0.0101		0.00988
			0.0100		0.00988
		Av. 0.0100		Av. 0.00988	
				91 ^a	0.00987
					0.00991
					0.00995
					Av. 0.00991
Zn as ZnNH ₄ PO ₄ (21, p. 142)	0.1168	50	0.1169	50	0.1168
			0.1166		0.1165
			0.1171		0.1169
		Av. 0.1169		Av. 0.1167	
Zn as ZnNH ₄ PO ₄ (4, p. 401-15)	0.1123	65	0.1121	65	0.1122
		&	0.1120	&	0.1119
		95	0.1121	91	0.1119
		Av. 0.1121		Av. 0.1120	
Cu as copper pyridinothiocyanate (19, p. 185)	0.0602	70	0.06037	70	0.06017
		&	0.05994	&	0.06060
		95	0.05981	91	0.06062
		Av. 0.0600		Av. 0.0605	
Ca as CaC ₂ O ₄ ·H ₂ O (5, p. 352)	0.1343	95	0.1354	91	0.1358
			0.1354		0.1359
			0.1356		0.1362
		Av. 0.1355		Av. 0.1360	
Ba as BaSO ₄ (5, p. 352)	0.1408	95	0.1414	91	0.1415
			0.1405		0.1408
			0.1411		0.1414
		Av. 0.1410		Av. 0.1412	
Ni as nickel dimethyl glyoxime (5, p. 352)	0.0552	95	0.05535	91	0.05515
			0.05523		0.05535
			0.05537		0.05525
		Av. 0.0553		Av. 0.0553	
Cl as AgCl (5, p. 352)	0.0998	95	0.1000	91	0.0995
			0.0997		0.1000
			0.1000		0.1001
		Av. 0.0999		Av. 0.0999	

^a Alcohol used for washing was saturated with the precipitate.

Calcium was separated from magnesium by precipitation according to the method given by Hillebrand and Lundell (11). The following amounts were recovered from a sample which contained 0.0102 gram of calcium oxide and 0.02383 gram of magnesium oxide:

Separation with ethanol:

CaO: 0.0108; 0.0101; Av. 0.0104
MgO: 0.02388; 0.02327; Av. 0.0236

Separation with 2-propanol:

CaO: 0.0100; 0.0092; 0.0103; Av. 0.0098
MgO: 0.02390; 0.02401; 0.02416; Av. 0.0240

Potassium and sodium chlorides were separated from magnesium chloride according to the procedure given by the same authors (11). The sample contained 0.07975 gram of combined alkali chlorides (1 to 1) and 0.0953 gram of magnesium oxide. Because the evaporation of the solution containing the sodium and potassium chlorides left a residue of organic matter which could not readily be removed only the magnesium was determined after separation.

Separation with ethanol:

MgO: 0.0954; 0.0941; 0.0948; Av. 0.0948

Separation with 2-propanol:

MgO: 0.0918; 0.09261; 0.0923; Av. 0.0922

A repetition of this procedure with 0.1129 gram of magnesium oxide in the presence of 0.0843 gram of sodium and potassium chlorides (7 to 10) gave the following results:

Separation with ethanol:
MgO: 0.1098; 0.1107; 0.1115; Av. 0.1107
Separation with 2-propanol:
MgO: 0.1121; 0.1125; 0.1131; Av. 0.1126

In a separation of the same elements according to the Palkin method (16) using 0.0843 gram of sodium and potassium chlorides (7 to 10) in the presence of 0.1129 gram of magnesium oxide the following results were obtained:

Separation with ethanol:
NaCl and KCl: 0.0884; 0.0881; 0.0886; Av. 0.0884
Separation with 2-propanol:
NaCl and KCl: 0.0846; 0.0843; Av. 0.0844

The magnesium was not determined in this separation. The alkali chlorides are precipitated in this determination by the addition of absolute alcohol and ether. A double precipitation is necessary with ethanol, but with 2-propanol a single precipitation completely separated the sodium and potassium chlorides.

TO DECREASE SOLUBILITIES. In some instances ethanol is used to decrease the solubility of precipitates which are too soluble to be precipitated from aqueous solution. Examples of this use are the determinations of strontium and calcium as sulfates. The procedure for calcium is given by Treadwell and Hall (21) and that for strontium by Mahin (14). Typical results are shown in Table VI.

TO WASH PRECIPITATES. Alcohol is used quite frequently for washing precipitates, generally for one of two reasons: the precipitate is less soluble in alcohol than in some other medium; or, there is some advantage in using a low-boiling washing medium either to obtain more rapid drying or to make it possible to dry at relatively low temperatures those precipitates which decompose at the ordinary drying temperatures.

Table VII contains the results of experiments to compare the suitability of ethanol and 2-propanol as washing media.

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Colorimetric Standards for Silica

H. W. SWANK AND M. G. MELLON, Purdue University, Lafayette, Ind.

ONE of the methods recommended for the colorimetric determination of small amounts of dissolved silica depends upon the formation of a yellow heteropoly compound, molybdisilicic acid, by the reaction of ammonium molybdate and the silica in the presence of a mineral acid. Since the usefulness of this procedure for routine work is limited by the instability of solutions of silica and of the yellow color, permanent standards have been proposed by various individuals.

The purpose of the present work was to study, by means of a spectrophotometer, these or other possible standards to determine the system most nearly meeting the requirements of an ideal colorimetric standard. The latter, in addition to being permanent and reproducible, should transmit the same amount of light at each wave length as the substance which it is to match, if the hues are to be identical under all conditions.

In the original recommendation of the method in 1898, Jolles and Neurath (5) used potassium molybdate and nitric acid as reagents and known solutions of silica for comparison. Winkler (14) modified the method by substituting hydrochloric for nitric acid and by introducing aqueous solutions of potassium chromate for standards. A solution containing 0.53 gram per liter of this salt was stated to be equivalent in color to 100 p. p. m. of silica. Dienert and Wandenbulcke (3) used ammonium molybdate and sulfuric acid and, as a standard, an aqueous solution of picric acid containing 35.9 mg. per liter, equivalent to 50 p. p. m. of silica. Atkins (2) employed the same concentration of this standard, but Thresh and Beale (12) recommended 40 mg. Believing the picric acid used by previous workers contained

moisture, King and Lucas (7) proposed 25.6 mg. of dried material as equivalent to 50 p. p. m. of silica. Thompson and Houlton (11) recently reported using picric acid standards. Steffens (9) thought the reddish yellow hue of the potassium chromate solution did not match the greenish yellow obtained with silica and ammonium molybdate, an observation confirmed by the work of Liebknecht, Gerb, and Bauer (8). Winkler's potassium chromate standards were adopted, however, by the American Public Health Association in 1933 (1).

EXPERIMENTAL WORK

PREPARATION OF MATERIALS. Several types of silica solutions were used, two being made from different samples of c. p. sodium silicate and a considerable number from definite amounts of c. p. silica or acid-washed sea sand fused with sodium carbonate. The former were standardized at intervals gravimetrically and kept in Pyrex glass bottles. The latter were discarded if more than 48 hours old. These solutions contained 500 to 5000 p. p. m. of silica and were diluted for use.

Picric acid recrystallized from benzene was used to prepare solutions of the concentrations recommended by King and Lucas and by Dienert and Wandenbulcke. Borax and potassium chromate were recrystallized. All the water used came from a special still built entirely of tin and Pyrex glass. Both c. p. ammonium molybdate and that prepared from molybdcic acid and redistilled ammonium hydroxide were used.

APPARATUS. A Keuffel and Esser spectrophotometer served for obtaining transmission data, using 20-cm. cells. In contrast to the usual practice with this instrument, the transmissions of the solution and solvent were determined separately and the transmittancy calculated from these values. Ordinary visual comparisons were made both in tall-form Nessler tubes with plane glass ends and in a Duboscq-type colorimeter by the substitution method (15).

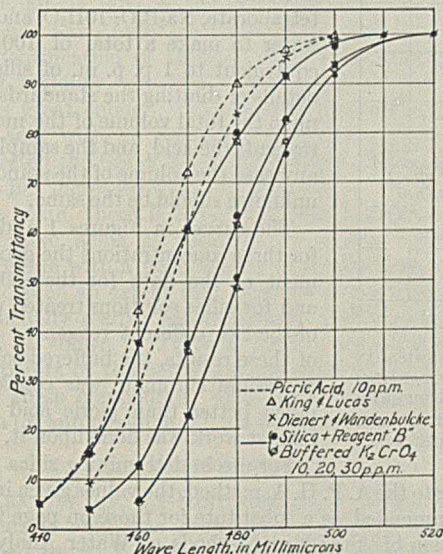


FIGURE 1. SPECTRAL TRANSMISSION CURVES FOR PICRIC ACID STANDARDS, BUFFERED POTASSIUM CHROMATE STANDARDS, AND SILICA SOLUTIONS WITH REAGENT B

A photoelectric colorimeter similar to that described by Story and Kalichevsky (10) proved to be both sensitive and rapid in determining the effect of different factors on the intensity and stability of the yellow color. Blue glass filters isolated the part of the spectrum in which yellow solutions absorb light. Galvanometer deflections were noted for a constant thickness of solution.

COLOR REACTION. The selection of satisfactory permanent standards presupposes a knowledge and control of the conditions likely to affect the stability and reproducibility of the color produced with the silica in the unknown. After surveying the work of others upon this point, different variations in reagents, concentrations, and other conditions were tried. On the basis of the results obtained, two reagents were selected for use in the study of permanent standards. For the first, now recommended by the American Public Health Association (A. P. H. A. Reagent), one adds to 100 ml. of unknown 10 ml. of a solution containing 200 ml. of hydrochloric acid (1 to 1), 30 grams of ammonium molybdate, and 400 ml. of water. For the second (Reagent B), adapted from Dienert and Wandenbulcke's recommendation, one adds to 100 ml. of unknown 4 ml. of 10 per cent ammonium molybdate and 1 ml. of 20 per cent sulfuric acid.

There seems to be an optimum amount of acid required for the full development of the yellow color. Either too much or too little gives decreased intensities, presumably from an effect on the heteropoly complex. The acidity of the A. P. H. A. Reagent is near the maximum. Acidities somewhat less gave just as satisfactory colors with this reagent.

Use of each of the two reagents mentioned gave a reproducible series of results, complete development of color occurring within 5 minutes and no fading within 30 minutes. However, the A. P. H. A. Reagent gave approximately 10 per cent greater intensity of color than Reagent B. The color

developed with these reagents is proportional to the silica, at least as high as 75 p. p. m. Transmittancy data were determined for each reagent for concentrations of silica of 10, 20, and 30 p. p. m., thus providing curves with which to compare those of possible permanent standards.

PICRIC ACID STANDARDS. In Figure 1 are shown spectral transmission curves for solutions of picric acid equivalent to 10 p. p. m., the concentrations being those recommended by King and Lucas and by Dienert and Wandenbulcke. A comparison of these curves with those for silica of the same concentration with Reagent B shows that the standards do not transmit the same amount of light at most wave lengths as the silica solution. The curve for Dienert and Wandenbulcke's solution of acid is fairly close to that for the corresponding silica solution, but no change of concentration would bring together the curves for the standard and the unknown. Similar data were obtained for solutions of picric acid designed to match other concentrations of silica, but only the curves for the latter solutions are shown. Although picric acid solutions show reasonable stability and conformity to Beer's law, the curves show that the system cannot be as satisfactory as one meeting more nearly the criteria of an ideal standard. In Nessler tubes differences are apparent between either of the two concentrations of standard and the corresponding silica solution.

POTASSIUM CHROMATE STANDARDS. In agreement with the report of Steffens, differences in hue could be noted easily in Nessler tubes between silica and potassium chromate solutions. The observations of Viterbi and Krausz (13), Hantzsch and Clark (4), and Jorgensen (6) concerning the

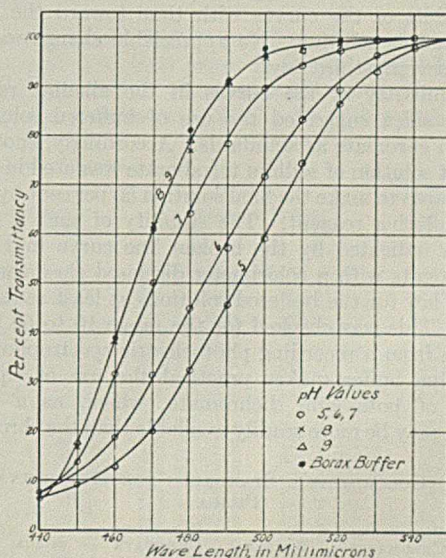


FIGURE 2. SPECTRAL TRANSMISSION CURVES FOR SOLUTION OF POTASSIUM CHROMATE AT DIFFERENT pH VALUES

variability of the chromate-dichromate equilibrium in solutions of potassium chromate gave a possible clue to the objection to this system as a standard. To determine the effect of hydrogen-ion concentration on the hue, a series of solutions equivalent to 10 p. p. m. of silica was prepared in buffer solutions to give pH values of 5, 6, 7, 8, and 9. From the curves in Figure 2 showing their transmittancy data, it is evident that a decrease in hydrogen-ion concentration caused a decided change in hue to a pH value of about 8, beyond which little change occurred. A fresh, unbuffered solution gave a curve indicating a pH value between 6 and 7. It is evident that such systems may be affected by absorption of carbon dioxide or alkali from the glass.

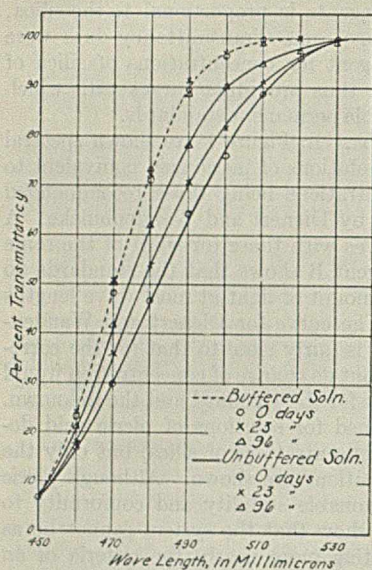


FIGURE 3. SPECTRAL TRANSMISSION CURVES FOR BUFFERED AND UNBUFFERED SOLUTION OF POTASSIUM CHROMATE AT DIFFERENT PERIODS OF TIME

In view of these facts, an unbuffered solution equivalent to 15 p. p. m. of silica was kept in a flint glass bottle for 3 months. The transmittancy data, shown in Figure 3, show a gradual shift of the curves with time toward the position for an alkaline solution. No appreciable change was noted after the seventy-third day.

The similarity of the curves in the alkaline region to those for silica suggested the use of buffered solutions of potassium chromate as standards. Accordingly, enough of a 1 per cent solution of sodium tetraborate was used in diluting the standards to make the final solution 50 per cent by volume of the buffering reagent. The stability of such a buffered system is indicated by the broken line curve in Figure 3. Measurements with a colorimeter disclosed close conformity to Beer's law for the buffered solutions at least as far as 100 p. p. m. This was checked for the range 10 to 50 p. p. m. with data from a recording photoelectric spectrophotometer. An alkaline buffer makes practical the use of equivalent amounts of potassium dichromate, which, as a primary standard, may be more readily available than the chromate.

TABLE I. COLORIMETRIC STANDARDS FOR DETERMINATION OF SILICA

POTASSIUM CHROMATE ^a	SILICA ^b	POTASSIUM CHROMATE	SILICA
Ml.	P. p. m.	Ml.	P. p. m.
0.0	0	8.0	16
1.0	2	9.0	18
2.0	4	10.0	20
3.0	6	11.0	22
4.0	8	12.0	24
5.0	10	13.0	26
6.0	12	14.0	28
7.0	14	15.0	30

^a 0.63 gram of potassium chromate per liter. The volumes specified are to be diluted with 25 ml. of a 1 per cent solution of borax and enough water to make a total of 55 ml.

^b When 50 ml. of sample are used, together with 5 ml. of reagent, as recommended in the A. P. H. A. method.

As a buffered solution of potassium chromate transmits more light than one unbuffered, it is necessary to use a concentration higher than that recommended by the A. P. H. A. method to give a color equal to a given amount of silica. In order to determine the amount to use, measurements were made with three different colorimeters, Nessler tubes, and the spectrophotometer, covering a period of

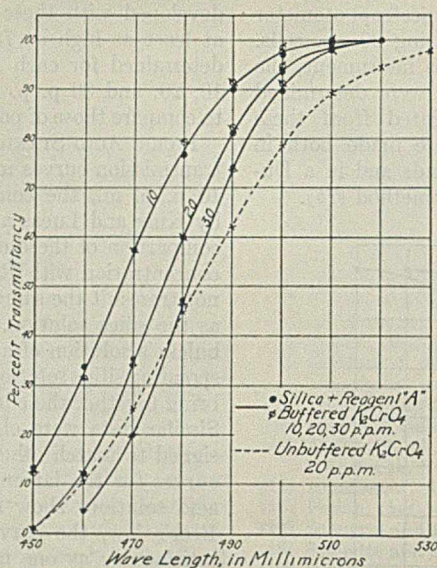


FIGURE 4. SPECTRAL TRANSMISSION CURVES FOR UNBUFFERED POTASSIUM CHROMATE SOLUTION AND FOR BUFFERED POTASSIUM CHROMATE STANDARDS AND SILICA WITH A. P. H. A. REAGENT

several months and using various solutions of silica and ammonium molybdate. To be equivalent to a silica solution of 100 p. p. m., the amounts recommended are 0.63 and 0.58 gram per liter for the A. P. H. A. Reagent and Reagent B, respectively. One milliliter of this stock solution, diluted with 50 ml. of a 1 per cent solution of sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and enough water to make a total of 100 ml., is equivalent to 1 p. p. m. of silica. The details of diluting the standards depend upon the total volume of the molybdate reagent, the acid, and the sample, but in any case the volume of the standard and unknown should be the same.

The curves in Figures 1 and 4 show for three concentrations the good agreement of the data for these standards and for silica solutions treated with one of the two different reagents. In view of these results, the buffered solution of potassium chromate was considered so much better than picric acid that no further work was done upon it.

For use in determining silica in water according to the A. P. H. A. method, the values given in Table I are recommended as a substitute for those on page 67 of the 1933 edition of "Standard Methods of Water Analysis." A careful gravimetric determination of the silica in a well water checked the value obtained colorimetrically with this table.

SUMMARY

A comparison of silica solutions and standards by means of visual and photoelectric colorimeters, Nessler tubes, and a spectrophotometer would seem to justify the following conclusions:

1. Either the A. P. H. A. reagent or an adaptation of that of Dienert and Wandenbulcke is generally satisfactory for producing the yellow color with silica.
2. Solutions of picric acid or unbuffered potassium chromate are not considered as meeting satisfactorily the requirements of a permanent standard.
3. A solution of potassium chromate suitably buffered, as with borax, provides a standard possessing none of the disadvantages of those now recommended.
4. To use the latter solution a new table is recommended.

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Identification of Amines as 2,4-Dinitrobenzoates

C. A. BUEHLER AND JOHN D. CALFEE, Department of Chemistry, University of Tennessee, Knoxville, Tenn.

THE amine salts of sulfonic (3, 6) and carboxylic (1) acids have been recommended as derivatives for the identification of amines. Such salts appear to be of sufficient stability, provided the strength of the acid employed is great enough. The success met with 3,5-dinitrobenzoic acid with an ionization constant of 1.55×10^{-3} (4) suggested the use of 2,4-dinitrobenzoic acid in which this constant has increased to 3.5×10^{-2} (4).

In the main, there is little to choose between these two dinitrobenzoic acids as reagents for amine identification. Both combine with a wide variety of aliphatic and aromatic amines to such an extent that isolation of the salts in a pure form is usually readily accomplished. The results with the 2,4 acid, as shown in Table I, include for comparison the melting points of the corresponding salts with the 3,5 acid. None of these compounds, with the exception of those of ammonia (5) and pyridine (7), has been found in the literature.

EXPERIMENTAL

PREPARATION OF 2,4-DINITROBENZOIC ACID. The 2,4-dinitrobenzoic acid was prepared by Curtius' method (2) as modified by E. L. Lafferty in this laboratory. The details are as follows:

With mechanical stirring 100 grams of 2,4-dinitrotoluene, Eastman's highest grade, melting point 69.5° to 70.5° C., were dissolved in 600 cc. of concentrated sulfuric acid at 50° C. A chromic acid solution was prepared by dissolving 158 grams of

powdered U. S. P. potassium dichromate in 200 cc. of water, and then adding cautiously 100 cc. of concentrated sulfuric acid. The chromic acid solution, kept near boiling to prevent solidification, was added dropwise through a separatory funnel to the 2,4-dinitrotoluene solution, which was being vigorously stirred in a round-bottomed flask placed in an ice bath. During this addition the temperature of the reacting mixture was not allowed to exceed 65° (60° to 65° C. appeared to be the most favorable range). When the addition was complete, stirring was continued for 15 minutes and the mixture was allowed to cool to room temperature, after which ice was added in a quantity sufficient to double the volume. When the ice had melted, the remaining solid was removed by filtration.

The filtrate, since it contained a small amount of the dinitrobenzoic acid, was thoroughly extracted with about 300 cc. of ether. After evaporating off the ether from the upper layer, the solid thus obtained was added to the original residue. In order to separate any unchanged dinitrotoluene, a strong solution of sodium bicarbonate was added to the combined residues until the solution became basic to litmus. The solid dinitrotoluene was then removed by filtration, after which an excess of concentrated hydrochloric acid was added to the filtrate to precipitate out the free 2,4-dinitrobenzoic acid. This acid, after being filtered and washed thoroughly with a cold dilute solution of hydrochloric acid, was redissolved in a saturated solution of sodium bicarbonate, an equal volume of water was added, and the solution thus obtained was made slightly acid with concentrated hydrochloric acid.

The precipitated acid, when filtered, washed with ice water, and dried on filter paper in the air, weighed about 45 grams (40 per cent of the theoretical amount). It had a yellow color and melted at 179° C. The color of the product

TABLE I. 2,4-DINITROBENZOATES OF AMINES

AMINE	RE-CRYSTALLIZED	COLOR	MOLAR RATIO	NEUTRALIZATION EQUIVALENT		NITROGEN		MELTING POINT		MELTING POINT OF 3,5-DINITROBENZOATE
				Calcd.	Found	Calcd.	Found	Obs. °C.	Cor. °C.	
Aniline	0 ^{a,b}	Pink	1:1	305	314	13.77	13.83	157.8-159.4	160.4-162.0	134.7
<i>o</i> -Toluidine	1	White	1:1	319	316	13.17	13.21	189.5-191.2	193.2-194.9	134.9
<i>m</i> -Toluidine	0 ^{a,b}	Yellow	1:1	319	312	13.17	13.18	142.0-143.6	144.5-146.1	139.0-144.0
<i>p</i> -Toluidine	1	Red	1:1	319	316	13.17	13.04	158.2-159.6	160.8-162.2	145.0-147.4
4-Amino-1,3-dimethylbenzene	1	Yellow	1:1	333	337	12.61	12.52	172.0-172.4	175.1-175.5	169.6-170.4
<i>o</i> -Chloroaniline	1	Yellow	1:1	340	335	12.38	12.41	135.6-136.4	137.9-138.7	152.7
<i>m</i> -Chloroaniline	1	Yellow	1:1	340	337	12.38	12.42	139.6-140.4	142.0-142.8	121.8
<i>p</i> -Chloroaniline	1	Yellow	1:1	340	336	12.38	12.40	161.8-162.4	164.5-165.1	133.0
<i>p</i> -Bromoaniline	1	Brown	1:1	384	383	10.94	10.91	179.0-179.6	182.6-183.2	126.9
<i>o</i> -Nitroaniline	No compound isolated									
<i>m</i> -Nitroaniline	1	Yellow	1:1	350	352	16.00	16.02	131.2-131.6	133.0-133.4	112.0-114.4
<i>p</i> -Nitroaniline	0 ^b	Yellow	1:1	350	358	16.00	16.01	116.0-116.9	117.3-118.2	128.6
<i>p</i> -Aminophenol	1	Brown	1:1	321	317	13.09	13.03	200.0-200.2	204.3-204.5	178.2-178.8
<i>o</i> -Aminobenzoic acid	1	Yellow	1:1	175	167	12.04	12.04	148.0-149.0	150.5-151.5	205.2-205.6
<i>m</i> -Aminobenzoic acid	1	White	1:1	175	177	12.04	11.93	184.5-186.0	188.1-189.6	167.0-172.2
<i>p</i> -Aminobenzoic acid	1	Yellow	1:1	175	171	12.04	12.18	165.4-166.0	168.3-168.9	196.7
Methylaniline	0 ^{a,b}	Brown	1:1	319	310	13.17	13.07	101.6-102.8	102.6-103.8	121.8
Dimethylaniline	0 ^{a,b}	Yellow	2:1	273	265	12.85	12.78	101.4-103.0	102.4-104.0	114.8-115.6
Benzylaniline	1	Yellow	1:1	395	385	10.63	10.77	120.0-120.8	121.4-122.2	133.0
Dibenzylaniline	No compound isolated									
Acetanilide	2 ^c	White	1:1	347	350	12.11	12.09	87.4-90.4	87.9-90.9	129.1-130.1
Diphenylamine	0 ^d	Gray	1:1	381	378	11.02	10.99		
Triphenylamine	No compound isolated								
<i>o</i> -Phenylenediamine	1	Yellow	1:1	320	318	17.50	17.46	193.2-193.6	197.5-197.9	177.3
<i>m</i> -Phenylenediamine	1	Yellow	1:1	320	324	17.50	17.52	193.0-193.2	197.3-197.5	158.7
<i>p</i> -Phenylenediamine	1	Golden yellow	1:1	320	319	17.50	17.57	177.8-179.0	181.4-182.6	177.3-178.0
α -Naphthylamine	1	Yellow	1:1	355	357	11.83	11.94	195.0-195.4	199.3-199.7	200.5
β -Naphthylamine	1	Yellow	1:1	355	355	11.83	11.98	177.8-178.2	181.4-181.8	156.5-157.2
Benzidine	1 ^f	Red	2:1	304	306	13.82	13.81	225.8-227.0	231.8-233.0	205.7
Pyridine	1	Brown	2:1	252	246			138.6-139.4	140.9-141.7	171.3
Quinoline	1	Brown	2:1	341	336	12.34	12.37	139.6-140.4	142.0-142.8	151.4-152.2
Ammonia	1	Yellow	1:1	229	233	18.34	18.30	213.4-215.4	218.5-220.5	246.7
Benzylamine	0 ^a	Yellow	1:1	319	325	13.17	13.14	194.8-195.8	199.1-200.1	210.0
Diethylamine	0 ^a	Yellow	1:1	285	281	14.74	14.74	145.0-146.6	147.5-149.1	163.4
Triethylamine	0 ^a	Yellow	1:1	313	317	13.42	13.59	80.6-82.5	81.0-82.9	138.0-150.0
Urea	1 ^c	Yellow	1:1	272	275	20.59	20.63	127.4-128.2	129.1-129.9	120.5
Acetamide	1	Yellow	1:1	271	264	15.49	15.52	109.8-110.8	111.1-112.1	93.9-103.9
Benzamide	1	Orange	1:1	333	328	12.62	12.52	116.8-117.8	118.1-119.1	138.6-140.4

^a Purified by washing in ethyl alcohol as described in Experimental.

^b Decomposition occurred on redissolving compound.

^c Prepared in and recrystallized from a mixture of alcohol and water.

^d Since this compound was extremely unstable, the melting point is of little significance.

^e Compound turned dark below melting point.

^f Prepared in and recrystallized from a mixture of alcohol and ether.

^g Nitrogen could not be determined by the Kjeldahl method.

is determined to some extent by the rapidity with which the acid is precipitated from solution. Rapid precipitation from the acidified bicarbonate solution yielded some very red crystals, while slow cooling of a saturated neutral bicarbonate solution gave long colorless needles.

PREPARATION OF SALTS AND ANALYSES. As a rule, to form the salts, 0.01 mole of each component was dissolved by heating in the least possible amount of absolute alcohol, after which the two solutions were poured together on a watch glass to crystallize. However, the compounds of aniline, *o*-toluidine, *m*-toluidine, methylaniline, dimethylaniline, benzylamine, diethylamine, and triethylamine were prepared by adding, in equimolecular amounts, the hot liquid amine to the very finely powdered acid. Although purification was usually accomplished by recrystallization from absolute alcohol (Table I), these latter-mentioned salts were purified almost entirely by pulverizing them in cold absolute alcohol,

followed by filtration. The number of crystallizations necessary for purity in each case is indicated in the second column of Table I.

The melting points, neutralization equivalents, and nitrogen analyses were determined as described previously (1).

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Determination of Organic Halogens

FRED E. BEAMISH, University of Toronto, Toronto, Ontario, Canada

IT HAS been reported by Jenkins, McCullough, and Booth (5) that the explosion method for organic halogen determination as outlined by Lemp and Broderson (6) produces consistently low results with ortho and para chlorinated diphenyls. Cook and Cook (3) also state that this method produces unsatisfactory results with halogenated diphenyls. Adams (1) and his co-workers have reported satisfactory results on halogenated diphenyl and diphenylbenzene compounds, using the bomb-explosion method.

The present investigation was undertaken to determine whether or not the substituted halogens of these compounds and others with which the author has experienced some difficulty could be completely converted to sodium halide when subjected to the sodium peroxide-sugar explosion. It has been the author's experience that certain variations introduced into the procedure for determination of organic halogens by the explosion method produce inconsistent and low results; however, the experience gained in this laboratory through many hundreds of analyses on organic halogens prompts the statement that this method is destined to be considered as generally applicable as the Dumas method for nitrogen. Contrasted with distillation methods and the Carius method it is extremely rapid and simple of operation, besides being as accurate as any reported macromethod for organic halogen determinations.

PROCEDURE

The sample used should be such that the silver halide will weigh not more than 275 mg., as much larger samples are not completely oxidized. Add 12 grams or 1 scoop of sodium peroxide and 200 mg. of lactose, shake the whole thoroughly for about 45 seconds, and place in the hottest part of the Bunsen flame for about 45 seconds. This should be done behind a protective screen. Drop the bomb into cold water and wash with distilled water. Dissolve the fusion and remove the cup in the usual manner. Add 50 cc. of 1 to 1 nitric acid slowly, and remove the gas by stirring or, if desired, boiling in the case of chlorides. Filter through a fine grade of filter paper and wash completely. Add very slowly while stirring excess 0.1 N silver nitrate. Stir to coagulate and filter through a Gooch crucible. Wash the silver halide with 300 cc. of water, dry at 140° C. for 1 hour, cool on copper block for about 20 to 25 minutes, and weigh.

Potassium nitrate has been reported by Elek and Hill (4), Lemp and Broderson (6), and others as a necessary constituent of the explosion mixture and has been used to some

extent in this laboratory. However, all results reported in this article and many others have been obtained without potassium nitrate, and it may be concluded that potassium nitrate is not a necessary constituent of the explosion mixture.

Table I is included to indicate the range of applicability and accuracy of the method.

TABLE I. TYPICAL RESULTS OBTAINED IN SOME COMPOUNDS ANALYZED^a

SUBSTANCE	HALOGEN	
	Calculated %	Obtained %
<i>m</i> -Chloronitrobenzene	22.50	22.45
2,5-Dichloronitrobenzene	36.88	36.96
1,2,4-Dichloroaniline	43.78	43.75
Hexachlorobenzene	74.71	74.56
<i>m</i> -Nitrobenzalchloride	34.43	34.43
<i>m</i> -Bromobenzoic acid	39.77	39.64
<i>p</i> -Chloroacetanilide	20.92	20.94
9,10-Dibromoanthracene	47.58	47.53
Chloroacetophenone	22.95	22.96
6-Chlorocoumarin	19.64	19.58
5,7-Dibromo-8-hydroxyquinoline	52.77	52.72
Trichlorobutyric acid	55.57	55.46
Propylene bromide	79.17	79.20
Iodopropionic acid	63.47	63.46
Chloroacetamide	37.92	37.96
Triphenylchloromethane	12.73	12.79
		12.75

^a Compounds were purified where necessary.

DISCUSSION

DETERMINATION OF HALOGENATED DIPHENYLS. A sample of the *o*- and *p*-chlorodiphenyl taken from the original stock was obtained from Jenkins, McCullough, and Booth (5). The results obtained on halogenated diphenyls and a substituted diphenylbenzene, together with those obtained by Huntress and reported by Jenkins, McCullough, and Booth (5), appear in Table II, and indicate that by means of the procedure here employed consistent and accurate results can be obtained on halogenated diphenyls. The sample of the substituted diphenylbenzene was provided by Roger Adams, University of Illinois.

TABLE II. RESULTS OBTAINED ON HALOGENATED DIPHENYLS

SUBSTANCE	HALOGEN CALCULATED	HUNTRESS' ^a RESULTS	HALOGEN FOUND
	%	%	%
<i>o</i> -Chlorodiphenyl	18.81	18.81	18.78
		18.79	18.76
			18.75
			18.74
<i>p</i> -Chlorodiphenyl	18.81	18.79	18.86
		18.90	18.85
		18.86	18.74
			18.80
			18.75
<i>p</i> -Bromodiphenyl	34.30	...	34.34
			34.37
4,4-Dibromodiphenyl sulfone	42.63	...	42.65
			42.69
C ₁₈ H ₂ Br ₄ (CH ₃) ₂ (OH) ₂ (a brominated diphenylbenzene)	48.30	...	48.18
			48.21

^a Carius method used.

EFFECT OF OVERHEATING BOMB CUP. In the procedure outlined by Lemp and Broderson (6) ignition is effected in the hottest part of the Bunsen flame, the heating being continued until the cup is red for at least one-fourth of its length. With certain organic bromine compounds when the stainless steel cup is used low results are obtained by so heating unless a suitable reducing reagent is employed. This was not observed when the nickel cup described by the author (2) was used, even though heating was continued until the gasket melted and flowed down the walls of the bomb.

The comparative results obtained using nickel and steel cups are illustrated in Table III. The explosion usually takes place about 20 to 35 seconds after the flame is applied to the bomb, so that further heating is unnecessary and rapidly depletes the life of the cup.

TABLE III. EFFECT OF OVERHEATING NICKEL AND STEEL CUPS

SUBSTANCE	TIME OF HEATING Min.	HALOGEN			
		Calculated %	Steel cup %	Nickel cup %	
Bromocamphor	0.5-0.75	34.59	34.50	34.58	
			...	34.48	34.55
	2	34.41	34.57
				34.41	...
				33.50	34.58
				31.30	34.45
3	32.33	34.52	
			...	34.52	
Bromodiphenyl ^a	0.5-0.75	34.30	34.81	34.89	
			...	33.91	34.84
		
Dibromobenzene	2	67.76	67.56	67.81	
2,4-Dinitrochlorobenzene	0.5-0.75	17.51	...	17.51	
			...	17.53	...

^a This sample of bromodiphenyl was not purified.

Overheating either steel or nickel cups containing the chlorinated organic compounds did not appear to affect the result. When heating was continued for only 35 to 45 seconds, using either the nickel or steel cups, reducing reagents were in no case found necessary with either bromine or chlorine compounds.

EFFECT OF DELAYED EXPLOSION. In most cases the effect of delay in exploding becomes important only after an interval of some hours and seems to affect only volatile compounds. With two compounds low results were obtained after a delay of 15 to 20 minutes. The amount of loss is illustrated in Table IV and, in some cases at least, does not appear to be due to leakage during the interval of rest.

DETERMINATION OF BLANKS. A great deal of the difficulty experienced in obtaining consistently accurate results may be traced to incorrect blanks. The crucible must be carefully prepared. A suitable method is to macerate a thin layer of asbestos with a fine stream of water, continuing until the filtered water shows no trace of suspended asbestos. The asbestos is then tapped down with the stirring rod. A fine grade of filter paper similar to Whatman's No. 32 must

be used for the first filtration. Too rapid filtering requires much wash water to eliminate the last traces of sodium halide. No appreciable opalescence should appear in the wash water after filtering through the Gooch crucible. Coagulation is aided somewhat by addition of alcohol to the silver nitrate solution. Stirring the solution is sufficient to coagulate the silver halide and boiling is not necessary.

TABLE IV. EFFECT OF TIME INTERVAL BETWEEN SHAKING MIXTURE AND EXPLOSION

SUBSTANCE	Immediate explosion %	HALOGEN		Calculated %
		After 15 to 20 minutes %	Over 15 hours %	
<i>p</i> -Dichlorobenzene	48.20	47.69	47.77	48.25
			47.45	
			47.71	
<i>m</i> -Dichlorobenzene	48.29	47.92	46.78	48.25
		48.39	48.04	
Bromobenzene	50.91	50.94	49.64	50.91
		50.89	50.94	
Chlorotoluene	28.16	28.02	27.55	28.02
		28.00	28.11	
Chloroform	89.00	88.67	69.55	89.11
		89.13	89.21	
Dibromobenzene	67.66	...	67.64	67.76
		67.76	...	

DETERMINATION OF HALOGEN IN COMPOUNDS WHICH SUBLIME. The author has experienced some difficulty with compounds which sublime. For instance, with dibromoanthracene it was observed that the yellow compound remained on the cover of the cup and the results were often inconsistent and low. This was overcome by covering with a layer of sodium peroxide about 1 cm. deep after mixing the explosion mixture. The results obtained are given in Table I.

INFLUENCE OF MELTING POINT. An intimate mixture of compound and explosion mixture apparently becomes essential only in the case of those substances with high melting points. Organic halogenated compounds with low melting points—i. e., up to about 90° C.—do not require a fine state of division. Liquids were weighed out in a glass bulb or tube. A thin glass rod sealed to the neck serves as a handle in filling, and should be broken off before placing the tube in the bomb cup. It is essential that the wall of the bulb be extremely thin.

SUMMARY

The determination of substituted halogens in diphenyl and diphenylbenzene compounds by means of the sodium peroxide-sugar explosion has been accomplished.

Continued heating of the steel cup after the explosion produces low halogen results with some bromine compounds, while overheating the nickel cup does not affect results.

Addition of supplementary oxidizing substances to the sodium peroxide-sugar explosion mixture is not necessary.

The results obtained on chloroform indicate that the method is adapted to volatile liquids, although results may be low if the explosion is delayed.

ACKNOWLEDGMENT

The author is indebted to J. Russell for checking results of analysis.

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Determination of Total Reducing Sugars, Dextrose, and Levulose in Raw Cane Sugars

F. W. ZERBAN AND M. H. WILEY, New York Sugar Trade Laboratory, New York, N. Y.

IN A PAPER published some time ago (?) the importance of determining dextrose and levulose in cane products was pointed out, and various ways in which this might be accomplished were discussed. It was concluded that Nijns's method (6) of estimating levulose by selective copper reduction promised to be useful for the purpose. It was also found that contrary to Nijns's statement, dextrose has a distinct reducing effect on the copper carbonate reagent, and that large quantities of sucrose reduce it measurably, especially in the presence of reducing sugars. Jackson (3) also found this to be true for a copper carbonate solution similar to Nijns's, but containing 25.3 instead of 15 grams of copper sulfate per liter. The method has been further studied by Jackson and Mathews (4), and their modification has been adopted by the Association of Official Agricultural Chemists (1). Because of the reducing effect of dextrose on the copper carbonate reagent, the determination of levulose in mixtures with other sugars requires a determination of total reducing sugars also. The tables given by Jackson and Mathews for this purpose are not directly applicable to the analysis of raw sugars.

Since raw sugars contain large quantities of sucrose with small quantities of dextrose and levulose, a correction for the reducing effect of the sucrose must be applied to the result of the copper carbonate reduction as well as to that of the total reducing sugar determination. While the first of these corrections is known from the work of Jackson and Mathews, the usual tables for reducing sugars in the presence of large

quantities of sucrose consider only invert sugar, but not dextrose and levulose in varying proportions. It was therefore necessary to establish such a table. Following the example of Jackson and Mathews, the Lane and Eynon volumetric method (5) was chosen because it is more practical for routine work than the gravimetric procedures and is rapidly gaining ground in the cane-sugar industry. The Lane and Eynon tables have been extended so as to include columns of factors for levulose and for dextrose in varying proportions, in the presence of large quantities of sucrose, and for 10 ml. of Soxhlet solution.

The procedure prescribed by Lane and Eynon was followed in every detail, several series of analyses being run with solutions containing 10 and 25 grams, respectively, of sucrose in 100 ml., plus dextrose alone, levulose alone, and invert sugar, ranging in quantity from 90 to 300 mg. of each. The solutions were titrated against 10 ml. of Soxhlet solution. The results were plotted, interpolated, and the final values are shown in Table I.

The factors for invert sugar are generally a little higher than those given by Lane and Eynon. This is no doubt due to small differences in manipulation, and each analyst should check these values under his own individual conditions, or construct his own tables of factors.

A few check analyses are given in Table II.

In confirmation of a statement made by Lane and Eynon, that in the presence of a large excess of sucrose small variations in the details of the procedure have a much greater

TABLE I. LANE AND EYNON FACTORS FOR MIXTURES OF LEVULOSE AND DEXTROSE

(10 ml. of Soxhlet solution)

TITER	A. IN PRESENCE OF 10 GRAMS OF SUCROSE IN 100 ML										TITER	B. IN PRESENCE OF 25 GRAMS OF SUCROSE IN 100 ML											
	100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L		0 D 100 L	100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L	0 D 100 L
15	46.1	46.3	46.5	46.6	46.8	47.0	47.2	47.4	47.7	47.9	48.1	15	42.9	43.1	43.2	43.4	43.6	43.7	43.9	44.1	44.3	44.5	44.7
16	46.0	46.2	46.4	46.5	46.7	46.9	47.1	47.3	47.6	47.8	48.0	16	42.9	43.0	43.2	43.3	43.5	43.6	43.8	44.0	44.2	44.4	44.6
17	46.0	46.2	46.4	46.5	46.7	46.9	47.1	47.3	47.5	47.7	47.9	17	42.8	42.9	43.1	43.2	43.4	43.5	43.7	43.9	44.0	44.2	44.4
18	45.9	46.1	46.3	46.4	46.6	46.8	47.0	47.2	47.5	47.7	47.9	18	42.7	42.8	43.0	43.1	43.3	43.4	43.6	43.8	43.9	44.1	44.3
19	45.9	46.1	46.3	46.4	46.6	46.8	47.0	47.2	47.4	47.6	47.8	19	42.7	42.8	42.9	43.1	43.2	43.3	43.5	43.6	43.8	43.9	44.1
20	45.8	46.0	46.2	46.3	46.5	46.7	46.9	47.1	47.3	47.5	47.7	20	42.6	42.7	42.9	43.0	43.1	43.2	43.4	43.5	43.7	43.8	44.0
21	45.7	45.9	46.1	46.2	46.4	46.6	46.8	47.0	47.2	47.4	47.6	21	42.5	42.6	42.8	42.9	43.0	43.1	43.3	43.5	43.6	43.7	43.9
22	45.7	45.9	46.0	46.1	46.3	46.5	46.7	46.9	47.1	47.3	47.5	22	42.5	42.6	42.8	42.9	43.0	43.1	43.2	43.4	43.5	43.7	43.8
23	45.6	45.8	46.0	46.1	46.3	46.5	46.7	46.9	47.1	47.3	47.5	23	42.4	42.5	42.7	42.8	42.9	43.0	43.1	43.3	43.4	43.6	43.7
24	45.6	45.8	45.9	46.0	46.2	46.4	46.6	46.8	47.0	47.2	47.4	24	42.4	42.5	42.6	42.7	42.8	42.9	43.0	43.2	43.3	43.5	43.6
25	45.5	45.7	45.8	45.9	46.1	46.3	46.5	46.7	46.9	47.1	47.3	25	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.1	43.2	43.4	43.5
26	45.4	45.6	45.7	45.9	46.0	46.2	46.4	46.6	46.8	47.0	47.2	26	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.0	43.2	43.3
27	45.4	45.6	45.7	45.8	46.0	46.2	46.4	46.6	46.7	46.9	47.1	27	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.1	43.2	43.3
28	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.5	46.7	46.9	47.1	28	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	43.0	43.1	43.2
29	45.3	45.5	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8	47.0	29	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.0	43.1
30	45.2	45.4	45.5	45.7	45.8	46.0	46.2	46.4	46.5	46.7	46.9	30	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9	43.0
31	45.2	45.4	45.5	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8	31	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9
32	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.3	46.4	46.6	46.8	32	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8	42.9
33	45.1	45.3	45.4	45.5	45.6	45.8	46.0	46.2	46.3	46.5	46.7	33	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7	42.8
34	45.0	45.2	45.3	45.5	45.6	45.8	46.0	46.2	46.3	46.5	46.7	34	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6	42.7
35	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.2	46.4	46.6	35	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6
36	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.1	46.2	46.4	46.6	36	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5	42.6
37	45.0	45.1	45.3	45.4	45.6	45.7	45.9	46.0	46.2	46.4	46.5	37	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5
38	44.9	45.0	45.2	45.3	45.5	45.6	45.8	46.0	46.1	46.3	46.5	38	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4	42.5
39	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4	39	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3	42.4
40	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4	40	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2	42.3
41	44.9	45.0	45.2	45.3	45.5	45.6	45.8	45.9	46.1	46.3	46.4	41	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1	42.2
42	44.9	45.0	45.2	45.3	45.5	45.6	45.7	45.9	46.0	46.2	46.3	42	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1
43	44.8	44.9	45.1	45.2	45.4	45.5	45.7	45.8	46.0	46.2	46.3	43	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0	42.1
44	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2	44	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9	42.0
45	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2	45	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8	41.9
46	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2	46	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7	41.8
47	44.8	44.9	45.1	45.2	45.4	45.5	45.6	45.8	45.9	46.1	46.2	47	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7
48	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1	48	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6	41.7
49	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1	49	40.6	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5	41.6
50	44.7	44.8	45.0	45.1	45.3	45.4	45.5	45.7	45.8	46.0	46.1	50	40.5	40.6	40.7	40.8	40.9	41.0	41.1	41.2	41.3	41.4	41.5

effect than in the absence of sucrose, it is found that the precision is not quite as high as when reducing sugars alone are present, but it is nevertheless satisfactory for routine analyses of raw sugars.

TABLE II. DETERMINATIONS OF TOTAL REDUCING SUGARS BY LANE AND EYNON'S METHOD

10 GRAMS OF SUCROSE IN 100 ML. OF SOLUTION								
Dextrose taken, mg.	120.0	108.2	70.5	125.0	43.5	43.6	72.7	64.1
Levulose taken, mg.	137.9	65.7	150.5	125.0	138.0	82.0	36.0	186.9
Total	257.9	173.9	221.0	250.0	181.5	125.6	108.7	251.0
Titer found, ml.	18.15	26.6	21.4	18.6	25.9	36.9	42.5	18.8
Total found, mg.	258.4	172.9	219.6	251.6	180.3	124.7	106.8	251.6
25 GRAMS OF SUCROSE IN 100 ML. OF SOLUTION								
Dextrose taken, mg.	237.9	156.0	85.5	156.5	123.0	41.5	56.5	50.0
Levulose taken, mg.	37.5	132.5	106.3	56.0	53.7	86.5	47.8	98.5
Total	275.4	288.5	191.8	212.5	176.7	128.0	104.3	148.5
Titer found, ml.	15.6	15.2	22.35	20.3	24.0	33.05	40.25	28.7
Total found, mg.	276.3	287.2	192.8	211.8	178.3	128.6	103.6	149.1

The use of Jackson and Mathews' modification of Nijns's method for the determination of levulose was next investigated from the standpoint of raw sugar analysis. An electrically heated water bath, with automatic thermostat control within 0.1° C., was employed for the purpose, and the directions of Jackson and Mathews were followed, except that 250-ml. flasks had to be used instead of the 150-ml. size which is no longer on the market. The reduced copper was determined gravimetrically, as in the previous investigation. A number of analyses were made with different quantities of levulose, and the bath temperature was so regulated that after 75 minutes' heating the results checked with those given in Jackson and Mathews' table. This was found to be the case when the water surrounding the immersed portion of the flasks indicated 55.2° C.

TABLE III. ANALYSES OF SUGAR MIXTURES BY A COMBINATION OF METHODS

	Su- crose G./20 ml.	TAKEN		FOUND					
		Levu- lose ^a	Dex- trose ^a	Copper Mg.	Copper cor- rected for sucrose Mg.	Lane & Eynon titer	Levu- lose %	Dex- trose %	
1	5	0.50	0.00	85.9	76.9	34.0	0.49	0.01	
2	5	0.375	0.125	67.7	58.7	33.8	0.38	0.13	
3	5	0.25	0.25	47.5	38.5	33.6	0.26	0.25	
4	5	0.125	0.375	27.8	18.8	33.5	0.12	0.38	
5a	5	0.00	0.50	8.4	-0.6	33.5	-0.05	0.55	
5b	5	0.00	0.50	8.4	3.8	33.5	0.00	0.50	
6	4	1.00	0.00	142.8	134.3	46.0	1.01	-0.01	
7	4	0.75	0.25	108.5	100.0	45.8	0.75	0.25	
8	4	0.50	0.50	73.2	64.7	45.4	0.49	0.52	
9	4	0.25	0.75	42.1	33.6	44.5	0.24	0.77	
10a	4	0.00	1.00	11.3	2.8	44.2	-0.05	1.06	
10b	4	0.00	1.00	11.3	6.7	44.2	0.00	1.01	
11	5	1.50	0.00	266.9	257.9	31.5	1.50	-0.02	
12	5	1.125	0.375	207.0	198.0	30.5	1.11	0.41	
13	5	0.75	0.75	142.9	133.9	30.6	0.75	0.75	
14	5	0.375	1.125	84.2	75.2	30.6	0.39	1.10	
15a	5	0.00	1.50	21.8	12.8	30.0	-0.07	1.58	
15b	5	0.00	1.50	21.8	17.2	30.0	0.02	1.49	

^a Per cent of sucrose.

Mixtures of levulose and dextrose in varying proportions, with 4 and 5 grams, respectively, of sucrose in 20 ml. total volume were analyzed next, and the corrections established by Jackson and Mathews for the effect of dextrose and sucrose were confirmed. One milligram of levulose has the same reducing power as 12.4 mg. of dextrose; 4 grams of sucrose reduce 8.5 mg. of copper, and 5 grams of sucrose 9.0 mg. of copper. When no levulose is present, however, the reducing effect of sucrose is much smaller. Jackson and Mathews found that 5 grams of sucrose alone give only 2.4 mg. of copper; the writers found 4.6 mg. copper reduced by 5 grams of sucrose plus 25 mg. of dextrose, or 4 grams of su-

crose plus 40 mg. of dextrose. This is of little importance in the analysis of raw sugars, because these always contain a certain proportion of levulose.

To test the combination of the Lane and Eynon and the Jackson and Mathews methods, mixtures of sucrose with 0.5, 1.0, and 1.5 per cent of total reducing sugars were prepared and analyzed as outlined above. In the case of the mixtures containing 1.5 per cent of total reducing sugars the Lane and Eynon titration was carried out after diluting 100 ml. of the original solution to 250 ml., and figuring back to the original concentration. The results, calculated as described by Jackson and Mathews, are shown in Table III.

For an indirect method, the results are satisfactory. When dextrose alone is present in addition to sucrose (Nos. 5, 10, and 15), the correction of 8.5 and 9 mg. of copper for the sucrose effect (a) is too high. A correction of 4.6 mg. in Nos. 5b and 10b gave zero levulose, in 15b 0.02 per cent of levulose; for 5 grams of sucrose and 1.5 per cent of dextrose (No. 15), the proper correction is 7.3 mg. of copper.

PROCEDURE

A number of raw cane sugars were next analyzed by the following procedure:

A solution of the raw sugar, containing 25 grams of sucrose in each 100 ml. is prepared (the direct polarization may be taken to equal the sucrose in most cases without serious error). A total of 250 ml. of solution is usually sufficient. The solution is clarified with neutral lead acetate solution before being made up to the mark. It is filtered, deaired with dry potassium oxalate, and refiltered. Two 20-ml. portions of the final solution are used to determine in duplicate the reducing effect on the copper carbonate solution, according to Jackson and Mathews. The copper in the precipitate is determined volumetrically by Mohr's ferric sulfate and permanganate method, since weighing usually gives too high results because of contamination; electrolytic reduction, or the chromic acid-ferrous sulfate method of Jackson and Mathews may also be used. The remainder of the filtrate is used for the Lane and Eynon titrations, and the factor is found from Table IB. If the titer is less than 15 ml., 100 ml. of the clarified solution are diluted to 250 ml., the new solution now containing 10 grams of sucrose in 100 ml., and the factor is found from Table IA. If, on the other hand, the titer of the original clarified solution is over 50 ml., a new solution of the raw sugar is prepared and a known quantity of levulose or invert sugar is added, as suggested for such cases by Eynon and Lane (2). The added reducing sugar is later corrected for.

CALCULATIONS

The method of calculation is shown in the following example:

Sucrose, per cent in raw sugar	96.75
Grams of raw sugar containing 100 grams of sucrose	103.36

A sample of 64.60 grams of raw sugar ($103.36 \times \frac{5}{8}$) was dissolved in a 250-ml. flask, and clarified as described above. The Lane and Eynon titer was found to be 18.13 ml. Since the ratio between levulose and dextrose is not known as yet, the first calculation is based on the factor for invert sugar in Table IB, which is 43.4. This gives $100 \times 43.4/18.13$ or 239.4 mg. of total reducing sugars, as invert, in 100 ml. of solution.

With the Jackson and Mathews method 76.9 mg. of reduced copper were found. Corrected for the reducing effect of the sucrose, this gives $76.9 - 9.0$ or 67.9 mg. of copper. According to Jackson and Mathews' table, this corresponds to 22.0 mg. of apparent levulose in 20 ml. of solution, or 110.0 mg. in 100 ml. of solution.

	Mg.
Total reducing sugars as invert	239.4
Apparent levulose, first approximation	110.0
Apparent dextrose, first approximation, 239.4 - 110.0	129.4
Equivalent levulose, 129.4:12.4	10.4
Apparent levulose, second approximation, 110.0 - 10.4	99.6
Apparent dextrose, second approximation, 239.4 - 99.6	139.8
Equivalent levulose, 139.8:12.4	11.3
Apparent levulose, third approximation, 110.0 - 11.3	98.7
Apparent dextrose, third approximation, 239.4 - 98.7	140.7

TABLE IV. DETERMINATIONS OF LEVULOSE AND DEXTROSE IN RAW CANE SUGARS

No.	ORIGIN	TOTAL REDUCING SUGARS		
		DEXTROSE %	LEVULOSE %	%
1	Cuba	0.542	0.382	0.924
2	Philippines	0.671	0.557	1.228
3	Hawaii	0.176	0.261	0.437
4	Puerto Rico	0.559	0.531	1.090
5	Florida	0.426	0.402	0.828
6	Santo Domingo	0.342	0.446	0.788

The levulose equivalent of the dextrose, 140.7:12.4, is again 11.3 mg., so that the figures for levulose and dextrose, third approximation, are not changed further.

The ratio between levulose and dextrose is thus found to be 98.7:140.7, or as 41:59. For this ratio Table IB gives a Lane and Eynon factor of 43.3 instead of 43.4, and the total reducing sugars are therefore not 239.4, but 238.8 mg. In this particular case a second calculation, on the basis of 238.8 mg. of total reducing sugars, is hardly necessary, because the difference is within the limits of error. If it is made, the second calculation gives 98.7 mg. of levulose and 140.1 mg. of dextrose in 100 ml. of

solution or in 25.84 grams of raw sugar. The final result is therefore 0.382 per cent of levulose, 0.542 per cent of dextrose, 0.924 per cent of total reducing sugars.

The results of the analyses of this and other raw sugars are compiled in Table IV.

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RECEIVED April 10, 1934. Presented before the Division of Sugar Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934.

Extraction of Gossypol from Cottonseed Meal

Effect of Moisture and Repeated Extraction with Ether by Different Procedures

J. O. HALVERSON AND F. H. SMITH, Agricultural Experiment Station, Raleigh, N. C.

IN A PREVIOUS paper (2) data were presented showing that moisture both in the cottonseed meal and in the ether exerted a marked influence on the amount of gossypol which could be extracted. These data suggested that there is no definite limit between the ether-soluble and bound gossypol. More data are presented here to substantiate those results and to show further what occurs when cottonseed meal is repeatedly moistened and extracted with ether, and with ether saturated with water.

Initial charges of 75 grams of cottonseed meal were moistened or conditioned (2) by passing a vapor of condensing steam over thin layers of meal for 5 hours, or, more conveniently, the proper amount of water was mixed in with a mortar and pestle. The conditioned meal was extracted for 72 hours and the gossypol estimated by a recently published modified method (1).

ETHER-SOLUBLE GOSSYPOL FROM MOISTENED COTTONSEED MEAL

The U. S. P. grades of ether (not for anesthesia) obtained from the General Chemical Company and J. T. Baker Chemical Company (designated in the text as G and B ethers, respectively) have consistently yielded discordant amounts of gossypol. Consequently, experiments were undertaken to determine the quantity of gossypol which could be extracted from the same cottonseed meal by the following procedure:

Group a, determinations 1 to 3 with G ether alone
 Group b, determinations 4 to 6, with B ether alone
 Group c, determinations 7 and 8, with B ether, 10 cc. of alcohol (95 per cent), and 5 cc. of water
 Group d, determinations 9 and 10, with B ether and 5 cc. of water

Preliminary work showed that meal conditioned by increasing its moisture content yielded more ether-soluble gossypol upon successive moistening of the charge of meal and

subsequent extraction. It was therefore decided to determine how much ether-soluble gossypol could be extracted from meal 1578, which had previously shown a total (bound and ether-soluble) gossypol content of 1.102 ± 0.006 per cent (3). The repeated conditioning and extraction of the charge was continued as long as appreciable amounts of gossypol could be obtained.

TABLE I. GOSSYPOL RECOVERED FROM MOISTENED COTTONSEED MEAL BY SUCCESSIVE EXTRACTIONS WITH ETHER BY DIFFERENT PROCEDURES

EXTRACTION PERIODS	(Average mg. of gossypol per 100 grams of meal)							
	GROUP a		GROUP b		GROUP c		GROUP d	
	Mois- ture %	Gossy- pol Mg.	Mois- ture %	Gossy- pol Mg.	Mois- ture %	Gossy- pol Mg.	Mois- ture %	Gossy- pol Mg.
AVERAGE GOSSYPOL AND MOISTURE PER DETERMINATION								
1 to 6	20.2	16.0	19.4	24.7	19.5	38.0	20.3	37.7
7 to 14	24.0	7.1	25.8	5.7	27.4	3.5	30.1	4.8
15 to 17	26.2	1.0	24.5	2.1	24.4	1.8	24.6	0.9
AVERAGE TOTAL GOSSYPOL PER DETERMINATION								
1 to 6		96.1		148.2		228.2		226.0
7 to 14		56.5		45.2		28.3		38.3
15 to 17		3.0		6.3		5.3		2.7
Per cent		0.1556		0.1997		0.2618		0.2670

In the first six successive periods of extraction an average of 16.0 mg. of gossypol per determination was obtained by the G ether in group a, compared to 24.7 mg. by the B ether in group b (Figure 1 and Table I). The moisture content of the charges in these groups does not vary greatly and is adequate for the extraction.

Groups c and d yielded an average of 38.0 and 37.7 mg. of gossypol per determination, respectively, considerably more than groups a and b. This large difference is apparently due to the addition of water to the ether in the receiving flask, since the moisture content of the charges in the various groups is approximately the same. The discrepancy in the yield of gossypol for groups a and b compared

to *c* and *d* is distinctly shown by the total amount of gossypol obtained per determination during extraction periods 1 to 6 (Table I).

Neither brand of ether without the addition of water or alcohol yielded as much gossypol in groups *a* and *b* in periods 1 to 6 as in groups *c* and *d* where water and alcohol were used with the solvent. Therefore, beginning with the seventh period of extraction, with groups *a* and *b* 10 cc. of alcohol (95 per cent) and 5 cc. of distilled water were added to the ether in the receiving flask of each determination. This procedure is similar to that employed from the first extraction period on in group *c*.

The average amount of gossypol obtained in extraction periods 7 to 14 was small even with this change in procedure for groups *a* and *b*, and in comparison with periods 1 to 6 was considerably less for all groups. The average moisture in the charge was adequate and quite uniform except in group *d*, where it increased, especially in extraction periods 11 to 13, but an appreciably higher yield of gossypol did not accompany this increase in moisture. The yield of gossypol in group *a* with the changed procedure in extraction is somewhat increased over that of the other groups for the tenth, twelfth, and thirteenth periods, probably because of the smaller amount of gossypol obtained in the first six periods of extraction.

The average amount of gossypol obtained per determination in extraction periods 7 to 14 for groups *a* to *d* does not vary much, but in groups *a* and *b* they are somewhat higher. The total amount of gossypol was less for groups *c* and *d*, although the moisture in the charge was somewhat higher for these groups than for groups *a* and *b*. With adequate moisture in the charge there is no correlation of yield of gossypol to moisture content.

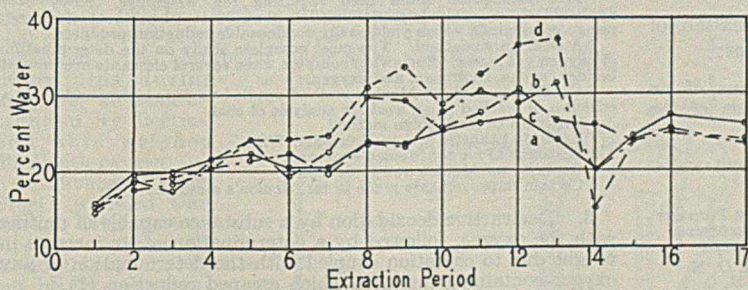


FIGURE 2. AVERAGE MOISTURE IN CHARGE OF COTTONSEED MEAL EXTRACTED

Later, further extractions of the cottonseed meal residues were made, consisting of the fifteenth to seventeenth periods, with the result that for all four groups small weighable amounts of gossypol were obtained. The average gossypol obtained and the average moisture content of the charges are fairly uniform throughout for the groups (Figures 1 and 2).

The total gossypol recovered from the meal by the four procedures is 0.1556, 0.1997, 0.2618, and 0.2670 per cent, respectively. The amounts are appreciably higher in groups *c* and *d*, where water was always present in the flask containing the ether. The alcohol added to the solvent in group *c* did not show any beneficial effect in the presence of sufficient moisture in the charge. The presence of water in the receiving flask with the solvent causes the yield of gossypol to be

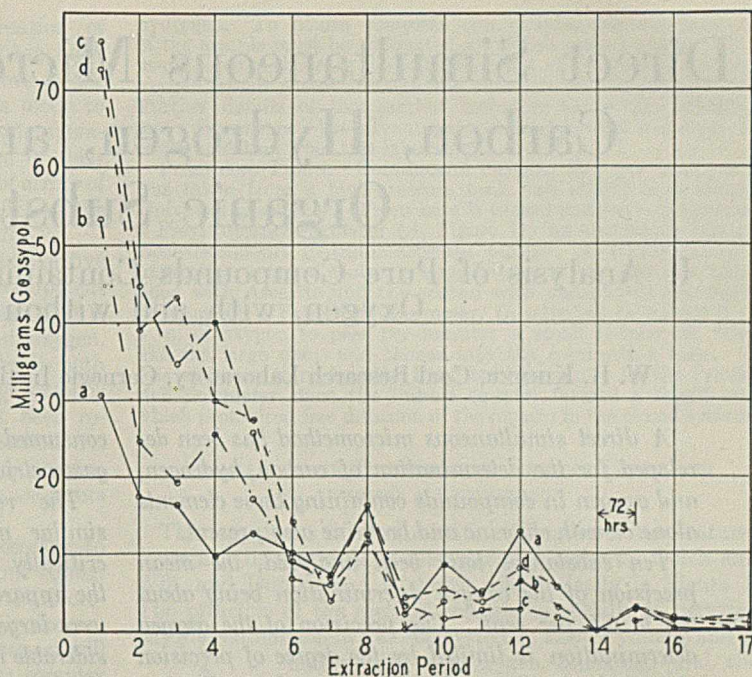


FIGURE 1. AVERAGE GOSSYPOL YIELDED BY GROUPS *a* TO *d* BY FOUR PROCEDURES OF EXTRACTION

larger but probably does not fully account for the difference in the behavior of the two brands of ether.

Of the total gossypol (1.102) in this meal, 24.2 per cent was gradually extracted by the ether in group *d* where water was always in contact with the solvent in the receiving flask.

SUMMARY

Experiments show that by repeatedly extracting the moistened meal or residue with wet ether, considerably more gossypol can be obtained than by extraction of the air-dry meal or by a single extraction of the moistened meal.

By this procedure 24.2 per cent of the total gossypol in a sample of cottonseed meal has been gradually extracted. The amount of gossypol obtained by prolonged extraction shows that there is no definite limit between ether-soluble and bound gossypol. The gossypol formerly considered to be bound can be partially extracted as ether-soluble when there is sufficient moisture both in the meal and in the ether.

The amount of gossypol that can be extracted from an air-dry cottonseed meal (as has been done in the past) varies, depending chiefly upon the moisture content. Because the moisture content also changes at times, such results give no

indication of the definite amount of gossypol present.

Probably the most reliable and practical indication of the amount of ether-soluble gossypol in cottonseed meal is obtained when the meal containing about 20 per cent of water is extracted for 72 hours with ether to which water has been added in the receiving flask. However, further extraction under these conditions will probably yield more gossypol.

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Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen in Organic Substances

I. Analysis of Pure Compounds Containing Carbon, Hydrogen, and Oxygen, with and without Halogens

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

A direct simultaneous micromethod has been developed for the determination of carbon, hydrogen, and oxygen in compounds containing these elements alone or with chlorine and bromine also present.

Ten substances have been analyzed, the mean precision of the oxygen determination being about 0.3 to 0.4 per cent. The precision of the oxygen determination is limited by the degree of precision obtainable in the carbon-hydrogen determination, any errors in the determination of the latter being multiplied by rather large factors. The oxygen

consumed during the combustion is determined gasometrically with considerable precision.

The results of previous investigators using similar macro- or semi-micromethods have been critically analyzed and the discovery made that the apparently satisfactory results obtained by them were largely due to compensation of errors of considerable magnitude.

The investigation is being continued on more complex compounds and will finally be extended to the analysis of coal and its products.

THE lack of a satisfactory method for the direct determination of oxygen in organic substances and the potential value of such a method as a control on all of the other determinations made on a substance are generally recognized. Oxygen continues, however, to be almost universally calculated "by difference," despite the fact that this calculation involves, especially in complex substances, the summation of errors made in the determination of the individual components.

The published methods for the direct determination of oxygen may be grouped into the following five classes:

1. Complete oxidation of the substance by means of an inorganic oxidizing agent, followed by a determination of the amount of oxidant consumed (Table I).

TABLE I. DETERMINATION OF OXYGEN USING INORGANIC OXIDIZING AGENTS

AUTHOR	INORGANIC OXIDIZING AGENT	ELEMENTS PRESENT IN COMPOUNDS STUDIED
Gay-Lussac and Thenard (15)	KClO ₃	C, H, O, N
von Baumhauer (1)	CuO	C, H, O
Stromeyer ^a (27)	CuO-Na ₂ CO ₃	C, H, O, N, S, Cl
Maumene ^b (16)	PbO-Ca ₃ (PO ₄) ₂	C, H, O, N, S, P, and halogens
Ladenburg (15)	AgIO ₃ -H ₂ SO ₄	C, H, O, N
von Baumhauer (2)	CuO-AgIO ₃	C, H, O, N, S, P, and halogens
Mitcherlich ^c (19)	HgO	C, H, O, N, S, P, and halogens
Phelps ^d (21)	Chromic acid-H ₂ SO ₄	C, H, O, N
Boswell (5)	CuO-asbestos	C, H, O
Strebinger ^e (28)	KIO ₃ -H ₂ SO ₄	C, H, O, S, N, and halogens
Staněk and Nemes ^f (24)	KIO ₃ -H ₂ SO ₄	C, H, O, S, N
Staněk and Nemes ^g (25)	KIO ₃ -H ₂ SO ₄	C, H, O, S, N, and halogens

^a Determined only oxygen consumed. Not applicable to nitro compounds or nitrates. Results always low.

^b No data given.

^c Technic very complex and tedious.

^d Nitrogen compound studied gave the poorest result.

^e Not applicable to nitrogen compounds which yield poor results on kjeldahlization—i. e., nitro-, azo-, and heterocyclic compounds, hydrazones, osazones, etc.

^f A micromethod. Has same limitations as cited in subscript ^e plus halogens. Oxygen calculated by difference. Oxygen consumed determined directly. Hydrogen calculated by means of involved equations.

^g Same as subscript ^f except difficulty due to halogens removed.

2. Destructive catalytic hydrogenation of the substance, followed by a determination of all resulting oxygen-containing substances (Table II).

TABLE II. DETERMINATION OF OXYGEN BY HYDROGENATION

AUTHOR	ELEMENTS PRESENT IN COMPOUNDS STUDIED
Wanklyn and Frank ^a (23)	C, H, O
Boswell ^b (6)	C, H, O
ter Meulen ^c (18)	C, H, O, N, S, and halogens
Schuster ^d (23)	C, H, O, and coal
Dolch and Will ^e (3)	C, H, O
ter Meulen ^f (17)	C, H, O, and coal
van Beek and de Ward ^g (5)	C, H, O, N, S, and fuels
Willa ^h (29)	C, H, O
Russell and Fulton ⁱ (22)	C, H, O

^a No data given.

^b Five absorption tubes used requiring ten weighings. Slow. Not applicable to compounds containing less than 30 to 40 per cent of oxygen nor to compounds which yield easily condensable reduction products.

^c A semi-micromethod. The most complete study on the determination of oxygen yet made. Somewhat complex when several elements are present besides carbon, hydrogen, and oxygen.

^d Confirmation of ter Meulen method applied to pure compounds, but a criticism of method when used for analysis of coal.

^e Criticism of ter Meulen method.

^f Reply to Schuster and to Dolch and Will.

^g Testimonial for ter Meulen's method.

^h Reply to ter Meulen and to Schuster.

ⁱ Certain improvements made in ter Meulen's method.

3. Destructive deoxidation by a substance capable of uniting with the oxygen, followed by a determination of its increase in weight due to oxidation coupled with the determination of any oxygen-containing products which escaped reduction (7).

4. Destructive chlorination of the substance followed by a determination of the oxygen-containing gaseous decomposition products (20).

5. Complete catalytic oxidation of the substance in a stream of gaseous oxygen, the carbon dioxide and water formed being simultaneously determined, together with a quantitative gasometric determination of the "oxygen consumed."

The gasometric determination of the oxygen consumed in the complete combustion of an organic substance, first carried out by Lavoisier about 160 years ago, has recently been developed by Glockler and Roberts (14) using semi-micro technic. The data given by these investigators, who confined their studies to the analysis of benzoic acid and one hydrocarbon, show that the mean error of their carbon determination was -0.12 per cent and of their hydrogen determination +0.41 per cent. The mean error reported for oxygen was -0.69 per cent, despite the fact that the summation of errors made in the carbon-hydrogen determination should make their oxygen values high. An analysis of their

results revealed that their gasometric determination of oxygen consumed was inaccurate, generally being too high, this error overcompensating the effect of the errors in the carbon-hydrogen determination. No attempt was made to correct accurately the gas volume due to changes in temperature and pressure, and the apparent concordance of their results was largely due to fortuitous compensation of errors of considerable magnitude. The same criticism applies to the results reported by Dolch and Will (9) and Dumke (10).

After considering the results obtained by the above five methods, it was decided to attempt the further development of the fifth method. This method has the advantage that it simultaneously determines carbon, hydrogen, and oxygen. However, considerably greater precision is necessary in both the carbon-hydrogen determination and in the gasometric determination of oxygen consumed than has yet been reported. It should be emphasized that in this method the determination of carbon and hydrogen must be very precise, since errors of 1 per cent in hydrogen and carbon cause errors of 8 and 2.67 per cent, respectively, in oxygen.

For the purpose of this laboratory it was necessary to employ a micromethod using samples weighing about 10 mg. The present paper reports the results obtained with the micromethod applied to compounds containing carbon, hydrogen, and oxygen, with and without halogens. A later report will present the results obtained in the analysis of more complex substances containing nitrogen and sulfur, and on coal.

MICRODETERMINATION OF CARBON AND HYDROGEN

Pregl's combustion apparatus was modified for this determination as follows:

ABSORPTION TUBES. The absorption tube fillings recommended by Pregl were not used in the present case because the tubes have to remain connected with each other and with the combustion tube for much longer periods than is customary in ordinary microcombustion practice. The use of absorbents for water—such as calcium chloride, dehydrite, anhydron, etc., which depend upon hydrate formation—was avoided and instead phosphorus pentoxide deposited on pumice was used, as recommended by Boëtius (4). Ascarite was used for absorption of the carbon dioxide. Both of these fillings have the advantage that one can tell at a glance to just what extent they have been exhausted. The absorption tubes were stoppered with tight-fitting pins during weighing, as recommended by Boëtius, and were weighed filled with oxygen.

COMBUSTION TUBE. Pregl's so-called Universal filling was first used, but on attempting to carry out blank quantitative oxygen transfers through the heated combustion tube, it was found that as much as 2 cc. of oxygen disappeared during each experiment. By a process of elimination, the loss of oxygen was traced to the copper oxide-lead chromate portion of the tube filling. Since the other portions of the Pregl filling were found to introduce no errors in the gas transfer, they were retained and it was merely necessary to replace the copper oxide-lead chromate filling with some other substance which would not cause this error. The successful use of a catalytic method in both macro- and micromethods (12) of combustion analysis suggested its trial for the present purpose. It was found that a 40 per cent palladium-asbestos catalyst, when used with the other reagents recommended by Pregl, gave accurate results for carbon and

hydrogen. To insure complete combustion, the vaporization of the sample must be conducted somewhat more carefully than usual, since in this case the oxidation must all be done by gaseous oxygen which passes through the tube during the combustion. Further details of this method including the results obtained and a discussion of the advantages will be presented in a separate communication from this laboratory.

PURIFYING TRAIN. Commercial oxygen, 99.5 per cent pure, was taken from a high-pressure tank and stored in a Haack Universal gasometer. From here it passed successively through a Pregl pressure regulator (A, Figure 1); an electrically heated Böck-Beaucourt platinum-asbestos purifier, B, which oxidized impurities; a spiral cooler; a large U-tube, C, the first arm being filled with Ascarite and the second with phosphorus pentoxide on pumice; a Friederich flowmeter, D, adjusted to permit 3 to 4 cc. of oxygen to pass per minute; a small U-tube, E, filled like the large one; and thence into the combustion tube. It was necessary to replace the Pregl bubble counter by the Friederich flowmeter since the bubble counter formed a liquid seal which prohibited free diffusion of the oxygen in the closed system.

APPARATUS FOR DETERMINING OXYGEN CONSUMED DURING A COMBUSTION

This apparatus is a combination of some of the features contained in the work of Glockler and Roberts, Dolch and Will, and Dumke and is shown schematically in Figure 1. The principle of the method consists essentially in carrying out the combustion in a closed system of known volume and in determining the oxygen consumed and the oxygen in the combustion products. To determine the oxygen consumed it is necessary to have the system at known equilibrium conditions of temperature and pressure both at the beginning and the end of the combustion.

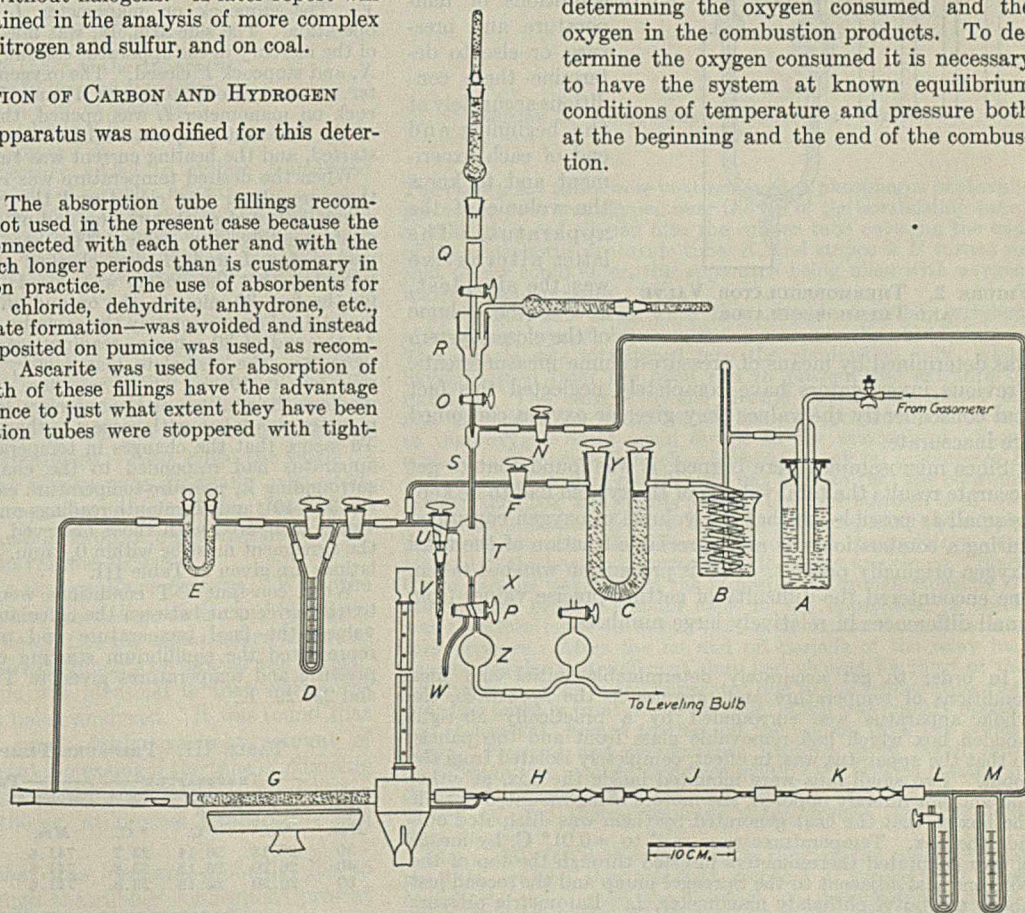


FIGURE 1. SCHEMATIC REPRESENTATION OF APPARATUS

Circulation of the oxygen over the sample during the combustion was maintained by means of the Sprengel pump *OSTP*, the rate of pumping being controlled by the rate of admission of mercury through stopcock *O* from a constant-level tube, *R*, supplied by a 100-cc. buret, *Q*. The oxygen from the pump is delivered to bulb *T* and thence through the flowmeter, combustion and absorption tubes, manometers, and back to *N*. The combustion of the sample is thus carried out by means of this

known volume of oxygen present in the system. As the oxygen is consumed during the combustion, it is displaced by mercury which collects in *T*. The total amount of oxygen finally consumed is then determined, after temperature and pressure equilibration, by running mercury out of bulb *T*, through the side tube, *W*, attached to stopcock *P* until the level reaches the scratch, *X*; the mercury is then weighed. From the weight of mercury thus obtained, the volume of oxygen which it has displaced can be calculated. The water and carbon dioxide formed during the combustion are absorbed in tubes *H* and *J* and from their increase in weight the oxygen content of these products can be calculated. With these data available, the oxygen in the sample can be calculated and is equal to the oxygen in the combustion products minus the oxygen consumed.

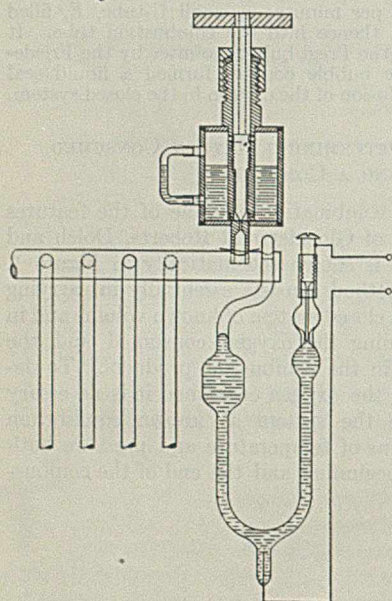


FIGURE 2. THERMOREGULATOR VALVE AND THERMOREGULATOR

DETERMINATION OF VOLUME OF CLOSED SYSTEM. In order to calculate accurately the weight of oxygen consumed during a combustion, it was necessary either to carry out the analyses under constant initial and final conditions of temperature and pressure, or else to determine these conditions accurately at the beginning and end of each experiment and to know the volume of the apparatus. The latter alternative was the simplest, and so the volume of the closed system

was determined by means of pressure-volume measurements. Previous investigators have completely neglected this fact and consequently the values they give for oxygen consumed are inaccurate.

Since microsamples were burned, it was found that to get accurate results the total volume of the system had to be kept as small as possible, so that the volume of oxygen consumed during a combustion was an appreciable fraction of the total oxygen originally present. If this precaution was not taken, one encountered the difficulty of getting precise values from small differences in relatively large numbers.

In order to get accurately determinable initial and final conditions of temperature and pressure in the apparatus, the whole apparatus was surrounded by a practically air-tight wooden box which had removable glass front and top panels, so that the apparatus was, in effect, completely isolated from the room. Two small fans were mounted inside the box, at either end and not directly opposed, the motors being mounted outside the box so that the heat generated by them was dissipated outside the box. Temperatures were read to $\pm 0.01^\circ \text{C}$. by means of two calibrated thermometers inserted through the top of the box, one just adjacent to the Sprengel pump and the second just above the butyl phthalate manometer, *L*. Barometric pressure was read on a precision Paulin barometer to $\pm 0.1 \text{ mm}$. using a magnifying glass. The pressure in the apparatus was determined by means of the butyl phthalate manometer which was read to $\pm 0.01 \text{ mm}$. of mercury. This manometer was provided with a stopcock so that it could be closed off during pumping periods or when the apparatus was not in use, thus avoiding the possibility of the manometer contents being sucked or blown out of the tube. A mercury manometer, *M*, also was used in the experiments on the determination of the volume of the apparatus and in controlling the pressure in the apparatus during pumping, and was read to $\pm 0.1 \text{ mm}$. To avoid sticking, the mercury was

lubricated with a small amount of butyl phthalate; it was found that before taking a reading it was necessary to shake the manometer slightly so as to wet the tube walls with the phthalate and thus lubricate the mercury columns. Since both manometers were in line with the air currents generated by the fans, the open ends of each were extended outside the box to atmospheric pressure.

In order to control the temperature in the box so that initial and final conditions were approximately the same, a thermoregulator and a pair of heaters were placed in the box. The temperature inside the box was brought a few degrees above that of the room and accurately maintained there to within $\pm 0.02^\circ \text{C}$. After the combustion, the final temperature was made approximately that present initially.

The heaters consisted of nichrome coils mounted on a circular Transite support in front of each fan, so that when the current was on the heated air was immediately put into circulation. The thermoregulator (Figure 2) was made of very thin copper tubing in the form of a grid (total width 45 cm., height 32 cm., with 10 pairs of staggered uprights connecting the two horizontal feeders), and was filled with toluene. The thermoregulator actuated the heater through a vacuum tube-operated relay, in a circuit shown in Figure 3. By means of this apparatus constant temperatures more or less independent of the room temperature were obtained in the box after about 30 minutes.

DETERMINATION OF VOLUME OF APPARATUS. The filled absorption tubes were put into position, completing the closed system, and oxygen was passed through the apparatus to displace any air, stopcock *U* being turned so that oxygen escapes to the atmosphere after passing through the entire apparatus; the entrance of moisture was prevented by the protection tube *V*. The stopcock on manometer *L* was closed during this operation. The side arm, *W*, was filled with mercury, the level of the mercury in the apparatus carefully adjusted to the scratch, *X*, and stopcock *P* closed. The oxygen from the supply gasometer was turned off, stopcocks *Y* and *F* were closed, the stopcock on manometer *L* was opened, the front and top sections of the constant-temperature box were put into place, the fans started, and the heating current was turned on.

When the desired temperature was reached, the valve on the thermoregulator was closed and the resistance in the heating circuit adjusted so that the on and off periods of the relay were approximately the same. The zero-point readings of the manometers *L* and *M* were checked and then stopcock *U* was turned so that the system was closed. No readings were taken for the first 30 minutes, the on and off times of the relay being maintained approximately the same by adjusting the resistances. At the end of 30 minutes readings were taken of the two thermometers, the phthalate manometer, and the barometer, and repeated at 40 and at 50 minutes. At the time of the last readings the position of the mercury level of the mercury manometer was taken with respect to the zero mark of the right arm. To insure that the changes in temperature and pressure in the apparatus had responded to the changes in the atmosphere surrounding it, pressure-temperature calculations were made for the 30-, 40-, and 50-minute readings and the calculated pressure values compared with those observed. For sufficient precision the agreement must be within 0.1 mm. Typical data and calculations are given in Table III.

When constant P-T conditions were obtained, as indicated by the agreement between the calculated and observed pressure values, the final temperature and pressure were noted and represented the equilibrium starting conditions. The starting pressure and temperatures given in Table III are 741.52 mm. and 299.29°K .

TABLE III. PRESSURE-TEMPERATURE DATA

READING	TEMPERATURE			PRESSURE			MERCURY LEVEL (M)
	Thermometer A	Thermometer B	Room	Barometer	Manometer L	Manometer R	
Min.	$^\circ \text{C}$.	$^\circ \text{C}$.	$^\circ \text{C}$.	Mm.	Mm.	Mm.	Mm.
30	26.18	26.14	23.7	741.6	+0.06	-0.04	...
40	26.20	26.18	23.8	741.6	+0.05	-0.03	...
50	26.20	26.18	23.8	741.6	+0.05	-0.03	+1.6

PRESSURE-TEMPERATURE CALCULATIONS

READING INTERVAL	P_1	T_2	T_1	P_2 (calcd.) ^a	P_2 (obsvd.)	DIFF.
Min.	Mm.	$^\circ \text{K}$.	$^\circ \text{K}$.	Mm.	Mm.	Mm.
30-40	741.50	299.29	299.26	741.58	741.52	0.06
40-50	741.52	299.29	299.29	741.52	741.52	0.00

^a P_2 is calculated from the equation: $P_2 = \frac{P_1 T_2}{T_1}$.

The heaters and fans were then turned off, the thermoregulator valve was opened, and the stopcock on manometer *L* closed.

The glass panel in front of the Sprengel pump was opened, the mercury in the leveling bulb raised until slightly above the level in the apparatus, and then stopcock *P* opened to permit mercury to enter bulb *T* on slowly raising the leveling bulb. This created a pressure in the entire apparatus which could be followed by its effect on the mercury manometer, *M*. When sufficient mercury had been added to give the maximum readable pressure on this manometer, stopcock *P* was closed, the heater and fans were again turned on, and the thermoregulator valve was again closed when the initial temperature was approximately reached. Establishment of equilibrium conditions was determined in the same manner as described in the preceding paragraph.

Since the increase in pressure in the closed system was caused by a decrease in the gas volume equal to the volume of mercury added to bulb *T*, it was necessary only to determine this volume of mercury in order to calculate from the initial and final equilibrium pressures and temperatures the volume of the closed system. The added mercury was run out through the side arm, *W*, and weighed, its volume being calculated from its density at the final temperature prevailing in the apparatus. The volume of the apparatus can then be calculated to the zero line of both manometers by means of the equation:

$$V = \frac{P_2 T_1}{P_1 T_2} (b - a) \frac{1}{1 - \frac{P_2 T_1}{P_1 T_2}}$$

where *V* = volume of free space in the apparatus

*P*₁ = initial pressure in mm. of mercury

*P*₂ = final pressure in mm. of mercury

*T*₁ = initial temperature in ° K.

*T*₂ = final temperature in ° K.

a = volume of mercury added to system (calculated from the weight of mercury added)

b = sum of volumes added or subtracted by depression or elevation of the manometer fillings from the zero mark (1 mm. on mercury manometer = 0.00208 cc.; 1 mm. on butylphthalate manometer = 0.00199 cc.)

The mean value obtained from five such determinations of the volume of the apparatus was 87.7 ± 0.27 cc. Greater precision was not necessary, since use was made of this figure only for correcting the volume of oxygen consumed because of changes of temperature and pressure in the conditions at the start and finish of the experiment. Also, since the small U-tube and absorption tube fillings were gradually exhausted, the volume gradually increased and on refilling the absorption tubes or the combustion tube it was impossible to fill them so that no change in volume occurred.

QUANTITATIVE GAS TRANSFER EXPERIMENTS. With the volume of the apparatus known, a large number of blank experiments were made to determine the quantitative nature of the gas transfer. In these experiments no sample was burned, but otherwise the technic was identical to that which was used when a sample was being analyzed. It was found that in every experiment a small, fairly constant amount of oxygen was lost, the amount increasing if the time of pumping was increased. The average value of this loss for twenty-five experiments was 0.166 cc. at normal temperature and pressure.

Experiment showed that this loss was probably due to diffusion of oxygen through the rubber connections present in the apparatus, although all the glass ends at such connections were abutted. Using the equation given by Edwards and Pickering (11), the area which would have to be exposed to give a loss such as observed is about 5 to 6 sq. cm., an entirely reasonable figure considering that there were 19 such rubber connections present in the closed system through which the oxygen might have diffused. Since the loss mentioned (0.166 cc.) was found to be quite constant, this correction was applied in all the actual combustions.

DIRECT MICRODETERMINATION OF CARBON, HYDROGEN, AND OXYGEN

PROCEDURE. The electrical heater was placed over the Böck-Beaucourt purifier and the current turned on so that the heater was at a dull red heat. The absorption tubes were attached and oxygen was passed through the apparatus and out through stopcock *U*. The mercury level in the Sprengel pump was accurately brought to the scratch, *X*. While oxygen passed through the cold combustion tube and displaced any air in the apparatus, a microsample for the combustion was weighed out, the amount depending somewhat on the percentage of oxygen in the sample.

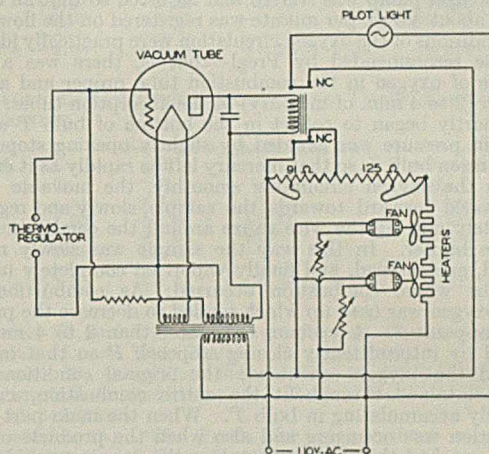


FIGURE 3. ELECTRICAL CIRCUIT FOR TEMPERATURE CONTROL

The absorption tubes were next removed, a phosphorus pentoxide protection tube was slipped over the tip of the combustion tube, a small glass rod slipped into the rubber tube covering the end of the phosphorus pentoxide tube, *K*, and stopcock *U* turned so that no air could enter, the apparatus being filled with oxygen under a slight pressure.

The absorption tubes were then wiped as usual, weighed after the appropriate interval, and replaced in the closed system. The sample was introduced into the combustion tube, while oxygen issued from the open end to prevent the entrance of moisture. The current to the electric heater was turned off and the heater removed from the box. Stopcock *U* was turned so that oxygen could again escape to the atmosphere. Stopcocks *Y* and *F* were then closed, the stopcock on manometer *L* was opened, the glass panels were put back so that the constant temperature box was tightly closed, the fans started, heat was turned on into the coils, and the oxygen coming from the supply gasometer turned off. When the desired temperature was reached in the box, the thermoregulator valve was closed. Since the apparatus was open to the atmosphere through stopcock *U*, atmospheric pressure should exist in the apparatus; a check was therefore made to insure that both manometers registered zero pressure. After the on and off periods of the relay had become regular and sufficient time had elapsed for most of the expansion to occur in the apparatus due to the temperature rise, the glass panel in front of the Sprengel pump was quickly opened and stopcock *U* turned to close off the system from the atmosphere. Pressure and temperature readings were taken until equilibrium was reached as determined by the criteria previously described. The current through the heating coils was then turned off, the thermoregulator valve opened, and the fans were stopped.

The middle top section and entire front of the constant temperature box were then removed, stopcock *U* turned so as to be completely closed, and the stopcock on manometer *L* closed. The leveling bulb was approximately leveled with the mercury at scratch *X*, and stopcock *P* turned to the position shown in Figure 1. Then the leveling bulb was lowered slightly until the mercury level in the apparatus was just at the bottom of the capillary below stopcock *P*. The long burner was then turned on low under the combustion tube and the expansion of the oxygen in the closed system forced mercury out into the expansion bulb, *Z*; any pressure generated was indicated on the mercury manometer and was avoided by occasionally lowering the leveling bulb and maintaining approximately atmospheric pressure in the apparatus. A Bunsen burner with a small

flame was then placed under the hollow mortar so as to bring its contents rapidly to the boiling point, gentle refluxing then being maintained by means of the microburner. The long burner was finally turned on full, keeping the pressure approximately equal to that of the atmosphere. Finally the movable burner was lighted, placed under the combustion tube at some distance behind the sample, and slowly turned up until it furnished the temperature desired; again, development of pressure was avoided.

After the tube had been heated for several minutes, stopcock *P* was closed and stopcock *U* opened to the system, the pressure by this time having been equalized so that on opening this stopcock no motion was observed in the levels of the flowmeter. The Sprengel pump was started and adjusted so that an oxygen flow of about 3.5 cc. per minute was registered on the flowmeter. The conditions of the oxygen circulation were practically identical to those recommended by Pregl—that is, there was a slight pressure of oxygen in the combustion tube proper and a slight vacuum (2 to 4 mm. of mercury) in the absorption tubes. Mercury shortly began to collect in the bottom of bulb *T* and increase in pressure was avoided by slightly opening stopcock *P* to expansion bulb *Z*, so that mercury left as rapidly as it entered.

With the oxygen circulating smoothly, the movable burner was pushed forward towards the sample, slowly and regularly, alternately moving the wire gauze around the combustion tube and the burner. In this way the sample was slowly melted, distilled, or sublimed, and finally vaporized completely into the hot tube where combustion occurred. As combustion took place, oxygen was used up which tended to decrease the pressure in the apparatus. A vacuum of greater than 2 to 4 mm. was avoided by intermittently closing stopcock *P* so that mercury replaced the oxygen consumed; the original conditions were thus maintained throughout the entire combustion, mercury gradually accumulating in bulb *T*. When the main part of the combustion was occurring and also when the products of combustion reached the absorption tubes, the oxygen was generally consumed at the same rate as mercury was added and during this time stopcock *P* was closed for a considerable length of time. If the vaporization of the sample was too rapid, a considerable vacuum was produced (as much as 30 to 40 mm.) and oxygen was consumed faster than mercury was added; in such cases it was usually found that low carbon-hydrogen values were obtained, the carbon particularly tending to be low because of incomplete oxidation. In general, the first combustion required about 75 to 85 minutes and the second (clean-up) combustion required about 15 minutes. After this the movable burner was turned out and oxygen was pumped for an additional 10 to 15 minutes. The complete time of pumping was thus 100 to 110 minutes. A total of about 60 to 65 cc. of mercury was added from the buret. During the entire combustion the mercury in the leveling bulb was kept at approximately the same level as the mercury in the expansion bulb.

The combustion was then stopped as follows: Stopcock *P* and then rapidly stopcock *O* were closed, leaving no drop hanging from the tip above *S*. Then, in order, the buret stopcock, stopcock *U*, and stopcock *N* were also closed, closing off the Sprengel pump completely from the rest of the apparatus. Stopcock *P* was then opened to the expansion bulb and some of the mercury ran out of bulb *T*. Oxygen was then transferred from the expansion bulb to bulb *T*, allowing more mercury to run out. This procedure was repeated until nearly all the mercury was removed from bulb *T* and capillary *S* completely cleared of mercury. The leveling bulb was then raised gradually until its level was a few millimeters above the level of the mercury in bulb *T* to avoid flow of oxygen out of the combustion tube; stopcock *U* was opened to the system, causing a slight flow of oxygen into the combustion tube. The long burner and microburner under the hollow mortar were turned off and the large wire tunnel over the combustion tube was removed. Any decrease in pressure in the system due to contraction of the oxygen on cooling was avoided by addition of mercury from the leveling bulb to bulb *T*. To hasten cooling, both fans were turned on and a stream of air was directed against the underside of the hollow mortar.

When the temperature of the apparatus had fallen to approximately that of the room, stopcock *N* was opened, stopcock *U* closed, and the stopcock on manometer *L* opened. Next, a vacuum of about 1 mm. of mercury was produced in the apparatus by lowering the leveling bulb and then stopcock *U* was again opened to the system. The top and front sections of the box were then put into place and the heaters turned on. By adjustment of the mercury level in bulb *T* by means of the leveling bulb, atmospheric pressure was maintained in the system. Equilibrium temperature and pressure were established following the same procedure as used for the initial conditions.

The heaters were then turned off, the thermoregulator valve

was opened, the fans were stopped, the front of the box was removed, the manometer stopcock closed, stopcocks *Y* and *F* were opened after being sure that the pressure regulator was filled with oxygen, and then stopcock *U* was opened to the atmosphere and oxygen passed through the apparatus for a few minutes while preparations were made to weigh the absorption tubes. The absorption tubes were then removed, wiped, and weighed after the appropriate time interval. The combustion apparatus, under slight oxygen pressure, was closed off from the atmosphere by means of phosphorus pentoxide tubes and could stand several days without the necessity of any conditioning.

After the absorption tubes were weighed, oxygen was again started from the supply gasometer and mercury run out of the Sprengel pump through the side arm until the mercury level was again at the scratch, *X*, the mercury being collected and weighed. From its weight the volume was calculated from the density at the final temperature of the experiment. All the data necessary for the calculation of the percentage of carbon, hydrogen, and oxygen in the sample were thus available.

RESULTS. Following the procedure outlined, determination of oxygen in seven pure compounds containing only carbon, hydrogen, and oxygen was first carried out. Then three compounds containing halogen were analyzed, two of them containing chlorine and the third containing both chlorine and bromine. To illustrate the method of calculation, the complete data are given for one of the compounds in Table IV.

TABLE IV. ILLUSTRATING METHOD OF CALCULATION

	<i>Mg.</i>
Weight of sample (benzoic acid)	9.118
Weight of carbon dioxide found	23.079
Weight of water found	4.087
	%
Carbon dioxide, found	69.03
Carbon dioxide, theory	68.83
Difference	+0.20
Water, found	5.01
Water, theory	4.95
Difference	+0.06
	<i>Cc.</i>
Volume of oxygen at start (740.37 mm.; 299.20° K.) *	87.713
Volume of oxygen at start, NTP	77.993
Volume of mercury added	13.838
Volume of oxygen at end (737.72 mm.; 300.09° K.)	73.864
Volume of oxygen at end, NTP	65.250
Volume of oxygen at end, NTP + correction (0.166 cc.)	65.416
Volume of oxygen consumed, NTP	12.577
	<i>Mg.</i>
Weight of oxygen consumed, found	17.973
Weight of oxygen consumed, theory	17.930
Difference	+0.043
Weight of oxygen in carbon dioxide, found	16.785
Weight of oxygen in carbon dioxide, theory	16.735
Difference	+0.050
Weight of oxygen in water, found	3.630
Weight of oxygen in water, theory	3.586
Difference	+0.044
Sum of oxygen in products of combustion, found	20.415
Sum of oxygen in products of combustion, theory	20.321
Difference	+0.094
Oxygen in sample, found (O ₂ in products - O ₂ consumed)	2.442
Oxygen in sample, theory (O ₂ in products - O ₂ consumed)	2.391
Difference	+0.051
	%
Oxygen in sample, found	26.78
Oxygen in sample, theory	26.22
Difference	+0.56

In Tables V and VI, which summarize the results obtained on 10 pure compounds, it is seen that the observed oxygen-consumed values are on the average too low by about 0.02 mg. The volumes are expressed to 0.001 cc. and calculated to 0.001 mg. (although the precision is not of this order), because the weighings were made to these limits and 0.001 cc. of oxygen weighs roughly 0.001 mg.

The tabulated data show that this method is capable of determining oxygen directly with a mean precision of about 0.3 to 0.4 per cent, this error apparently being independent of the percentage of oxygen in the sample. In order to get this precision, the determination of hydrogen must be accurate to within 0.05 per cent. With this error in hydrogen as a maximum, the error in the determination of carbon must be very small if one is to obtain a final precision of 0.4 per cent. The rather high multiplication of error is an inherent

TABLE V. MICRODETERMINATION OF CARBON, HYDROGEN, AND OXYGEN IN COMPOUNDS CONTAINING ONLY THESE ELEMENTS

COMPOUND	WEIGHT OF SAMPLE Mg.	FOUND				O ₂ consumed Mg.	DIFFERENCE FROM THEORY			
		C %	H %	O %	C %		H %	O %	O ₂ consumed Mg.	
Benzoic acid	9.118	69.03	5.01	26.78	17.973	+0.20	+0.06	+0.56	+0.043	
	11.384	68.80	4.99	26.06	22.426	-0.03	+0.04	-0.16	+0.040	
	9.203	68.81	5.01	26.70	18.087	-0.02	+0.06	+0.48	-0.010	
Benzalacetophenone <i>p</i> -Phenylphenol	7.321	86.42	5.83	8.09	19.666	-0.08	+0.02	+0.40	-0.036	
	7.088	84.54	5.95	9.59	18.648	-0.13	+0.03	+0.18	-0.022	
	7.754	84.42	5.98	10.14	20.351	-0.25	+0.06	+0.73	-0.074	
<i>p</i> -Cyclohexylphenol	6.965	81.48	9.18	9.68	19.536	-0.28	+0.02	+0.59	-0.079	
	7.810	81.76	9.19	9.59	21.979	0.00	+0.03	+0.50	-0.015	
	7.139	83.56	6.38	10.63	18.766	+0.06	-0.00	+0.51	-0.021	
Methyl- β -naphthyl ether	7.331	83.33	6.37	10.22	19.246	-0.17	-0.01	+0.10	-0.046	
	9.611	80.70	3.94	15.75	22.172	-0.05	+0.06	+0.37	-0.001	
	9.523	80.55	3.86	15.31	21.917	-0.20	-0.02	-0.07	-0.053	
Anthraquinone	8.130	80.73	3.94	15.58	18.779	-0.02	+0.06	+0.20	+0.023	
	9.324	42.14	6.46	51.46	10.465	+0.07	-0.02	+0.02	-0.001	
	13.605	42.15	6.47	51.41	15.288	+0.07	-0.01	-0.03	+0.020	
					Mean =	-0.06	+0.03	+0.29 \pm 0.04	-0.015 \pm 0.005	

TABLE VI. MICRODETERMINATION OF CARBON, HYDROGEN, AND OXYGEN IN COMPOUNDS CONTAINING THESE ELEMENTS PLUS CHLORINE AND BROMINE

COMPOUND	WEIGHT OF SAMPLE Mg.	FOUND				O ₂ consumed Mg.	DIFFERENCE FROM THEORY			
		C %	H %	O %	C %		H %	O %	O ₂ consumed Mg.	
<i>o</i> -Chlorobenzoic acid	9.390	53.67	3.28	21.47	13.867	-0.01	+0.06	+1.02	-0.053	
	11.436	53.77	3.25	21.16	16.928	+0.09	+0.03	+0.71	-0.025	
<i>sym</i> -Trichlorophenol	12.478	36.53	1.54	8.33	12.638	+0.05	+0.01	+0.22	-0.005	
	<i>p</i> -Chlorophenacyl bromide	12.400	41.18	2.64	7.24	15.315	+0.05	+0.05	+0.38	+0.016
					Mean =	+0.05	+0.04	+0.58 \pm 0.04	-0.017 \pm 0.008	

fault of this method and is the limiting factor in obtaining higher precision. The presence of halogens in the sample adds no complications to the method, but reduces the precision of the oxygen determination.

It may be emphasized that this is the first time that a true micromethod has been attempted for the direct determination of oxygen. As is often the case, the micromethod has pointed out large sources of error in the macro- and semi-micromethods previously described.

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RECEIVED JUNE 2, 1934. Presented before the Division of Organic Chemistry at the 88th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 14, 1934.

PRECISE MEASUREMENT OF AIR PERMEABILITY OF PAPER. A sensitive instrument has been developed by the Bureau of Standards for measuring the rate at which air passes through paper and other porous materials in sheet form. A preliminary survey indicated that the most common sources of error in existing instruments for testing the air permeability of paper are leakage, especially at the edges of the specimen, fluctuations in driving pressure, lack of sensitivity, and restricted range. The new instrument contains a permeability cell of novel design, in which an annular cell surrounds the inner testing cell. The air flow is so regulated that there is no lateral pressure gradient at the boundary of the inner cell, and hence no leakage into or out of it. The pressure regulator is a form of automatic diaphragm valve designed to maintain a very steady pressure drop across the instrument. The amount of air, which in a given time reaches

the inner cell by flowing through the specimen under the influence of this constant pressure difference, is measured with a capillary flowmeter containing four carefully calibrated capillary tubes. Results are reproducible on an identical area to within a few tenths of one per cent.

The range of the new instrument is about a thousand times that of most other instruments available for the purpose. It will accommodate materials of any thickness up to half an inch, and it is not necessary to cut them in order to make the test. Tests can be made rapidly, since the element of time is taken care of in the calibration and the duration of the test need not be measured. The test area is larger than is usually found in air permeability instruments, in order better to sample the material. The instrument is well adapted to the testing of leather and some other sheet materials.

Colorimetric Determination of Silica in Boiler Water

M. C. SCHWARTZ,¹ Louisiana Steam Generating Corporation, Baton Rouge, La.

INFORMATION (3, 13) on the formation and methods of prevention of silica boiler scale is becoming increasingly more important in considering the design of modern high-pressure steam plants. The analytical determination of silica is naturally of fundamental importance in the consideration of such problems and is capable of high accuracy (6), but the length of time required to complete the analysis is too long for certain types of investigations. In such instances one must resort to a more rapid method of analysis, such as colorimetry.

Solutions containing dissolved silica react with acid solutions of ammonium molybdate to form colored silicomolybdates; soluble phosphates and iron salts likewise form complex colored molybdates. The reactions (1, 2, 4, 7-12, 14-16) are complicated and, although various complex molybdates have been isolated and prepared in a pure state, their existence in solution is somewhat conjectural, owing to the important effect of the hydrogen-ion concentration on the various equilibria existing.

APPARATUS. Two colorimeters were used, a 40-mm. Bausch and Lomb Duboscq type and a 50-mm. Hellige Duboscq. A Macbeth daylight lamp was used as the source of illumination. Hydrogen-ion measurements were made using the hydrogen-saturated calomel electrode and the quinhydrone-saturated calomel electrode combinations.

STANDARDS. Picric acid and potassium chromate solutions have been used as permanent liquid standards. A spectrophotometric comparison (prepared by A. C. Hardy, Massachusetts Institute of Technology) of these liquids with a silicate solution is shown in Figure 1.

REAGENTS. Calcium chloride: 111 grams of c. p. anhydrous calcium chloride per liter of solution (1 M). Ammonium molybdate: 10 and 25 per cent solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. Hydrochloric acid: concentrated acid and 1 to 1 acid (by volume). Blank tests should be made on these reagents for the presence of silica.

EXPERIMENTAL RESULTS

EFFECT OF VARYING pH. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 2 ml. of 10 per cent ammonium molybdate solution and the various amounts of acid indicated in Table I to make up 50 ml. The colored solutions were compared with the appropriate silica stand-

ards standardized in a similar fashion against silica solutions. Figure 2 represents the data of Table I.

TABLE I. EFFECT OF VARYING pH ON COLOR INTENSITY

HYDROCHLORIC ACID ML.	APPARENT SILICA CONCENTRATION		pH ^a
	P. p. m.		
0.25 (1 to 1)	35.0		1.85
0.5 (1 to 1)	35.9		1.39
1.0 (1 to 1)	36.7		1.12
1.5 (1 to 1)	36.0		0.85
1.0 Concentrated acid	35.5		0.71
1.0 Concentrated acid + 0.5 ml. (1 to 1)	34.5		0.62
2.0 Concentrated acid	13.8		0.41

^a Determined with quinhydrone-saturated calomel electrode. The pH values although definitely reproducible are not precise measurements of hydrogen-ion concentration because of some reducing effect of quinhydrone on the silicomolybdate present in solution.

EFFECT OF AMMONIUM MOLYBDATE CONCENTRATION. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 1 ml. of a 1 to 1 solution of hydrochloric acid and the various amounts of molybdate solution indicated in Table II to make up 50 ml. Figure 3 represents the data of Table II.

TABLE II. EFFECT OF VARYING AMMONIUM MOLYBDATE CONCENTRATION ON COLOR INTENSITY

MOLYBDATE SOLUTION		APPARENT SILICA CONCENTRATION
ML.	%	
0.5	10	13.3
1.0	10	38.2
2.0	10	39.7
2.0	25	38.6
4.0	25	32.0

EFFECT OF TIME. Two milliliters of calcium chloride solution were added to 100 ml. of boiler water. After 1 hour the solution was filtered, and enough of the filtrate was added to 2 ml. of 10 per cent ammonium molybdate solution and 1 ml. of 1 to 1 hydrochloric acid to make up 50 ml. Figure 4 represents the data of Table III.

TABLE III. EFFECT OF TIME ON COLOR INTENSITY

TIME Min.	APPARENT SILICA CONCENTRATION
	P. p. m.
0	43.7
10	43.7
25	43.7
45	43.0
70	41.5
90	40.0

EFFECT OF INITIAL pH. Either sodium hydroxide or hydrochloric acid was added to 125 ml. of boiler water to produce the desired initial pH. Two milliliters of calcium chloride solution were added and the solution filtered after 1 hour. Two milliliters of ammonium molybdate and 1 ml. of 1 to 1 hydrochloric acid were added to 50 ml. of sample. In some instances the volume and concentration of the acid added had to be varied to maintain a colorimetric pH value of about 1.1. Somewhere between a pH of 12.69 and 12.87 calcium hydroxide precipitates from the solution. Figure 5 represents the data of Table IV.

EFFECT OF BUFFER SOLUTION. The quantities of buffer solution indicated in Table VI were added to 100-ml. samples of boiler water. The data of Table VI are represented in Figure 6.

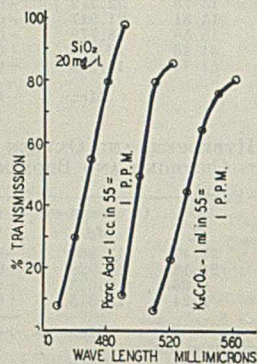


FIGURE 1. SPECTROPHOTOMETRIC COMPARISON OF STANDARDS

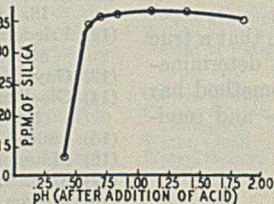


FIGURE 2. EFFECT OF VARYING pH ON COLOR INTENSITY

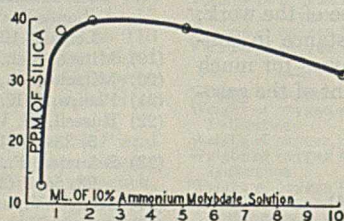


FIGURE 3. EFFECT OF AMMONIUM MOLYBDATE CONCENTRATION ON COLOR INTENSITY

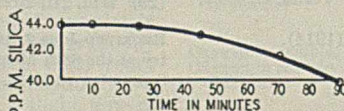


FIGURE 4. EFFECT OF TIME ON COLOR INTENSITY

¹ Boiler Feedwater Fellow, Institute of Industrial Research, Louisiana State University.

TABLE IV. EFFECT OF INITIAL pH OF BOILER WATER ON ERROR IN DETERMINING SILICA

	INITIAL pH ^a	SILICA FOUND		FINAL pH ^c
		P. p. m.	ERROR ^b P. p. m.	
1	8.62	59.1	+18.1	0.98
2	9.24	48.9	+7.9	1.01
3	9.61	46.0	+5.0	0.99
4	9.97	41.1	+0.1	1.10
5	10.12	41.1	+0.1	1.09
6	10.32	41.2	+0.2	1.10
7	10.46	40.7	-0.3	1.10
8	10.68	40.7	-0.3	1.10
9	10.96	39.8	-1.2	1.08
10	11.14	31.9	-8.1	1.09
	11.14	31.3	-8.7	0.76
11	11.63	10.1	-30.9	1.15
	11.63	Too faint to be read		0.30
12	12.10	3.7	-37.3	1.64
	12.10	4.4	-36.6	1.16
	12.10	4.2	-36.8	0.80
	12.10	Too faint to be read		0.52
13	12.37	<3.7	>37.3	1.24
	12.37	Too faint to be read		0.82
14	12.69	Too faint to be read		1.00
15	12.87
16	13.07	4.2	-36.8	1.88
	13.07	5.0	-36.0	0.66
17	13.58	16.8	-24.2	1.25
18	13.85	11.1	-29.9	0.28

^a Determined with hydrogen-saturated calomel electrode.^b Average result of gravimetric analysis, 41.0 p. p. m.^c Determined with the quinhydrone-saturated calomel electrode, represents the pH value of the solution after addition of ammonium molybdate and hydrochloric acid.

TABLE V. EFFECT OF PHOSPHATE PRECIPITATION ON INITIAL pH OF BOILER WATER

INITIAL pH ^a	EQUILIBRIUM pH ^a (AFTER PHOSPHATE PRECIPITATION)
9.61	7.36
9.97	7.38
10.12	7.69
10.32	7.84
10.46	7.92

^a Determined with the hydrogen-saturated calomel electrode.

In order to determine the proper range of pH for phosphate precipitation more precisely, the fractional precipitation of calcium phosphate and silicate was investigated with the use of a series of buffer solutions (Table VII).

TABLE VI. EFFECT OF ADDING BORATE-SODIUM HYDROXIDE BUFFER^a SOLUTION (4) ON pH VALUES OF BOILER WATER

BUFFER SOLUTION ADDED M.	pH BEFORE PHOSPHATE PRECIPITATION ^b	pH AFTER PHOSPHATE PRECIPITATION ^b
0	11.05	7.26
10	10.91	9.52
20	10.78	9.69
30	10.68	9.81
40	10.61	9.86
50	10.53	9.89
100	10.46	10.00

^a Borate solution, 12.404 grams of H₂BO₃ and 100 ml. of M NaOH per liter. Sodium hydroxide solution, 0.1 M. The buffer solution consists of equal parts of borate and sodium hydroxide solution.^b Determined with hydrogen-saturated calomel electrode.

Fifty milliliters of buffer solution were added to 110 ml. of boiler water and the pH was determined. Two milliliters of

calcium chloride solution were added and the solution was filtered after 1 or 2 hours. The pH was redetermined. Two milliliters of ammonium molybdate solution and 1 ml. of 1 to 1 hydrochloric acid were added to 50 ml. of solution and the silica and pH determined. The data of Table VIII are represented in Figure 7.

TABLE VIII. COLORIMETRIC DETERMINATION OF SILICA IN BOILER WATER

(In presence of phosphate)					
pH ^a OF BUFFER SOLUTION	INITIAL pH ^a	pH AFTER PPTN. ^a	SILICA ^b P. p. m.	ERROR ^c P. p. m.	FINAL pH ^d
10.43	10.83	10.47	59.5	+0.5	1.25
10.26	10.61	10.29	58.8	-0.2	1.25
9.92	10.12	9.94	59.6	+0.6	1.25
9.93	9.72	9.60	59.5	+0.5	1.25
9.41	9.48	9.40	59.4	+0.4	1.25
9.17	9.23	9.10	61.8	+2.8	1.25
9.02	9.13	9.00	62.5	+3.5	1.19
8.48	8.79	8.62	64.8	+5.8	1.14
8.04	8.46	8.28	68.0	+9.0	1.10
7.61	8.19	8.04	71.9	+12.9	1.04
7.27	8.02	7.83	75.0	+16.0	1.04

^a Determined with hydrogen-saturated calomel electrode.^b Dilution factor, 1.54.^c Average result of gravimetric analysis, 59.0 p. p. m.^d Determined with quinhydrone-saturated calomel electrode.

EFFECT OF ALUMINUM. Solutions of boiler water were prepared containing the proper amounts of aluminum and the initial pH was adjusted by adding hydrochloric acid. Two milliliters of calcium chloride solution were added. The sample was filtered after 1 hour and the pH determined. The silica was determined colorimetrically and the pH was determined again. The data of Table IX are represented in Figure 8.

TABLE IX. EFFECT OF SOLUBLE ALUMINUM ON COLORIMETRIC DETERMINATION OF SILICA IN BOILER WATER

INITIAL pH ^a	pH AFTER PHOSPHATE PRECIPITATION ^a	ALUMINUM ADDED ^b P. p. m.	FINAL pH ^c	SILICA ^d P. p. m.
10.23	9.09	0	1.03	62.2
10.25	8.85	5	1.03	45.0
10.24	8.95	10	1.05	33.6
10.24	8.78	20	1.07	15.9
10.25	8.81	30	1.07	9.1
10.25	8.87	50	1.08	approx. 3

^a Determined with hydrogen-saturated calomel electrode.^b Source of aluminum, aluminum chloride.^c Determined with the quinhydrone-saturated calomel electrode.^d Average result of gravimetric analysis, 64.2 p. p. m.

TABLE X. EFFECT OF IRON ON COLORIMETRIC DETERMINATION OF SILICA IN BOILER WATER

INITIAL pH ^a	pH AFTER PHOSPHATE PRECIPITATION ^a	IRON ADDED ^b P. p. m.	SILICA ^c P. p. m.	FINAL pH ^d
10.24	9.72	0	61.3	1.04
10.24	9.75	2	61.1	1.05
10.22	9.75	5	60.5	1.04
10.26	9.73	10	52.5	1.04

^a Determined with hydrogen-saturated calomel electrode.^b Source of iron, ferric chloride.^c Average result of gravimetric analysis, 63.0 p. p. m.^d Determined with quinhydrone-saturated calomel electrode.

TABLE VII. BUFFER SOLUTIONS

COMPOSITION ^a	EXPECTED pH	ACTUAL pH ^b	TEMPERATURE ° C.	REFERENCE (4)
75 ml. I + 75 ml. II	10.93	11.08	24	p. 208 (5 borate + 5 NaOH)
80 ml. I + 70 ml. II	10.43	25	p. 208
82.5 ml. I + 67.5 ml. II	10.36 ^c	10.26	24	p. 208 (5.5 borate + 4.5 NaOH)
82.5 ml. I + 67.5 ml. II	10.36 ^c	10.22	25	
90 ml. I + 60 ml. II	9.87	9.92	25	p. 208 (6 borate + 4 NaOH)
105 ml. I + 45 ml. II	9.60	9.63	25	p. 208 (7 borate + 3 NaOH)
120 ml. I + 30 ml. II	9.44	9.41	25	p. 208 (8 borate + 2 NaOH)
150 ml. I	9.19	9.17	24	p. 208 (10 borate)
135 ml. I + 15 ml. III	9.04	9.02	24	p. 209 (9 borate + 1 HCl)
97.5 ml. I + 52.5 ml. III	8.47	8.48	24	p. 209 (6.5 borate + 3.5 HCl)
37.5 ml. V + 112.5 ml. IV	7.94 (18°)	8.04	24	p. 213 (2.5 borate + 7.5 HCl)
18 ml. V + 132 ml. IV	7.46 (18°)	7.61	23	p. 213 (1.2 borax + 8.8 H ₂ BO ₃)
9 ml. V + 141 ml. IV	7.09 (18°)	7.27	23	p. 213 (0.6 borax + 9.4 H ₂ BO ₃)

^a Buffer solutions:I, 12.404 grams of H₂BO₃ and 100 ml. of M NaOH per liter.

II, 0.1 M NaOH.

III, 0.1 M HCl.

IV, 12.404 grams of H₂BO₃ per liter.V, 19.108 grams of Na₂B₄O₇.^b Buffer solutions were not prepared rigorously. Values determined with the hydrogen-saturated calomel electrode.^c Interpolated values.

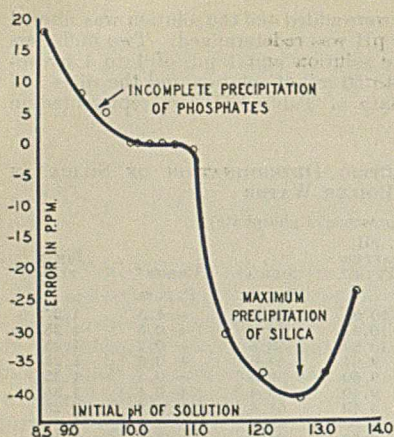


FIGURE 5. EFFECT OF INITIAL pH ON ERROR IN DETERMINING SILICA

EFFECT OF IRON. Solutions of boiler water were prepared containing the proper amounts of iron and the initial pH was adjusted by adding sodium hydroxide. Where 2 p. p. m. of iron were added, a slight turbidity appeared, as well as precipitates in the subsequent samples. However, the solutions were not filtered. Two milliliters of calcium chloride solution were added. The sample was filtered after 1 hour and the pH determined. Silica was determined colorimetrically and the pH was re-determined. The data of Table X are represented in Figure 9.

SUMMARY OF RESULTS

The yellowish green color of the silicomolybdate complex (approximate silica concentration 50 p. p. m.) develops its maximum intensity (1) at a pH of approximately 1.1; (2) at a concentration of ammonium molybdate corresponding to approximately 2 ml. of a 10 per cent solution; (3) practically instantaneously if the molybdate and acid solutions are added in quick succession; and remains so for approximately one-half hour, after which it diminishes.

The precipitation of phosphates from boiler water by calcium chloride results in a drop in the pH of the solution.

The proper initial pH range of the boiler water for complete removal of phosphates without precipitation of silica is 9.5 to 10.5.

The use of a sodium hydroxide-borate buffer solution of pH 10 maintains the proper pH for the removal of phosphates.

The presence of aluminum in the boiler water as an aluminate reduces the determined silica concentration of the boiler water, particularly near pH values of 10, by actual reaction in the presence of calcium chloride.

Although very little iron can exist in solution in boiler water of pH approximately 11, the effect of adding iron on the colorimetric determination of silica has been determined as resulting in an apparent decrease probably due to adsorption of silica on ferric hydroxide.

PROCEDURE

As a result of the preceding work, the following reagents and procedure were developed:

SODIUM HYDROXIDE-BORATE BUFFER SOLUTION. Solution A, 12.40 grams of boric acid plus 100 ml. of *M* sodium hydroxide per liter. Solution B, 0.1 *M* sodium hydroxide. The buffer solution is made by taking 6 parts of solution A and 4 parts of solution B. The buffer is kept in a hard-rubber bottle.

CALCIUM CHLORIDE SOLUTION. 1 *M* calcium chloride.

AMMONIUM MOLYBDATE SOLUTION. Ten per cent solution of $(\text{NH}_4)_2\text{MoO}_4 \cdot 4\text{H}_2\text{O}$.

HYDROCHLORIC ACID. Three volumes of concentrated acid to 2 volumes of distilled water.

Calcium chloride, ammonium molybdate, and hydrochloric

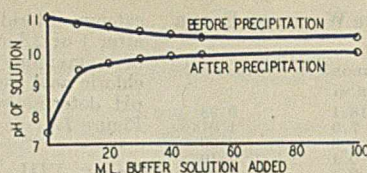


FIGURE 6. EFFECT OF BUFFER SOLUTION ON pH VALUES

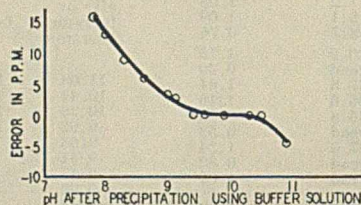


FIGURE 7. DETERMINATION OF SILICA IN PRESENCE OF PHOSPHATE

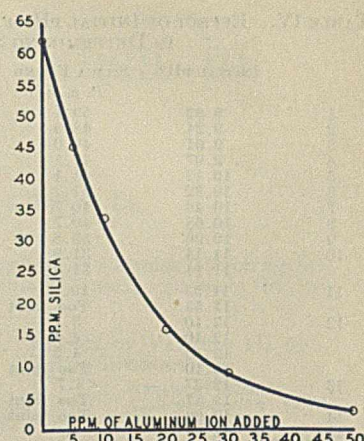


FIGURE 8. EFFECT OF SOLUBLE ALUMINUM ON COLORIMETRIC DETERMINATION OF SILICA

acid are kept in Pyrex glass bottles. Silica blanks should be taken on the reagents.

PROCEDURE. To 110 ml. of boiler water add 50 ml. of buffer solution, 2 ml. of calcium chloride solution, and stir vigorously. A flocculent precipitate of calcium phosphate forms which settles rapidly. Allow the solution to stand for approximately 2 hours (in any event, at least 1 hour) with occasional stirring, and then filter. To 50 ml. of the filtrate add 2 ml. of ammonium molybdate solution and 1 ml. of 3 to 2 hydrochloric acid solution. After allowing the solution to stand for 10 to 15 minutes, compare the silica color intensity with an appropriate potassium chromate or picric acid silica standard. Subtract the buffer blank from the calculated reading and multiply the result by the dilution factor (1.54).

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RECEIVED May 16, 1934. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934. The present paper includes a portion of a program of boiler feedwater research being carried out at the Louisiana Steam Generating Corporation under the general direction of E. B. Powell, Stone and Webster Engineering Corporation, Boston, Mass., with the cooperation of the Institute of Industrial Research, Louisiana State University, and with the collaboration of S. T. Powell, Baltimore, Md.

A Microscope Cold Stage with Temperature Control

C. W. MASON AND T. G. ROCHOW, Cornell University, Ithaca, N. Y.

THE microscopist may be called upon to examine a specimen below room temperature in order that he may observe temperatures, appearances, and optical properties of the specimen during freezing and thawing, transformation, or chemical reaction. The apparatus to be described consists of a cold stage and devices for controlling the temperature, and is designed for use at temperatures down to -25°C . and even lower. Accurate control of the temperature, to within 0.1°C ., is considered important but means are also provided for quickly changing the temperature.

A simple cold stage has been described by Chamot and Mason (1), and was used in 1928 in her study of the freezing of emulsions by Miss Newcomer (2), who cooled the stage with alcohol, flowing by gravity through a cooled copper spiral. The present apparatus represents an improvement in the design of the circulatory system so as to include an air lift for pumping the liquid around the system and a shunt for more accurate control of the temperature of the stage.

APPARATUS

COLD STAGE. The cold stage, part *S* of Figure 1, may be made by any competent mechanic from a plate of aluminum about $70 \times 100 \times 10$ mm.; the upper surface of this plate is channeled and a second plate, 3 mm. thick, is fastened tightly upon it by means of a lead foil gasket, *G*, and closely spaced screws. The channel thus constitutes a tube for circulation of a cooling agent through what is substantially a block of aluminum. An opening, 19 mm. in diameter, is provided for the specimen, and recessed at its edges to take windows of 25-mm. round cover-glasses, the lower one sealed

in place by vaseline. A hole for the reception of a low-temperature thermometer extends into the central chamber. The whole stage is insulated by 5-mm. sheet cork, held in place by pins and rubber cement. Several layers of aluminum foil, cemented by rubber cement, protect the insulation from sweating. The cold stage is clamped on any microscope having a fairly roomy stand, preferably after removal of the rotating stage.

CIRCULATORY SYSTEM. The complete system for circulating cooled liquid through the stage is also shown in Figure 1. Dried air passes into the air lift, *L*, where the liquid of the cooling system is forced up into the reservoir, *R*. From there the liquid flows down into the cooling coil, *C*, and then either through the cold stage, *S*, or across the shunt, *H*, to return to the air lift, completing the circuit.

AIR LIFT. The air lift, *L*, is constructed as follows:

One end of a piece of 6-mm. glass tubing is drawn and bent into a curved nozzle with 2-mm. opening. Another piece of tubing is drawn out, 10 mm. from the end, into a neck about 25 mm. long and 3.5 mm. in diameter at its narrowest part. The bent nozzle is inserted into the second tube at the lower end of its constriction. The straight parts of the two members are separated by pieces of cork and are bound together by copper wire. The assembly is placed in a large test tube, 2.8×25 cm., which is filled with the liquid to be circulated and sealed with a rubber stopper with holes for the two tubes of the air lift and another hole for the return-line.

The air, admitted from a low-pressure air line, has its velocity further reduced by means of two stopcocks in a side-arm U-tube, containing calcium chloride for drying the air so as to avoid diluting the circulating liquid with condensed water from the air. A T-tube, *T*, with a stopcock in the branch, is inserted between the U-tube and the air lift.

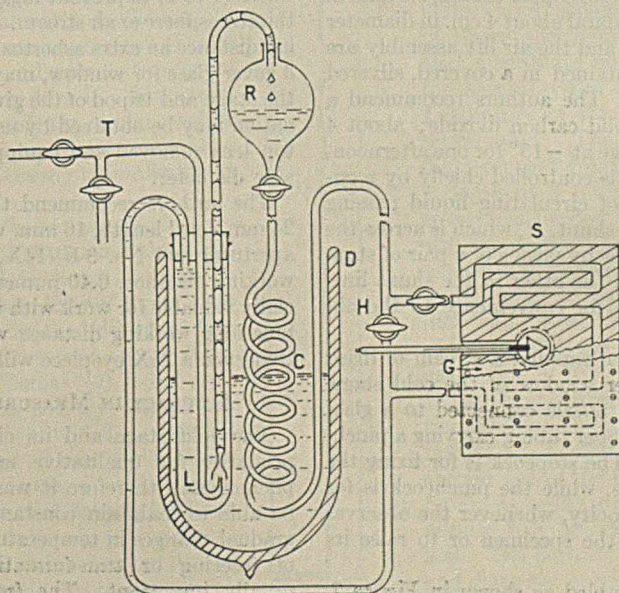


FIGURE 1. DIAGRAM OF COLD STAGE AND COOLING SYSTEM

The T-tube serves both as a safety outlet for any liquid which may be sucked back if the air pressure fails, and as a means for draining the apparatus of circulating liquid by applying air pressure at the top of the reservoir, *R*. The reservoir, a separatory funnel with stopcock, is about 50 cm. above the stage so as to provide static head for the liquid. In the operation of the air lift the air is admitted through the bent nozzle into the constricted tube at such a rate as to cause alternate slugs of air and liquid to rise in the delivery tube to the separatory funnel, from which the air escapes through a thistle tube (not shown) which also serves for the replacement of liquid lost by evaporation.

The advantages of the air lift as a pump in this apparatus are its simplicity of design and ease of construction; its high thermal efficiency due to the low conductivity of glass and

air; its small size and convenient shape, permitting its placement in the cooling bath; its complete lack of moving parts; and the ease in the adjustment of the velocity of the circulating liquid.

The disadvantages of the air lift are loss of circulating liquid by evaporation before the system has been cooled appreciably; and the need for a chamber, such as a separatory funnel, in which to separate air from liquid, and where heat is transferred to the liquid despite insulation of the chamber.

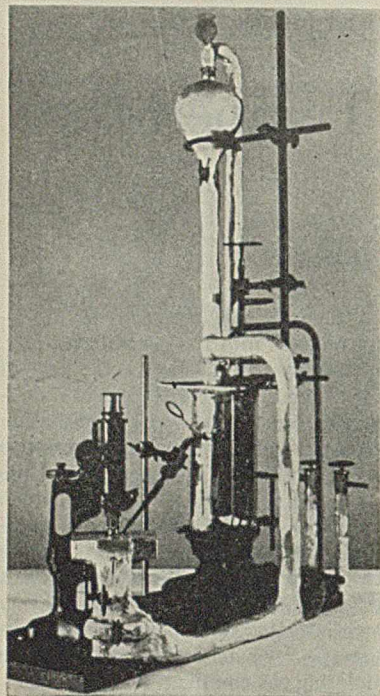


FIGURE 2. COLD STAGE, AS USED

flows down into the cooling coil, *C*, of copper tubing, 6.5 mm. in outside diameter, wound into a spiral about 4 cm. in diameter and 18 cm. long. Both the coil and the air lift assembly are immersed in a cooling bath contained in a covered, silvered Dewar beaker, *D*, 12 × 27 cm. The authors recommend a cooling bath of acetone and solid carbon dioxide; about 4 pounds (1.9 kg.) will keep the stage at -15° for one afternoon.

The temperature of the stage is controlled chiefly by regulating the relative proportions of circulating liquid passing through the stage and through a shunt, *H*, which is across the inlet and outlet tubes. Control is by means of a pair of stopcocks, one in the outlet line and the other in the shunt line. Both are located near the stage for convenience to the observer.

In order to warm the specimen rapidly, a stream of dried air is directed against the upper window of the cold stage. The air is emitted from a glass nozzle connected to a glass stopcock which is attached to rubber tubing carrying a pinchcock near the glass stopcock. The stopcock is for fixing the velocity of the air at the nozzle, while the pinchcock is for releasing the air at the fixed velocity, whenever the observer wishes to arrest the cooling of the specimen or to raise its temperature quickly.

The units described are assembled as shown in Figure 2. The U-tube, Dewar beaker, air lift, cooling coil, and stirrer

are all fastened to a large iron ring stand by means of iron clamps. The shunt and its stopcocks are mounted on a small wooden block, screwed to the baseboard. The cold stage is fastened to the microscope with an iron clamp. The microscope may be removed simply by unfastening the clamp and a single screw at the heel of the microscope base.

Lines for carrying air or circulating liquid are of 6-mm. glass tubing. The tubing carrying liquid is insulated with a layer of asbestos cement, approximately 1 cm. thick, and painted with powdered aluminum in lacquer to give a waterproof and reflecting surface. All glass tubing is fastened to the baseboard or to the larger parts of the apparatus, and thus, by having all the parts of the cold stage and its circulatory system fastened to the board, the apparatus is made portable as a unit.

OPERATION OF APPARATUS

By means of the apparatus described, the specimen in the cold stage may be cooled either slowly or rapidly and, likewise, warmed again either slowly or rapidly. If the specimen is to be cooled slowly it is placed in the stage at room temperature and the liquid is circulated, using the shunt so as to lower the temperature as gradually as desired. If the specimen is to be cooled rapidly the stage is first brought to the correct temperature and then the specimen is introduced into the stage. In either event, some of the liquid specimen should preferably make contact with the cold aluminum wall of the stage in order to give localized chilling; otherwise, the specimen being insulated all around by air, supercooling will be probable and final freezing may be too sudden. If the temperature of the specimen is to be raised gradually, the shunt and its stopcocks will serve the purpose. If a rapid rise in temperature is desired, or if cooling is to be arrested, the air current is released by pressing the pinchcock. The air may be preheated, if desired.

The specimen is mounted in a small watch glass or cell, or between two 18-mm. cover-glasses, and is supported above the lower window of the stage by means of a tiny wire tripod in close proximity to the bulb of the thermometer. If the tripod is 9 mm. high, the specimen is brought near enough to the upper glass window to permit the use of an 8-mm. objective (working distance, 1.5 mm.). After the specimen is in place the upper glass window is dropped in place, after being cleaned with Bon Ami and coated with a thin film of glycerol-water (1 to 1) to prevent fogging by condensed moisture from the atmosphere or air stream. With objectives of longer working distance an extra asbestos cover, 1.5 mm. thick, with a No. 3 cover-glass for window, may be placed over the well. With the stage and tripod of the given dimensions, dark-field illumination may be obtained by using an Abbe condenser with its top lens removed and equipped with a central stop of suitable diameter.

The authors recommend the Leitz objectives No. 2 (6X, 24 mm. focal length, 16 mm. working distance, 0.20 numerical aperture) and No. 3-b (14X, 13 mm. focal length, 3.2 mm. working distance, 0.40 numerical aperture). They are especially valuable for work with the cold stage because they combine long working distance with numerical aperture so high that even a 25X eyepiece will yield "useful" magnification.

ACCURACY IN MEASUREMENT OF TEMPERATURES

The cold stage and its circulatory system were designed primarily for qualitative examination of low-temperature phenomena; therefore it was considered most important to be able to maintain constant temperatures and to produce gradual changes in temperature. Quantitative measurement of freezing or transformation temperatures, however, is usually important. The freezing point of distilled water placed between cover-glasses in the well of the stage was

measured by an alcohol-filled thermometer graduated from $+50^{\circ}$ to -50° C. in degrees. With the bulb of the thermometer in the periphery of the field of a 6X objective and with the asbestos cover in place, readings for the temperature of ice, melting slowly or in equilibrium with water, were consistently 1.5° lower than those recorded with the same thermometer immersed in melting ice to the same extent as when in the cold stage; they were 2° lower than the freezing point indicated by "cooling curve" data. Undoubtedly a temperature gradient exists between top and bottom of the stage, and horizontal or vertical variations in the position of the thermometer bulb may also affect the temperatures it registers to the extent of one or two degrees.

Therefore a specific constant for the stage at a given temperature should be obtained by comparisons with pure compounds of known melting or transformation point, and with the thermometer in a definite location which should be maintained. The temperature at different places in the specimen is in reality reasonably free from any horizontal gradient, since freezing may start or progress equally well from any point.

POSSIBLE IMPROVEMENTS

Based on experience gained from three years' use of the apparatus described, the following modifications are suggested:

The cold stage might well be made thicker to provide a deeper well, so as to decrease the temperature gradient between top and bottom of the cell. The ledges for holding the windows should be made deeper; the bottom one so that

the condenser may be brought nearer the object, the upper one so that objectives of shorter working distance may be used. The stage, as described, cannot be rotated as is desired between crossed Nicol prisms or in the measurement of angles. This limitation is removed if pieces of rubber tubing are inserted in the inlet and outlet lines near the stage, long enough to allow the stage to be rotated 45° to the left and right. The rubber tubing would also permit the horizontal movement of the stage so that more of the specimen might be explored than is possible by moving the cover-glass in the small free space between the cover-glass and the walls of the well.

By cementing the lower window in place, the well could be filled with liquid of low freezing point and immiscible with the specimen. Replacing the air in the well by a liquid would have the advantage of providing quicker and more uniform distribution of heat among stage, specimen, and thermometer. A circulation line of larger capacity, including larger tubing and stopcocks, would provide both quicker extraction of heat from, and lower possible temperatures of, the specimen. The return and feed lines could be shortened by placing the Dewar flask nearer the microscope and the shunt controls on the same side of the microscope as the Dewar flask.

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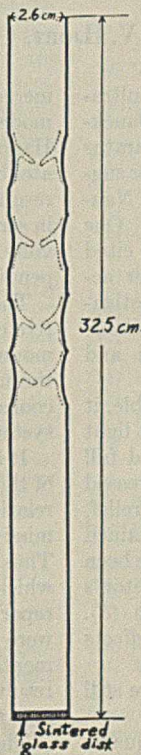
RECEIVED June 8, 1934.

Sintered Glass Absorber for Determining Carbon by Wet Combustion

P. A. WELLS, O. E. MAY, AND C. E. SENSEMAN, Bureau of Chemistry and Soils, Washington, D. C.

THE method of Friedemann and Kendall (2) has been used for several years in the Color and Farm Waste Division for the determination of carbon in fermentation solutions, and is suited for this purpose except for the glass bead absorption column. This type of absorber is inherently inefficient, as Friedemann and Kendall have emphasized that a 50 per cent excess of alkali must be present to insure complete absorption of carbon dioxide. Moreover, it has been found difficult to wash the column of glass beads free of alkali, and ordinary glass beads after several weeks of use are so attacked by the alkali that they can no longer be used.

Various gas-washing bottles have been studied recently by several workers (3, 4, 7, 8), and the spiral and sintered glass (5) filter-plate types found to be the most efficient. Sintered glass disks of Pyrex glass can be made according to the method described first by Bruce and Bent (1) and more recently by Kirk, Craig, and Rosenfels (6). Thomas (9) found that the latter type of absorber was entirely satisfactory for absorbing carbon dioxide, provided a suitable surface tension depressant was added to the alkali. Butyl alcohol used for this purpose appreciably decreased the size of the bubbles and caused frothing, which was desirable. Using butyl alcohol in a concentration of 0.4 per cent, complete absorption of carbon dioxide was possible until practically all the alkali was neutralized.



This type of absorber seemed suitable for the authors' purpose because of its simplicity and its efficiency under the widely varying conditions which are possible. Because suitable commercial bubblers were not available, a number of disks for these absorbers were constructed somewhat after the method of Bruce and Bent (1), the principal variation being that a graphite mold (a type used with satisfaction for several years by the Fertilizer Investigation Laboratory of this bureau) was substituted for the nickel mold. The mold was approximately 5 cm. in diameter and 1 cm. thick, machined out centrally to a depth of 3 mm. and a diameter of 2.7 cm. No cover was needed. Ground Pyrex glass of 80-mesh size was tamped into the mold, after which it was placed in a muffle furnace heated to about 800° C. and allowed to remain for 2 minutes. The sintered disk can be removed immediately from this type of mold, and the mold is then ready for further use.

The type of absorption tower shown in the illustration was found best suited for the purpose. The indentations are necessary to prevent spray from being carried out of the tube. With a tube of this size and 50 cc. of solution, flows of air up to 100 cc. per minute can be used without danger of mechanical loss. The porosity of the disk, as well as the height and diameter of the tube, can be varied to suit individual needs.

The absorber was tested by the method of Friedemann and Kendall (2), in which it was substituted for the usual glass bead column. After complete combustion of the sample (30 minutes' digestion period) the absorber was raised to a convenient height above the bottom of the flask and the alkali washed out with hot water free from carbon dioxide. Usually three washings of 40 cc. each were sufficient. In order to hasten the washing, a hand aspirator connected with a soda-lime tube was used to force the water out of the absorber. The carbonate was then precipitated by adding barium chloride solution, and the stoppered flask was protected with a soda-lime tube while cooling. It has been found convenient to use a mechanical stirrer while titrating the excess alkali. To obtain consistent results, carbon dioxide-free air should be passed over the solution while titrating, particularly when using mechanical agitation, because otherwise air is drawn into the flask. Blanks should be run in exactly the same manner as the determination, to correct for carbon dioxide in the apparatus and reagents.

TABLE I. DETERMINATION OF CARBON BY WET COMBUSTION USING SINTERED GLASS ABSORBER

CARBON TAKEN (AS SODIUM OXALATE)	(Butyl alcohol added, 0.5 per cent)		CARBON FOUND
	SODIUM HYDROXIDE USED IN ABSORBER ^a	PER CENT OF ORIGINAL SODIUM HYDROXIDE UNNEUTRALIZED	
Gram			Gram
0.1435	0.5 N	4.2	0.1430
0.1436	0.5 N	4.2	0.1430
0.1435	0.5 N	4.2	0.1430
0.0722	0.5 N	51.8	0.0724
0.0717	0.5 N	52.2	0.0718
0.0719	0.5 N	52.0	0.0719
0.0278	0.1 N	7.4	0.0277
0.0277	0.1 N	7.6	0.0275
0.0279	0.1 N	7.0	0.0277

^a 50 ml. used.

Typical results with the absorber described, given in Table I, show that the determination of carbon can be carried out successfully with complete absorption of carbon dioxide when less than 5 per cent of the alkali remains unneutralized. This was further evidenced by the fact that no precipitate appeared in a trap tube to which barium hydroxide solution (0.3 N) had been added and through which the air was passed after leaving the absorber.

SUMMARY

The sintered glass absorber described has several advantages over the glass bead absorber previously used for this determination. It is unnecessary to maintain a large excess of alkali and consequently the method has a wider range of application. Washing the alkali from the absorber is easier. Difficulties due to the disintegration of the glass beads by the alkali are eliminated.

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A New Ultraviolet Microscope Illuminator

Preliminary Studies of Its Use with Rayons

THOMAS HILL DAUGHERTY AND ELMER V. HJORT, University of Pittsburgh, Pittsburgh, Pa.

THE analytical uses of fluorescence effects due to ultraviolet irradiations have been summarized by Danckwortt (4) and by Radley and Grant (17). Apparatus for both macro and micro observation has been built or suggested by Lehmann (7), Wasicky (24), Reichert (18), Naumann (11), Auer (2), Silverman (21), and Singer (23). One or more of the following factors limit the equipment cited above: the expense of quartz lenses, slides, and other accessories; unsuitability for both macro and micro investigations; lack of flexibility in making the microscope available for other work; lack of suitable ultraviolet intensity; and inability to use the higher powers of the microscope.

To eliminate these undesirable features as far as possible, it was decided to make use of an oblique cone of ultraviolet light impinging on the object, securing thereby an even and full illumination with the elimination of shadows, an increased depth of focus causing uneven structures to appear in relief, and the production of as true color values as can be obtained with artificial light. For visible light these results have been obtained with the Silverman illuminator (20, 22), Preston's top light illuminator (15), and the Leitz ultrapaque (8). For fluorescence, the last named has secured these effects using glass equipment.

The apparatus described below was designed to secure still further advantages.

The apparatus consists of an enclosed annular quartz

mercury arc (Figures 1 and 2). The experimental quartz model of the arc was built to the writers' specifications by the Hanovia Chemical and Manufacturing Co. This arc operates on line voltages from 110 to 220 direct current, with best results at about 155 volts, and a lamp bank resistance is used in series, such that the voltage drop across the arc is about 85 volts. From 1 to 2 amperes are required for starting, depending on the voltage.

The arc is mounted just above the stage, so that the objective can occupy the position shown in Figures 1 and 2. The mounting is light-proof except for the filters which transmit the ultraviolet rays to the object under examination. It is cooled by fins attached to the arc and by a circulating water system.

It is necessary to use a filter to remove as much as possible of the visible light emitted by the mercury arc (4), because its relative intensity obscures the fluorescence. The transmissivity of different filters may cause confusing phenomena. Thus Kögel (6) reported that certain filters transmit red rays which may be mistaken for red fluorescence. The published reports of fluorescence work often fail to specify what filters were used, and in most reports the use of only one filter is mentioned. To avoid the resulting confusion in reporting results, data obtained with a number of commercially available filters were recorded.

The best results with rayons were obtained by using Heat-

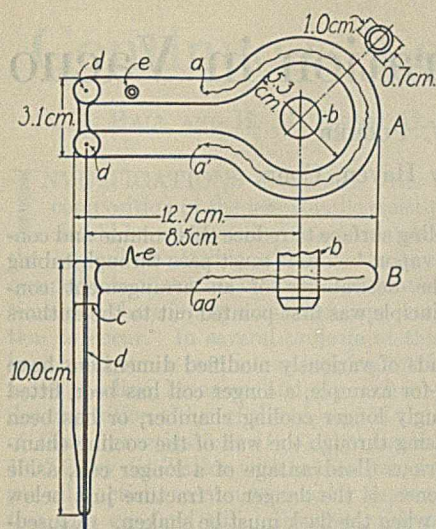


FIGURE 1. ANNULAR MERCURY ARC

- A. Plan
B. Elevation
aa'. Luminous path of arc
b. Position of objective
c. Mercury
d. Tungsten electrodes
e. Evacuation tip (must be on cool part of arc)

with the work of Lewis (10), who showed that the best region for the fluorescence of cellulose products lies in a region of shorter wave length. The silvered quartz filter completely excludes the visible, but is weak in the ultraviolet. Consequently, poor results were obtained with it.

FLUORESCENCE OF RAYONS

The chemical and microscopic methods (1) for the identification of rayons are still tentative. The chemical method is laborious. The use of fluorescence for identifying natural fibers (5, 9, 13) is fairly successful, but the results for rayon are conflicting (12, 14, 16).

The results obtained from the examination of thirty-seven undyed, unmordanted fibers, using the filters which gave the best results, are summarized in Table I. These fibers are authentic samples secured from the leading manufacturers of this country. The word "shadows" as used in the table refers to transmitted visible colors which simulate fluorescence, in accordance with the descriptions used by Nopitsch (12).

TABLE I. FLUORESCENCE CHARACTERISTICS OF RAYONS

FIBER	FILTERS	
	HEAT-RESISTING RED PURPLE ULTRA, 587	UVET GLAS-1 COMBINED WITH UVET GLAS-2
Raw silk	Yellow to buff; brighter than nitrate rayons, paler than viscose	Yellow to buff, much brighter than nitrate and viscose rayons
Cuprammonium rayon	White with purple shadows; bright, whereas acetate rayons are dull	White; bright whereas acetate rayons are dull and tend to be tinted
Nitrate rayon	Pale yellow, without the brown tints present in silk or viscose	Dull, pale yellow without the brown tints in silk; distinction from viscose a matter of observer's experience
Acetate rayon	Dull, white, with or without tinted shadows; much less bright than cuprammonium rayon	Dull, white, usually with tinted shadows; much less bright than cuprammonium rayon, which is not tinted
Viscose rayon	Deep yellow to brown; deeper than the tints of nitrate rayon or raw silk; less bright than raw silk	Faint yellow to buff; easily distinguishable from raw silk; distinction from nitrate rayon a matter of observer's experience

Easily bleached dyed fibers gave substantially the same results as the undyed, and could be recognized even if a slight additional hue was present.

Mixed fabrics revealed the fluorescence of the constituent fibers microscopically, but showed macroscopically a single

Resisting Red Purple Ultra, No. 587 (3), and a combination of the Uvet Glas filters, Nos. 1 and 2 (19), possibly because of a suitable range in the ultraviolet, together with low intensity in the visible. In the case of Violet Ultra, No. 586 (3), the visible is nearly excluded, but no lines are shown with the mercury arc below 3300 Å. The results with this filter were poor, in accordance

color which was a combination of the constituent hues. Although the same type of product made by different manufacturers shows slight differences in the tints obtained, these differences cannot be utilized for identifying the source of the fiber, because they may result from the fluorescence of impurities incidental to the manufacturing and finishing processes.

The method will require study of authentic samples by anyone contemplating using it because of the difficulty of exact description of the colors observed. Further work is desirable, not only for the study of specimens which are difficult to bleach, but also with other ways of treating fibers before testing.

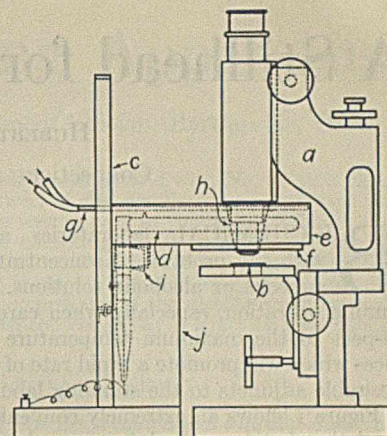


FIGURE 2. USE OF ANNULAR ARC WITH MICROSCOPE

- a. Microscope
b. Slide
c. Arc support
d. Circular arc
e. Shield to enclose arc
f. Filter, 7.94 cm. (3.125 inch) square, with hole in center 1.7 cm. (0.67 inch) diameter. The filters slip into a slot for easy interchanging
g. Water cooling system
h. Metallic cone to shield objective from heat of arc
i. Cooling fins
j. Auxiliary shield

ACKNOWLEDGMENT

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A Stillhead for Rapid Concentration in Vacuo

HUBERT BRADFORD VICKERY AND GEORGE W. PUCHER

Connecticut Agricultural Experiment Station, New Haven, Conn.

BIOCHEMICAL laboratories are frequently faced with the problem of concentrating large volumes of aqueous or alcoholic solutions. This is a time-consuming operation, especially when care must be taken with respect to the maximum temperature permissible, and devices which will promote a rapid rate of distillation are highly desirable adjuncts to the standing laboratory apparatus.

Figure 1 shows an extremely convenient and efficient stillhead that has been used for general concentration purposes in this laboratory during the past 4 years. When this is

together with a cooling surface to reduce this volume and condense a part of the vapor, before it must pass through tubing of small size. The desirability of an arrangement constructed on this principle was first pointed out to the authors by H. A. Spoehr.

A number of heads of variously modified dimensions have been constructed—for example, a longer coil has been fitted into a correspondingly longer cooling chamber, or has been sealed to tubes passing through the wall of the cooling chamber. The most serious disadvantage of a longer coil, aside from its inconvenience, is the danger of fracture just below the rubber stopper when the flask must be shaken. A fused-in coil is more difficult to construct, but is necessary if the presence of rubber must be avoided.

The heads are suspended from an overhead bar by a length of brass chain which contains a spiral spring of the type used for bird cages; this flexible arrangement cares for the rise of the flask in the water bath as the load diminishes, and permits agitation of the flask by hand should this be necessary. The Graham condensers are likewise suspended from chains. These are placed at the end of the bench, or pass through holes cut to accommodate them, and are protected by being wrapped with a single layer of stiff wire gauze. Large filter flasks are employed as receivers; stopcocks in the vacuum line to each permit the stills to be used singly when desired. The supply of water to the cooling coils is controlled independently from that to the condensers.

To begin a distillation, screw pinchclamp *A* on the rubber connection between stillhead and condenser is closed, and the receiver is evacuated. The ring-neck flask is then placed in position in the hot-water bath with the air-inlet tube reaching to the bottom (this tube should not be constricted at the lower end), and the short length of rubber tube at the top is clamped. The neck of the flask is held firmly against the lower surface of the rubber stopper while pinchclamp *A* is opened. Water is admitted to the condenser, and a slow stream of air is allowed to flow through the air-inlet tube. After distillation has begun and any tendency of the solution to froth has subsided, water is admitted very gradually to the cooler coil. The rate of distillation immediately accelerates, and great care must be exercised with many solutions to prevent frothing over. Should this become imminent, the water supply to the cooler is immediately shut off and clamp *A* is closed. New supplies of solution may be added to the flask as needed through the air-inlet tube; when this is done, however, clamp *A* must be closed and the water supply to the cooler shut off. Alternatively, a short length of 2-mm. tubing through the stopper of the flask may be used, with proper connections, to admit a continuous slow stream of fresh solution.

Although primarily designed for the rapid distillation of large volumes of solutions, the stillhead is also advantageous when only small volumes are to be concentrated. The reversed rubber stopper permits the use of ring-neck flasks as small as 500 cc., and the less convenient side-neck distillation flasks are not required. This has many advantages when concentrating a solution previous to crystallization.

RECEIVED June 18, 1934. The expenses incurred in the design of this apparatus were shared by the Connecticut Agricultural Experiment Station and the Carnegie Institution of Washington.

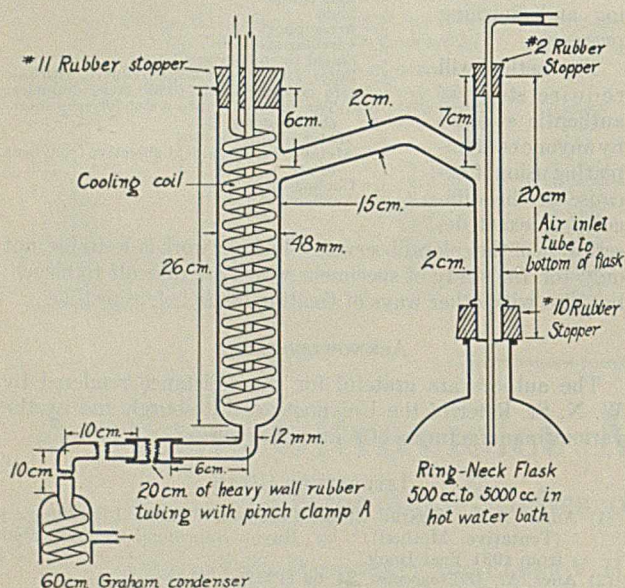


FIGURE 1

attached to a 5-liter flask, a distillation rate of 2 liters of water an hour can be maintained from solutions that do not froth badly, while from alcohol solutions the rate can easily be made to exceed 3 liters an hour. A similar apparatus, on a scale somewhat more than twice as large, and provided with a 5-liter bulb on the vapor tube, when attached to a Pfaunder steam-jacketed laboratory still, permits from 10 to 11 liters of water an hour to be distilled. The cooler coil in this apparatus is constructed of block-tin pipe, and a baffle plate is hung inside the bulb so as to intercept spurts of liquid from the still.

The dimensions given in the diagram are those of the stillheads set up in pairs on each workbench. The apparatus consists of a vapor tube constructed of 2-cm. tubing, furnished with a side arm of the same diameter, which is sealed into the wall of a cooling chamber 48 mm. in diameter. The cooling chamber contains a coil of about 14 turns of 8-mm. tubing suspended from the rubber stopper in the top. The advantage of the apparatus is the provision of relatively large-bore tubing to accommodate the hot expanded vapor,

Continuous Laboratory Topping Apparatus

H. T. RALL AND H. M. SMITH, U. S. Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

INVESTIGATIONS concerned with the character and composition of the less volatile constituents of petroleum should be conducted with material as little changed from the original as possible. This means that the more volatile components of a crude oil must be removed under such conditions that there is only a minimum opportunity for decomposition to occur. In several projects at this station there has been need for a continuous topping method that would remove gasoline, kerosene, and gas oil from petroleum without decomposition either of the tops or of the residuum. In two of these investigations (1, 2) the gasoline was removed at 100° C. by distillation with natural gas, and the kerosene and gas-oil fractions were subsequently removed by steam distillation in a gas-fired still. However, this necessitates heating the oil to several hundred degrees Centigrade, and even with steam there is considerable possibility for decomposition where the oil is in contact with the hot still walls, particularly with certain types of crude oil. In connection with some work now under way, it seemed advisable to develop means of topping that would remove all of the lighter constituents up to oil having a viscosity of about 50 seconds Saybolt without heating the crude above 150° C. The fundamental principle used to accomplish this was that of isothermal evaporation from a thin, heated film of oil at pressures of 2 to 5 mm. of mercury. A few experiments indicated that, in addition, a short fractionating column and the sweeping action of a small stream of inert gas would help considerably in obtaining the desired objectives. The fractionating column virtually eliminated overlap between distillate and residuum, while the small gas stream, countercurrent to the oil flow, besides substantially reducing the effective evaporation pressure of the oil, continuously removed the more or less stagnant layer of heavy vapors formed by evaporation from the oil film.

DESCRIPTION OF APPARATUS

As a result of several experiments the apparatus shown in Figure 1 was developed. It consists essentially of two independent parts, the heating circuit and the topping system

The heat needed by the process is supplied by the hot vapors of a liquid boiling in the flask, A. These vapors ascend through line B, enter the outside chamber of isothermal heating unit C at the top, and pass through the chamber and out at the bottom to D, where they are condensed and returned to the boiler, completing the circuit for the heating medium. The temperature of the vapor leaving the bottom of the still is determined by thermometer E. In practice, the vapor stream should have a velocity and volume sufficient to maintain this temperature constant, whether or not the topping section is being used.

The topping system may be considered conveniently by following first the path of the crude oil through the apparatus and then the course of the gas and vapors. The crude oil to be topped is poured into storage flask F through strainer G and drawn by the vacuum in the system through line H and control cock I into degasser and foam breaker J. The crude then enters the top of the isothermal heating chamber C through stopcock K and dripper L. The heating chamber is simply an eight-bulb condenser; the four top bulbs are packed with No. 18 steel jack chain, and the four bottom bulbs are empty. The chain provides much surface and serves as a heat reservoir to heat the cool, incoming crude oil quickly. The oil passes downward through the still and eventually runs out of dripper M into topped-oil receiving flask N. By proper manipulation of stopcock O, flask N may be removed, emptied, and re-evacuated without stopping the distillation.

While the crude oil is flowing downward through the heater, a small stream of inert gas is admitted in the center of the bottom bulb at P. This gas rises countercurrent to the descending oil film and carries the vapors evaporated from the crude into frac-

tionating tower Q, which is also packed with No. 18 jack chain. Here the heavier fractions of the distillates are separated and washed back, while the vapors pass to condenser R where they liquefy, the condensate collecting in the receiver, S. The gas passes through flask S and line T to the vacuum pump and thence to the atmosphere. It is essential that receiver S be kept cold enough so that the vapor pressure of the distillate will be negligible. For the same reason condenser R must be cold enough to liquefy all vapors.

The operating procedure is as follows:

The entire topping system is evacuated to a constant minimum pressure which should be 2 mm. or less.¹ Nitrogen or natural

¹ If the apparatus is absolutely free of leaks and of material having a measurable vapor pressure at the temperature of the manometer, the pressure indication should be zero. In practice these conditions are not completely fulfilled.

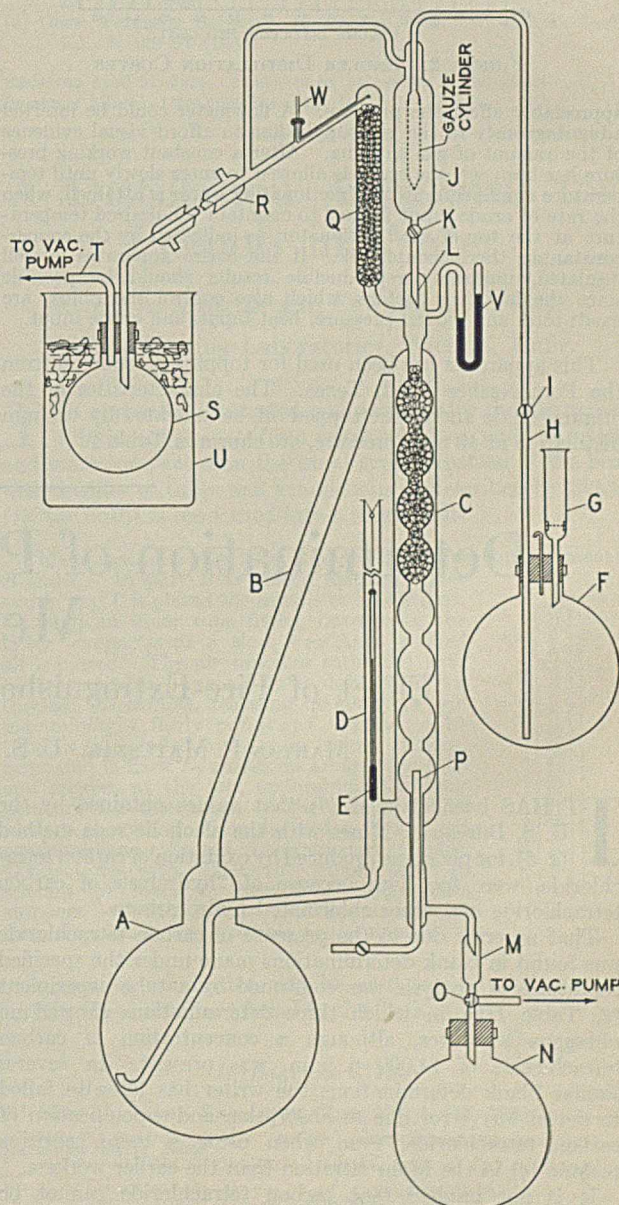


FIGURE 1. ISOTHERMAL CRUDE OIL TOPPING UNIT

gas is then admitted until the manometer remains constant at the working pressure, generally 8 to 20 mm. of mercury, depending upon the extent of topping desired. This gas supply is easily controlled by a fine needle valve which has a constant pressure of one pound per square inch (0.07 kg. per sq. cm.) gage on the inlet side, so that in effect the needle valve acts as a flowmeter, and, once the initial evacuation pressure and working pressure have been fixed, there will be no fluctuation unless leaks develop. There will be small amounts of dissolved gas evolved from the crude, but, if the pump has ample capacity and the crude input to the degasser is kept reasonably constant, these gases will not

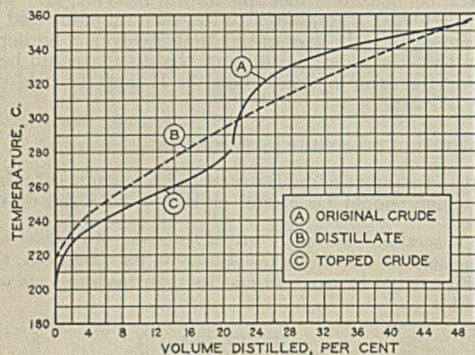


FIGURE 2. ENGLER DISTILLATION CURVES

appreciably affect the pressure. A flowmeter could be inserted advantageously in the gas supply line to afford visual evidence of the amount of gas entering. After a constant working pressure has been set, the crude is allowed to enter slowly until temperature equilibrium in the fractionating tower is attained, when the rate of crude input is fixed to maintain the desired temperature at the top of the fractionator, as indicated by the copper-constantan thermocouple, *W*. If the entire apparatus is well insulated, uniformly reproducible results should be possible since the following factors, which also control the reflux, are fixed: total and partial pressure, heat input, and crude input.

This apparatus has been used for topping a crude oil from the Port Neches Field, Texas. The characteristics of the original crude and of the topped oil, as indicated by vacuum distillation at 40 mm. pressure, are shown in Table I.

TABLE I. VACUUM DISTILLATION AT 40 MM. PRESSURE

Initial temp., ° C.	ORIGINAL CRUDE 114	TOPPED CRUDE ^a 194
Per cent distilled at 125° C.	1.35	0.0
150° C.	6.60	0.0
175° C.	15.70	0.0
200° C.	26.20	1.2
225° C.	35.75	11.5
250° C.	43.55	21.0

^a Topped at 158° C. (boiling turpentine) and 19 mm. total pressure with about 16 mm. partial pressure of natural gas.

A four-unit apparatus has also been constructed, in which the units are connected in parallel to the crude-oil source, topped-oil receiver, gas inlet, distillate receiver, and vacuum pump. Topped oil from this apparatus, using nitrogen as the inert gas and a temperature of 158° C., shows virtually the same characteristics as that given in Table I. There is a small gap between the topped oil and the distillate, as shown in Figure 2, where distillation curves for the crude oil, topped oil, and distillate are given. These are all made with a standard Engler apparatus. The curves indicate that the separation is fairly sharp.

The apparatus described is very flexible from an operating standpoint. Liquids covering a wide range of boiling points may be used as the heating medium, and pressures may be varied over a considerable latitude. The partial pressures of the gas used may also be changed to suit conditions, as may the kind of gas used. It is obvious that the capacity of such an apparatus is small. The four-unit set-up has a capacity of 200 to 300 grams of topped oil per hour when used with the crude oil mentioned above under conditions removing about 21 per cent of the crude. The apparatus may be constructed readily from materials usually available in the laboratory.

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RECEIVED May 25, 1934. Presented before the Division of Petroleum Chemistry at the 12th Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., May 3 to 5, 1934. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Determination of Phosgene by the Soda Method

Effect of Fire-Extinguisher Chlorinated Hydrocarbons

MARYAN P. MATUSZAK,¹ U. S. Bureau of Mines, Pittsburgh, Pa.

IT HAS been claimed (6) that values obtained by the U. S. Bureau of Mines with the alcoholic soda method (2, 3), for phosgene produced by oxidation of carbon tetrachloride, were too high because of "hydrolysis of carbon tetrachloride and other chlorinated hydrocarbons."

That no error due to the presence of carbon tetrachloride was found in blank determinations made under the specified conditions of analysis was confirmed by a tube experiment (2, Table III), in which three determinations showed no phosgene whatever, although a concentration of carbon tetrachloride of 14,000 p. p. m. was present. In several similar blank determinations the writer has likewise failed to detect any error due to absorption and saponification of carbon tetrachloride, even when using a more sensitive technic (4) in the Mohr titration than the earlier workers.

It is not implied that carbon tetrachloride cannot be

¹ Present address, 301 South Creek Ave., Bartlesville, Okla.

saponified by alcoholic soda. But if the conditions of analysis used in the earlier work—absorption, at 0.5 liter per minute, of 4 or 5 liters of air containing carbon tetrachloride up to 5850 p. p. m., or of 0.5 to 1 liter containing up to 14,700 p. p. m., by a petticoat-bubbler absorber containing 50 cc. of *N* sodium hydroxide in 85 per cent alcohol—are maintained, and if neutralization is not unreasonably delayed, no error due to this compound is present.

Chloroform, the next most abundant component of commercial fire-extinguisher liquids, saponifies more readily than carbon tetrachloride (5). Hence, experiments were made to determine the concentration at which it causes a detectable error under the conditions of analysis.

Chloroform-containing air samples, 5.08 liters in volume, were absorbed by 50 cc. of *N* sodium hydroxide in 85 per cent alcohol in a petticoat-bubbler absorber during 10.5 minutes. The Mohr determinations were made with great care. Neutrali-

zation was made to phenolphthalein with nitric acid, concentrated at first and 0.25 *N* near the end. Although no effort was made to hurry the work, neutralization was usually made within about 10 minutes after absorption. Heat liberated during neutralization was removed by cooling with tap water, to avoid decreasing the sensitivity of the chromate indicator. Then 1 cc. of *M* sodium bicarbonate was added, to insure a pH of about 9, and 1 cc. of 10 per cent potassium chromate.

Comparison of the titrated solution was made by reflected (not transmitted) yellowish light against a gray background with a freshly prepared reference solution containing similar amounts of reagents and a slight excess of sodium chloride. Some flasks of Pyrex glass made the yellow solution appear darker than others, an effect that appeared to be independent of wall-thickness; hence, the flasks used were matched to eliminate this effect. Titrations were continued until the reddish end point persisted for at least 5 minutes. This sometimes took 15 minutes or more, for although an apparently permanent end point was reached with the first 2 or 3 drops of 0.00818 *N* silver nitrate, a much larger volume could be added after several minutes. The data are given in Table I.

TABLE I. ABSORPTION AND SAPONIFICATION OF CHLOROFORM

CHLOROFORM <i>P. p. m.</i>	APPARENT PHOSGENE <i>P. p. m.</i>	CHLOROFORM <i>P. p. m.</i>	APPARENT PHOSGENE <i>P. p. m.</i>
1000	0	3990	43
1410	3	6410	89
1430	2	6780	92
1496	3	8170	113
1950	16	10920	153
2810	44	14500	196
2830	43	14600	190

Since, in the fire experiments (2, Table II), the concentration of fire-extinguisher liquids varied from 2000 to 5130 p. p. m. (calculated as carbon tetrachloride) and since only about 10 per cent of this was introduced as chloroform, no error due to absorption and saponification of this compound was present. Such error, even with the more sensitive titration technic, does not begin to appear until the chloroform concentration is at least twice the maximum introduced in the fire experiments.

In the tube experiments (2, Table IV) the initial concentration of chloroform was of the order of 1400 p. p. m. But, even if it all escaped decomposition or oxidation—which could scarcely have been true, as the total concentration of chlorinated hydrocarbons decreased by about 38 per cent—a detectable error was unlikely, as the air samples and the absorption periods were only one-fifth or one-tenth as large as those used in obtaining the data of Table I. Moreover, any possible error must have been negligible in comparison with the phosgene reported, 3700 to 3800 p. p. m.

Other experiments showed that Pyrene, a typical fire-extinguisher liquid (2, No. 1), was several times more resistant to saponification than chloroform, indicating that the values of 15 to 60 p. p. m. for phosgene found in fire-gases by the Bureau of Mines were not subject to any appreciable error because of chlorinated hydrocarbons introduced as fire-extinguisher liquids.

The alleged high soda values obtained by other workers (6) were probably due to insufficient removal of hydrogen chloride or precipitation of silver carbonate in the Mohr titration (4). The former appears to account for the only numerical data published in support of the alleged error, which were obtained with the unpurified gas from a toluene solution of phosgene and not with purified fire-gases; the latter, for the high values obtained in experiments on the thermal decomposition of mixtures containing carbon tetrachloride, for which no numerical data were published. Such error would be the more prominent the larger the air samples taken for analysis.

The soda method can be improved by acidifying with nitric acid and boiling out the carbon dioxide before neutralizing and titrating, and can also be rendered less objectionable by eliminating the use of alcohol. Aqueous *N* sodium

hydroxide absorbs phosgene very effectively and is more stable and absorbs less chlorinated hydrocarbons.

The method of purification of fire-gases with zinc and mercuric sulfide (1) is preferable to the original method of purifying with silver nitrate and antimony trisulfide (2). The principal objection to the older method—that nitric acid, formed in the removal of hydrogen chloride by silver nitrate, reacts with antimony trisulfide to give hydrogen sulfide—is obviously inoperative if the gas is passed first over antimony trisulfide and then over silver nitrate, for any hydrogen sulfide formed by reaction of the former with hydrogen chloride is removed by the latter.

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A Distillation Apparatus for Phenols in Water

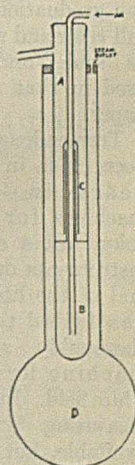
ELDON A. MEANES AND EDWARD L. NEWMAN

Wichita Testing Laboratories, Wichita, Kans.

THE apparatus illustrated was designed for the steam distillation of phenols from water solutions, and is simpler and more compact than the usual type. Instead of the box with a series of tubes and connections as described by Shaw (1), the outfit is condensed into a single unit.

This consists of a glass tube, *A*, divided into two compartments *B* and *C*. In part *B* is placed distilled water and in part *C* is placed the sample to be distilled. Through an inner tube fitting down into the lower compartment a slow stream of washed air is passed. The air becomes saturated with moisture and passing up is deflected down through the sample, releasing its moisture and maintaining a fairly constant volume. The tube is surrounded by a glass jacket. Steam, generated in flask *D*, passes up around the tube and escapes at the top, maintaining the temperature for distillation of the sample. The phenols present are thus distilled over and are condensed and collected in a graduated cylinder. Connections with which the vapors come in contact are made by means of ground-glass stoppers. No rubber tubes or stoppers are used, thus eliminating any possible contamination.

Any suitable indicator may be used to ascertain the amount of phenol in the distillate.



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RECEIVED July 11, 1934.



The Tonometer

Study of Color and Brightness of White Films

L. A. WETLAUFER, E. I. du Pont de Nemours & Co., Inc., Philadelphia, Pa.

A STUDY of the paint and enamel films commonly referred to as whites reveals that very few can be classified spectrophotometrically as nonselective, and among those which are nonselective none reflect 100 per cent of the light. In other words, these opaque surfaces generally either contain coloring matter or are gray with respect to pure white. In fact, those who manufacture or use white coatings frequently complain that there are more significant visual color and brightness differences among commercial whites than among any common group of full colors.

These small variations in color are of more importance than is generally recognized. The question of whether a white is pleasing to the eye often depends on small traces of unsuspected color, and in the manufacture of quality white coatings a close control of color is both necessary and difficult. In addition, all organic coatings change slowly in color on aging, and the nature and amount of these changes frequently measure the practical value of the coating.

In dealing with whites, the three factors of major importance are brightness or total reflection, the hue toward which the sample deviates from pure white, and the extent of this deviation. This latter, which is the most important, might be called depth of tint, but Ridgway (5) has spoken of the graduations between a full color and white or black as "tone," and the term is used in that sense in this paper.

Tremendous strides have been made in the last few years in developing machines for measuring color, but a survey of the instruments on the market and of the literature (1, 4) has failed to disclose a thoroughly satisfactory machine for the so-called white field. Instruments for measuring brightness are available, but they do not satisfactorily measure color. The ordinary color analyzer, which measures the relative intensity of the reflected light at various wave lengths, is not sufficiently practical in the region ap-

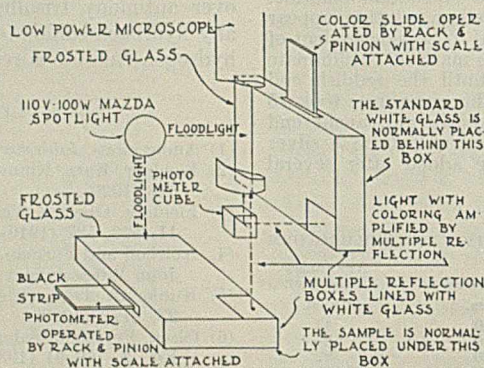


FIGURE 1. DIAGRAM OF TONOMETER

proaching white, because the variation in the intensity between different wave lengths is small compared with the total intensity at all wave lengths. Instruments, such as the Pfund tintometer (manufactured by the Munsell Color Company), fail to allow for important hue variations.

Fortunately, the problem of measuring the color of commercial whites is simplified by the fact that the deviation from pure white is almost always toward some member of the yellow family, or toward the complementary blues which are added to neutralize the yellow color

of all common organic vehicles. The problem in its simplest form consists therefore of measuring the yellowness or blueness of these white coatings. Based on this principle, the Pfund tintometer measures the yellowness of the coating by measuring the amount of blue glass which must be inserted into the reflection from the sample to neutralize the yellow present. The accuracy is greatly increased by using the principle of multiple reflection to intensify the tone to the point where it can be accurately measured. Difficulty is encountered in securing a permanent blue glass which is the true complement of yellow, and no allowance is made for the fact that

hue variations in the yellow present have an important bearing on the appearance of the white. In spite of these disadvantages, it is felt that the Pfund instrument has greater merit for the purposes under consideration than any of the color instruments examined.

The instrument described in this paper utilizes the multiple-reflection principle of the Pfund tintometer, but measures normally the amount of yellow glass which must be inserted into the reflection from a standard white to match the color of the sample. Standard yellow glasses of good color permanence have been secured in graded steps to cover the range of yellow hues commonly encountered in white coatings. This includes the range from green-yellow to red-yellow. This instrument has been designed for practical use in the ordinary control or research laboratory. It is simple in

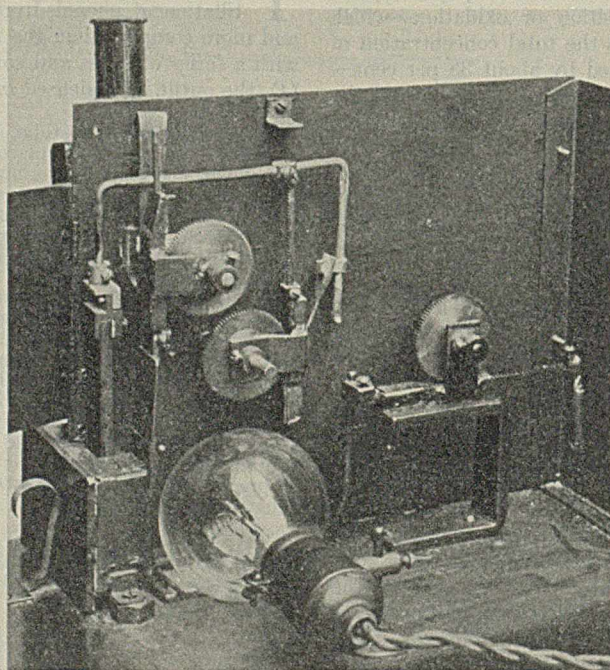


FIGURE 2. TONOMETER WITH BACK AND ONE SIDE OF HOUSING REMOVED

Racks and pinions control movements of black-strip photometer, color slides, and auxiliary shutter over upper reflecting box. Projecting into top of reflecting box is one of color slides. Other reflecting box is directly beneath lamp.

design and operation; is relatively inexpensive to construct; requires only a short time for each reading; and gives almost no bleaching of the sample during the test. The readings have a direct significance and permit easy visualization of color differences from an inspection of tabulated data.

In use for the last six months, the instrument has proved of value in connection with a number of important problems. It has been used to maintain a constant standard in controlling

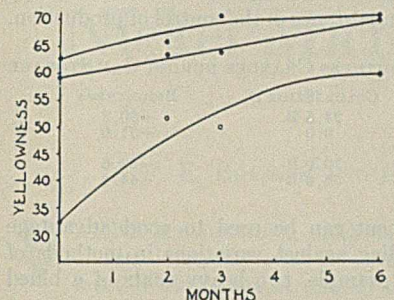


FIGURE 3. YELLOWING OF WHITE AIR-DRY ENAMELS EXPOSED TO DIFFUSED LIGHT

the production of certain products, where both dry plate and wet standards have a tendency to drift. It has been used to study the effect of film thickness and baking conditions on color, and has proved invaluable in following the changes in color which take place during the aging of white coatings under various conditions of exposure.

APPARATUS AND METHOD

Some of the instruments for measuring color, such as the Razez-Mulder (2), the Keuffel and Esser (3), and the Pfund, have means for amplifying color differences either by scale readings or appearance of actual color. In developing the tonometer, account was taken of these two types of amplification. Scale amplification is a simple mechanical problem. Color amplification is accomplished by the use of multiple reflection boxes. The instrument is self-contained and mounted on a base-board 19.25 inches long and 10 inches wide. Its working parts are built in and around a housing of aluminum 11 inches long, 8.75 inches high, and 6 inches deep. It should be possible to construct the instrument in the average plant shop for less than \$200. A diagrammatic representation is shown in Figure 1.

Two boxes, each 2 inches wide, 3 inches long, and 1 inch deep, are used to obtain the degree of multiple reflection desired. These boxes are lined with an opal glass far enough on the blue side of theoretical white, so that the majority of readings are in one direction from this arbitrarily selected glass standard. The openings through which the light enters are covered with diffusing glass in order to obtain even diffusion of light. The boxes are illuminated by a 110-volt, 100-watt Mazda spotlight. The light emerges from the end opposite the light entrance and the two fields are brought into juxtaposition by means of a photometer cube. The combined fields are then viewed through a lens system, a low-power microscope being used in the present assembly.

A slot is cut in one side of the upper reflecting box, as indicated. A color slide is introduced through this slot to vary the yellowness of the light which is directed into the eyepiece. The opal glass covering one 2 x 3 inch side of each box is easily removable to permit substitution of a sample to be measured. Normally, commercial whites are on the yellow side of the arbitrary standard, and the sample then is placed over the box opposite that in which the color slide is used. Employing this procedure, it will be seen that the instrument is a color synthesizer rather than a color analyzer.

Obviously, as a color slide is introduced into one of the fields, the brightness of that field is reduced, making a color depth (saturation) match difficult. To compensate for this undesirable feature, a slot, similar to the one through which the color slide is operated, is cut in one side of the other box through which a black strip may be introduced to equalize the brightness of the two fields while obtaining the color match. This black strip may be used, with the color slide removed, for making actual brightness determinations. A difficulty arises, however, in that the eye is not capable of entirely eliminating the effect of color differences when attempting to compare brightness. To obviate

this, a green glass is placed over the photometer cube, thus covering both fields. Green successfully masks color differences in the normal range of hues encountered. It is not satisfactory for the purples, but these hues seldom occur in commercial whites.

Both color slide and black strip are attached to racks and pinions for convenience of operation. Scales are attached to these racks and pinions, so that quantitative measurements of color depth and brightness may be recorded. The scales are divided into arbitrary units of such magnitude that, when taking into account the degree of multiple reflection employed, the least significant figures represent differences slightly greater than the average eye is able to detect.

The opal glass standard is checked against magnesium oxide, the accepted standard for whiteness. The magnesium oxide is applied to a flat surface (a piece of the white glass is suitable) by burning magnesium ribbon and allowing the oxide to condense on the surface. After a coat about 0.002 inch in thickness is obtained, a reading for color should yield a value of 39.3 Y, indicating that the opal glass is 39.3 points on the blue side of pure white. The "black-strip" photometer is checked at the same time and should yield a value of +67.5, indicating that the opal glass is 67.5 points on the gray side of pure white. Table I is a typical set of calibration readings.

TABLE I. CALIBRATION OF WHITE GLASS vs. MAGNESIUM OXIDE

	COLOR 4		BRIGHTNESS	
	First operator	Second operator	First operator	Second operator
Magnesium oxide	40 Y	38 Y	+67	+71
Magnesium oxide check	40 Y	39 Y	+67	+65
Magnesium oxide check	38 Y	42 Y	+68	+68
Magnesium oxide check	40 Y	41 Y	+67	+69
Magnesium oxide check	38 Y	39 Y	+66	+67
Magnesium oxide check	38 Y	39 Y	+67	+68
Average	39 Y	39.7 Y	+67	+68

The color slides vary from green-yellow to red-yellow. Each slide is cut so that a sample will yield essentially the same yellowness reading with the two slides closest to it in hue, thus indicating that all slides have for practical purposes the same yellow saturation. Five slides are in use at present, selected on the basis of practical experiments. These slides are numbered, the greenest yellow being No. 1 and the reddest yellow No. 5. Table II shows some of the results from which the final series was selected.

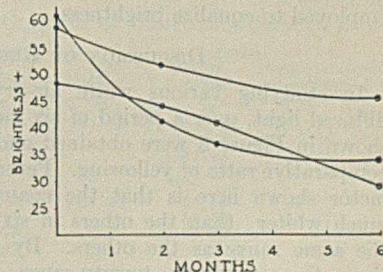


FIGURE 4. BRIGHTNESS OF WHITE AIR-DRY ENAMELS EXPOSED TO DIFFUSED LIGHT

TABLE II. CALIBRATION VALUES FOR SELECTION OF COLOR SLIDE SERIES

FILM	YELLOW GLASS	YELLOWNESS
Excessive red tone	4	84 Y
	5	84 Y (best match)
Red tone	3	60 Y
	4	55 Y (best match)
	5	55 Y
Natural white	1	84 Y (best match)
	2	84 Y
Natural white	1	83 Y (best match)
	2	82 Y
Blue tone	1	65 B (best match)
	2	65 B
Badly yellowed panel (slight red tone)	1	106 Y (best match)
	2	110 Y
	3	104 Y

One bulb (Figure 2) illuminates both reflecting boxes. Any variation in light intensity is therefore equalized in both fields. The lamp is attached to a post by means of a set screw, and may be moved in a vertical direction or a

horizontal circular motion. This permits flexibility in establishing the position of the lamp, which gives the best match when the standard opal glass is placed over both fields.

An actual determination ordinarily requires but a few minutes. If the sample is yellower than the standard opal glass, it is placed over the reflecting box opposite the one in which the color slide is introduced. If it is bluer than the standard, it is placed over the box in which the color slide is used. Having properly placed the sample, a color slide is attached and run into the field. If the hue is not right—e. g., if it is too red—a color slide less red in hue is tried. With relatively little experience, the correct slide can be quickly selected. With this slide in position, its depth in the field is varied, at the same time adjusting the brightness with the photometer. When a match is obtained, the reading on the color scale is observed. When the sample is yellower than standard, the letter Y is used in connection with the numerical value, and when it is bluer the letter B is used. In addition, the number of the color slide employed is recorded, and indicates the hue position in the color slide series. An example of a recorded measurement is Color (No. 3), 62 Y.

Now, by removing the color slide from the field and placing the green glass over the photometer cube, a brightness measurement may be made. If the sample is brighter than the standard, it is placed over the box in which the black strip is employed, or, if less bright than the standard, over the other box. The photometer is now adjusted until a match is obtained. If brighter than standard, the plus sign is used with the numerical value, and if less bright than standard, the minus sign is used. An example of a recorded measurement is Brightness, +45. At least three readings each for color and brightness must be made and averaged for final results.

In practically all cases, films which are yellower than the opal glass are also brighter. In rare instances, however, a yellower but less bright film is encountered, which is difficult to handle in that, while obtaining the color measurement, the black strip cannot be used for equalizing brightness. For this purpose a sliding shutter, attached above the light entrance to the box in which the color slide is used, may be employed to equalize brightness.

DISCUSSION OF RESULTS

In studying various white air-dry enamels exposed in diffused light, over a period of six months, the color results shown in Figure 3 were obtained and show at a glance the comparative rates of yellowing. Perhaps the most significant factor shown here is that the enamel which was initially much whiter than the others in six months yellowed into the same range as the others. By actual computation of time, these readings, twenty-seven in number (three for each point), required less than one-half hour. To have made comparisons at periodic intervals against freshly prepared control panels would have required much tedious work and would have been limited in value by possible color changes in the can during aging. Brightness measurements, shown in Figure 4, indicate a gradual graying on aging in all cases, although the rate of graying varies considerably.

TABLE III. EFFECT OF TEMPERATURE VARIATIONS ON COLOR AND BRIGHTNESS

	TEMPERATURE OF BAKE ° F.	COLOR (SLIDE 3)	BRIGHTNESS
1	258	48.3 Y	+40.3
	263	51.6 Y	+37.3
2	258	53.8 Y	+34.3
	261	55.2 Y	+44.6
3	258	48.0 Y	+47.6
	263	49.6 Y	+40.8

Another series, represented by Figure 5, was designed to measure the changes which occur in white baking enamels during the first few days of exposure. The exposures were outdoors, diffused light, and dark. Practically no change is noted in the panel exposed in the dark, appreciable bleaching and then gradual yellowing is seen in the diffused light

exposures, and rapid bleaching and then fairly rapid yellowing in the outdoor exposure. Brightness measurements during this period show no appreciable change.

The instrument has also been used to detect the effect of temperature variations in baking, as shown in Table III.

Valuable data are being obtained upon color and brightness changes in the can upon aging. Two blued whites yielded the results shown in Table IV. These variations represent very appreciable differences to the unaided eye and appear of especial importance in the control of production.

TABLE IV. COLOR BRIGHTNESS CHANGES DURING CAN STORAGE

	COLOR (SLIDE 1)	BRIGHTNESS
Initial 1 month	24.5 B	+30.3
	0.0	+31.0
Initial 3 months	70.0 B	-52.6
	56.0 B	-44.0

Finally, the instrument can be used to good advantage in studying and guarding against variations in methods of film application. For example, two heavy coats of a blued

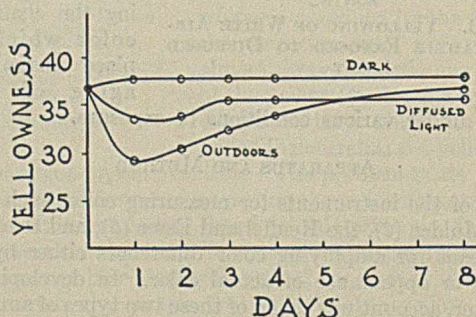


FIGURE 5. BLEACHING AND YELLOWING OF WHITE AIR-DRY ENAMELS DURING INITIAL STAGES OF EXPOSURE

enamel sprayed on steel yielded the readings 15 Y and +40. One coat on steel gave readings of 40 B and -20. The film thickness of the two coats was 0.005 inch and of the one coat 0.0013 inch.

Differences in gloss apparently do not affect the readings for color and brightness. This has been checked by lightly sand-blasting a piece of the white glass used as standard and comparing it with a piece of the glass as normally employed. This comparison, representing a wide difference in gloss, revealed no significant differences in color and brightness.

SUMMARY

There is need for a more practical color instrument designed primarily for the measurement of yellowness in white films, which will yield approximate general hue matches, and which can also be used for brightness measurements. Such an instrument must offer a direct, rapid, and accurate method; must be extremely simple to operate; must yield results which are of immediate practical significance; and must be relatively inexpensive to construct. The instrument which is described may be used for studying the initial yellowness and brightness of white coatings and for classifying them with respect to other hues which may be present; for the study of film aging with respect to these properties; for determining the effect of temperature variation; for determining can stability with regard to yellowness and brightness; and for measuring the effect of variations in film application, due particularly to differences in film thickness.

ACKNOWLEDGMENT

Acknowledgment is made to C. F. Rassweiler and H. H. Hopkins for helpful suggestions and to J. B. Gregor for assistance in calibration and development of data.

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RECEIVED April 26, 1934. Presented before the Division of Paint and Varnish Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 25 to 30, 1934.

Nickel Microbomb for Microestimation of Organic Arsenic

F. E. BEAMISH AND H. L. COLLINS, University of Toronto, Toronto, Ontario, Canada

VARIOUS macrofusion methods for the determination of organic arsenic have been proposed from time to time, most of which may be roughly divided into two classes: In the one decomposition is brought about by wet methods and in the other the compound is subjected to a dry fusion in an open crucible. Many of these procedures are not only tedious of operation, but cannot be applied to compounds such as cacodylic acid which are difficult to decompose.

St. Warunis (5) fused the organic compounds with sodium peroxide and sodium nitrate in a nickel crucible, and determined the arsenic as magnesium pyroarsenate. Pringsheim (4) used sodium peroxide and a silver crucible, determining the arsenic as the pyroarsenate. Parr (2) determined the arsenic in inorganic substances by means of a sodium peroxide explosion using a bomb, but he does not state in detail the method used.

It was decided to determine whether or not a sodium peroxide-sugar explosion in a microbomb could be used to convert organic arsenic completely to sodium arsenate, and also whether the delay of a subsequent precipitation could be avoided. The steel bomb described by the author (1) was at first tried. A precipitation of arsenic was found necessary because of the presence of iron and chromium in the products of corrosion from the steel cup. The method then became lengthy and offered no advantage over present micromethods.

In order to avoid this complication the nickel cup was made, as described (1). The lock used was made similar to that provided as standard equipment for the standard macro sulfur bomb. A handle, designed for removing the cap, facilitates manipulation. The amount of corrosion was much less than that obtained from the steel cup, and proved to have no effect on the direct titration against the iodine liberated from potassium iodide by the sodium arsenate formed.

PROCEDURE

Place 20 to 25 mg. of sucrose, measured by means of a scoop constructed for the purpose, in the bomb and add the weighed sample, which is adjusted to contain about 1.5 to 3 mg. of arsenic. Add approximately 1 gram of sodium peroxide, also measured by means of a scoop. Place the lid on the cup, taking care that a nonpitted gasket is in place. Mix the charge thoroughly by shaking the bomb violently for at least 2 minutes. Tap the bomb on the table several times to insure that the charge is all in the bottom of the cup. Ignite by heating in the tip of a small hot flame for 35 to 40 seconds. Allow the bomb to stand in the air for 5 seconds and then cool and rinse it by immersing in cold distilled water.

Remove the lid from the bomb, washing it off into a Pyrex tube of 35-mm. inside diameter and 155-mm. inside length. Add almost enough water to cover the cup, which has been placed on its side in the bottom of the test tube, and warm to bring about the solution of the fusion. When the fusion is dissolved remove the cup by means of a looped nickel wire and rinse it with hot water.

At this time the volume of the liquid should be about 25 to 30 cc. Boil the solution in the test tube by means of a low flame

from a microburner. A few glass beads aid in preventing bumping. The boiling should be continued until the volume has been reduced to about 10 cc. This also insures the removal of hydrogen peroxide. Cool the solution and add 12 cc. of 12 *N* hydrochloric acid which has been previously freed from chlorine and dissolved oxygen by boiling for 2 minutes as recommended by Pregl (3). Cool the solution to room temperature by placing the tube in a water bath. Add 1 cc. of freshly prepared 10 per cent potassium iodide solution, allow the solution to stand for exactly 3 minutes, and then titrate with 0.01 *N* sodium thiosulfate solution until only a faint yellow color remains. Add 3 drops of freshly prepared 1 per cent starch solution and titrate to the usual end point. The color should not return for at least 5 minutes, but may become darker on prolonged exposure to the air. A blank, determined for the reagents being used, should be deducted. The blank is quite consistent and should not amount to more than 0.3 cc.

The method was found to apply over a range of typical organic arsenic compounds, and Table I shows a few of the results obtained on some of the compounds employed.

TABLE I. ARSENIC CONTENT OF COMPOUNDS ANALYZED

SUBSTANCE	WEIGHT OF SAMPLE Mg.	ARSENIC		
		Calculated %	Determined %	Pregl standard micromethod %
Butylarsonic acid	6.855	41.17	41.35	41.16
	6.540		41.38	41.31
	6.225		41.45	41.30
	5.760		41.50	...
Cacodylic acid	4.585	54.26	54.18	54.04
	5.019		54.12	54.31
	4.979		53.98	...
	4.693		54.09	...
Phenylarsonic acid	5.925	37.10	36.93	36.64
	7.925		36.51	36.96
	4.705		36.64	36.72
	5.635		36.95	...
Triphenylarsine	9.716	24.49	24.44	24.35
	11.918		24.43	24.42
	11.624		24.43	...
	11.464		24.55	...
Sodium-p-hydroxyphenylarsonic acid	9.550	28.61	29.95	29.83
	7.258		30.04	29.62
	9.825		29.88	...
	9.705		29.85	...

This method was found to be equally effective with semi-microsamples (Table II).

TABLE II. ARSENIC CONTENT OF COMPOUNDS ANALYZED USING SEMI-MICROSAMPLES

SUBSTANCE	WEIGHT OF SAMPLE Mg.	ARSENIC		
		Calculated %	Semi-micro %	Pregl standard micromethod %
Triphenylarsine	22.254	24.49	24.47	24.35
	19.375		24.51	24.42
	18.996		24.33	...
Cacodylic acid	12.370	54.26	53.91	54.04
	8.447		54.14	54.31
	7.027		54.17	...

The procedure employed is similar to that given above. The amount of sodium peroxide should be increased to 1.5 grams, the volume reduced to 15 cc., and 15 cc. of hydrochloric acid added.

Before titrating, 3 cc. of 10 per cent potassium iodide are added and the customary 3 minutes allowed to elapse. The titration is then carried out as above, using 0.03 *N* sodium thiosulfate. It will not be necessary for all operators to use starch in detecting this end point.

The 0.01 *N* sodium thiosulfate solution is standardized by means of pure arsenious oxide, treating from 2.5 to 3.5 mg. A blank should be run and deducted.

In order to check the arsenic factor thus obtained, the sodium thiosulfate was also titrated against resublimed iodine and against the iodine liberated from potassium iodide by potassium iodate. The three factors obtained checked within experimental error.

SUMMARY

The arsenic content of organic compounds may be determined by means of a sodium peroxide-sugar explosion in a

nickel microbomb much more rapidly than by existing micro-methods and with the same degree of accuracy. A duplicate determination, including the weighings and final titrations, may be made in 50 minutes.

ACKNOWLEDGMENT

The authors are indebted to H. E. Woodward and F. Bremner who checked the analyses using the standard micromethod of Pregl (3).

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RECEIVED June 8, 1934.

Removal of Samples of Oil from Oil-Impregnated Paper

JOHN D. PIPER, The Detroit Edison Company, Detroit, Mich.

WHEN oil and paper high-voltage cable insulation is subjected to conditions of service or to laboratory treatments simulating such conditions, certain definite changes frequently take place in the oil. In order to investigate these changes, it is necessary to remove the oil from the paper without contaminating the oil. Extraction methods have been found to interfere with the viscosity and hydrophil tests (2, 4) used by this company. As is well known, the removal of the last traces of solvent from a heavy oil is a difficult and uncertain process. Since the viscosity of a system of two components of widely differing viscosities is greatly changed by small variations in the concentration of the component of lower viscosity (1), efforts to follow chemical changes in oils by means of viscosity measurements are partially invalidated by the presence of variable traces of solvent. Another objection to the use of a solvent is that in addition to removing the oil from the paper, it may remove certain substances which are not soluble in the oil and which are not wanted in the specimen obtained, as, for instance, natural resins. In such cases the values obtained by using the hydrophil test to measure the extent of oxidation are too high.

In order to avoid these errors, several mechanical methods, other than those requiring the use of solvents, have been tried in this company. It was recognized that the oil obtained by such methods might not be entirely representative of the total oil in the paper, owing to the selective adsorption by the paper of some of the impurities present. While the matter

has not been investigated thoroughly, the work done here indicates that the magnitude of such errors is small as compared with those due to the use of a solvent. In the first two mechanical methods tried, both of which involved pressing the oil from the paper, difficulty was experienced in obtaining the oil free from fine paper fibers which interfere with viscosity measurements and in obtaining sufficiently large samples of oil from tapes of relatively low oil content.

A centrifuge method, that is rapid as well as effective, has been found to eliminate the difficulties enumerated.

The apparatus is shown in Figure 1. Except as otherwise indicated, all measurements are outside dimensions.

In use, a tape from which oil is to be removed is wound on the reel, A. After the reel has been reversed a few times to loosen the winding, the roll is pushed off the shaft by means of the sliding guide and is placed in the funnel with the axis of the roll parallel to that of the funnel, as shown. The wide end of the funnel is then covered with a rubber cap to prevent

air from circulating through the apparatus during the centrifugalizing process. The apparatus is assembled by dropping into the centrifuge tube, in the order given, the lower mounting complete with vial, the upper mounting, and finally the loaded funnel, the stem of which projects just inside the mouth of the vial.

The length of time and the speed required to centrifugalize most of the oil from the tapes vary, of course, with the nature of the samples. Often a 20-minute period at about 2000 r. p. m. suffices. By continuing the process, so much oil may be removed that the paper is

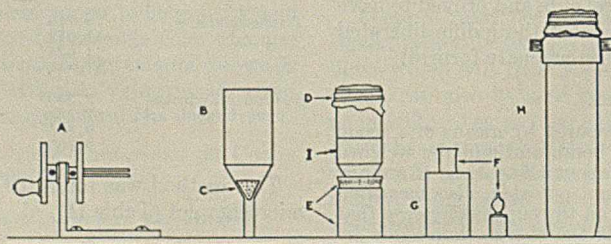


FIGURE 1. APPARATUS FOR REMOVING OIL FROM PAPER BY CENTRIFUGALIZING

- A. Reel with slotted shaft and sliding guide
- B. Pyrex funnel. Body, including taper: 90 mm. long \times 38 mm. diameter, stem angle 58°. Stem 30 mm. long, 7 mm. diameter
- C. Platinum filtering cone, angle 60°
- D. Rubber cap
- E. Upper mounting: aluminum cylinder 39 mm. long \times 38 mm. diameter, 6 mm. wall. Top 12 mm. beveled on inside to 1 mm. thickness to support rubber ring which fits both cylinder and shoulder of funnel
- F. Weighing vial with glass stopper
- G. Lower mounting: aluminum cylinder 52 mm. long \times 38 mm. diameter \times 3 mm. wall. Cylinder holds two gum rubber stoppers, the upper bored to fit vial F
- H. Assembly complete in centrifuge tube 137 mm. long \times 39 mm. inside diameter
- I. Roll of impregnated sample in tube

no longer translucent but is opaque. Even when a longer period is required, the time consumed is not considered excessive.

Unless fine suspended matter is present in the oil in the paper, the sample obtained by the method is clear and free from sediment. The use of the filtering cone is recommended for straining out cable wax or bits of torn paper. Paper fibers do not seem to be dislodged during centrifugalizing.

Not only is the method satisfactory for ordinary samples, but it has also been found to be applicable to samples containing abnormally low quantities of very viscous oils. Since the oil is deposited in a small weighing vial, it can be weighed for test and used without loss.

As has been intimated, one of the reasons the device was designed was to obtain oil for viscosity tests. That the vis-

cosity of the oil taken from radial samples of aged cable varies was observed in the investigations in this company. The possible significance of this phenomenon as regards electric transmission cable life in service is reported in the literature (3).

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RECEIVED May 14, 1934. This work forms part of a general research on the deterioration of high tension underground cable being undertaken by The Detroit Edison Company.

Ter Meulen Method for Direct Determination of Oxygen in Organic Compounds Containing Nitrogen

W. WALKER RUSSELL AND MAURICE E. MARKS, Metcalf Laboratory, Brown University, Providence, R. I.

IT HAS been shown recently (3) that when certain modifications are employed, the ter Meulen method for the direct determination of oxygen in organic combination yields very satisfactory results in the case of compounds containing carbon, hydrogen, and oxygen. By using a very active, thoria-promoted nickel catalyst, all the oxygen in the organic compound was converted to water which was completely retained by the first calcium chloride tube of the absorption train, since no oxides of carbon escaped methanation. Under such conditions the analysis of organic compounds also containing nitrogen should yield hydrogen, hydrocarbons, nitrogen, water, and ammonia. Since calcium chloride absorbs ammonia to a certain extent, ter Meulen (1) has proposed the use of a special tube carrying a charge of standard acid and in a second compartment calcium chloride. Any ammonia evolved during analysis is retained by the acid which is back-titrated at the end of the run. Thus the gain in weight of the tube due to ammonia can be evaluated and the water absorbed ascertained by difference. It appeared to the authors that in the absence of oxides of carbon in the effluent gases, procedure might be considerably simplified if an efficient water absorbent could be found which would not absorb ammonia. Reagent-grade sodium hydroxide in pellet form proved to meet these requirements. Pellets are to be preferred to a more finely divided form because they offer little chance for mechanical retention of ammonia.

APPARATUS AND METHOD

The apparatus previously described elsewhere (3) can be used without modification other than the replacement of all calcium chloride and ascarite with pellets of reagent-grade sodium hydroxide. A 5-inch (12.5-cm.) Schwartz tube charged with this sodium hydroxide served to retain completely the water corresponding to the oxygen in the sample. A second and third tube similarly charged, to act as guard tubes, complete the absorption train.

The method of analysis is identical with that already described (3), except that for compounds containing much nitrogen the time for an analysis may well be extended to 1.25 or 1.5 hours, in order to allow ample time for sweeping am-

monia from the system. A relatively large amount of catalyst—5 to 10 grams—is desirable to prevent the appearance of oxides of carbon in the effluent gases to be absorbed by the sodium hydroxide. Such an amount of active catalyst gives persistent blanks. Thus the blank per half hour may be as high as 2 mg. with a freshly prepared catalyst. The initial blank gradually decreases with continued use of the catalyst to a few tenths of a milligram, owing to the slow reduction of the last traces of nickel oxide. Therefore, the values of these blanks must be carefully ascertained and used to correct the results obtained. In case there is a difference between the blanks determined before and after an analysis, the average blank is best employed.

TABLE I. RESULTS OF ANALYSES BY MODIFIED TER MEULEN METHOD

SUBSTANCE	WEIGHT OF SAMPLE Gram	TEMPERATURE OF CATALYST ° C.	OXYGEN		NITROGEN CONVERTED TO NH ₃ %
			Found %	Calculated %	
Acetamide	0.20685	350	27.14	27.10	85
	0.1910	350	27.14		58
Dimethylglyoxime	0.18615	350	27.50	27.57	45
	0.2117	350	27.61		53
Urea	0.1939	300	26.59	26.65	33
	0.1497	350	26.71		
3,5-Dinitrobenzoic acid	0.1596	350	45.11	45.27	60
	0.2010	350	45.22		
<i>p</i> -Nitroacetanilide	0.20745	350	26.70	26.66	58
	0.1946	350	26.88		
<i>p</i> -Nitrobenzeneazoresorcinol	0.2295	350	24.53	24.70	54
	0.2337	350	24.61		

RESULTS

The results of analyses made upon high-grade organic chemicals containing nitrogen, with sodium hydroxide employed as absorbent, are given in Table I. In addition to the oxygen content found, the percentage of the calculated nitrogen appearing in the exit gases as ammonia is also given. Although over 50 per cent of the nitrogen frequently appears as ammonia, it is improbable that a simultaneous de-

termination of oxygen and nitrogen (as ammonia) can be arranged because of the activity of the cracking surface in liberating nitrogen in difficultly reducible form, probably as free nitrogen, from the compounds studied. More stable nitrogenous compounds may prove an exception, since Smith and West (4), who have obtained excellent results in the nitrogen analysis of organic compounds containing nitrogen in the ring, and also of nitrogen derivatives of chaulmoogric acid by catalytic hydrogenation (2), have found it desirable to preheat strongly the gases evolved from the

heated sample before passing them over the nickel catalyst. It is proposed to study this situation further.

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RECEIVED July 16, 1934.

Identification of Common Glycosides

KIRBY E. JACKSON AND WILLIAM M. DEHN, University of Washington, Seattle, Wash.

WHEREAS many individual tests for the glycosides are found in the literature, hitherto they have not been applied to all glycosides and no systematic method for their identification has been available. The authors have found that known reactions, modifications of known reactions, and new color reactions with simple reagents will enable one to identify the more common glycosides.

The glycosides in Table I are best identified in the order

given. (Picrotoxin, a compound closely related to the glycosides, is included in this study.) In all cases a few milligrams of each are treated at room temperature for about 2 hours with the reagents shown in Table II, so that effects of all reagents used on these glycosides are now determined and disclosed.

(For various confirmatory tests, see especially Merck's Reagenzien Verzeichnis, 1924.)

TABLE I. IDENTIFICATIONS

	a	b	c	d	e	f	g	h	i	k	l	
Phlorhizin	+	garnet	-	-	Br	Y	Y	Y	yR	Y	-	ltY, Or, rBr
Arbutin	-	Bl	-	-	Br	Y	BrG	Or	Y	Y	-	Or, BrBk
Digitonin	-	-	+	-	Y	Br	-	-	Y	Y	-	-
Picrotoxin	-	-	-	+	Y	Y	-	-	Br	-	-	Y, Or
Colocynthin	-	-	-	+	Cr	rBr	yBr	Y	BrR	ltY	Y	gold Y
Scillitoxin	-	-	-	+	brBk	Br	Br	Or	brG	Br	P	rBr
Amygdalin	-	-	-	-	dkG	Ca	-	-	-	-	-	Ca
Salicin	-	-	-	-	brBk	Cr	Ca	Y	R	-	-	Cr, dkR
Strophanthin	-	-	-	+	brBk	G	Y	-	rBr	Br	Y	Br, brBk
Digitalin	-	-	-	-	Blood R	rBr	chR	-	R	P	Y	chR, dkR
Convallarin	-	-	-	-	dkBr	rBr	Y	pink	R	R	P	Y, Or, Br
Saponin	-	-	-	-	Br	rBr	rBr	-	Ca	R	-	ltY, orR, dkbrR
Sapotoin	-	-	-	-	Br	rBr	pink	-	rY	V	Y	ltY, orR
Convallamarin	-	-	-	-	brY	rBr	pink	-	yBr	R	P	or, Br
Absinthin	-	-	-	-	-	Y	-	Y	rBr	brY	-	-

Bl = blue Ca = carmine G = green R = red
 Bk = black Cr = crimson Or = orange V = violet
 Br = brown Ch = cherry P = purple Y = yellow
 Small letters = lighter shades; dk = dark; lt = light; comma = changing to

TABLE II. REAGENTS

REAGENT	SOLVENT	PER CENT OF REAGENT	LITERATURE	REMARKS
a HIO ₃	Dil. AcOH	1 to 5	(4)	Phlorhizin dyes silk yellow to blood red
b FeCl ₃	H ₂ O	1	(11)	Arbutin becomes blue
c Cholesterol	Alcohol	10	(13)	Precipitates additive compound of digitonin
d Fehling's	Dil. K tartrate	3		Positive in 2 hours for picrotoxin, colocynthin, and scillitoxin
e NH ₄ VO ₃	H ₂ SO ₄	0.5	(9)	Colors in few minutes
f H ₂ SO ₄	H ₂ O	92	(2, 3)	Colors in few minutes
g FeCl ₃	AcOH	Trace	(8)	Over H ₂ SO ₄ containing trace of FeCl ₃
h HNO ₃	H ₂ O	25	(6)	
i Ac ₂ O		100	(10, 12)	Solution in Ac ₂ O over concd. H ₂ SO ₄
j H ₂ PO ₄	H ₂ O	85	(5)	1 hour's standing
k ZnCl ₂	15 per cent HCl	3	(1, 7)	Immediate colors
l Urotropin	H ₂ SO ₄	0.05		Immediate colors

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RECEIVED June 16, 1934.

PERU USES NEW METHOD OF EXTRACTING QUININE FROM CINCHONA. Some publicity has recently been given by the Callao-Lima press to a more economic method of extracting quinine from the bark of the cinchona plant, which is found in abundance in the jungle regions of Peru. Experiments conducted by Señor Franciles Zamorra Silva in the laboratories of Señor Hersino V. Sanchez, at Monzon, Peru, have resulted in a new process of obtaining quinine alkaloids and salts which may greatly affect the local production and exportation of this drug.

The production of quinine salts and alkaloids from cinchona bark produced in Peru during the past few years is not equal to the local demand. The public health statistics indicate that an average of over 2000 cases in the charity hospitals of the city of Lima alone are annually treated with quinine, and epidemics of malaria necessitating its use occur frequently throughout the provincial districts of the Republic. Any method leading to the greater economic production of this drug receives the attention of the Peruvian Government.

Constant-Temperature High-Pressure Laboratory Autoclave

FRED J. DYKSTRA AND GEORGE CALINGAERT, Ethyl Gasoline Corporation, Detroit, Mich.

A SMALL high-pressure autoclave, particularly suited for liquid-phase hydrogenation, was described by Peters and Stanger (1). The unit is heated electrically and well lagged on the outside. Stirring is obtained by rocking and the connection to the source of hydrogen is by means of a coil of flexible copper tubing. This design avoids the use of packing glands, since there are no moving parts inside the autoclave. Equipment of similar type, but smaller in size, is now available from supply houses as regular laboratory equipment.

While well suited for the preparation of many compounds by hydrogenation, autoclaves of this type are not particularly well adapted to a study of catalysts, especially active cata-

lysts, which prevents splashing of the liquid up into the reflux condenser, *E*. The jacket is heated on the outside by means of strip heaters, *F*. Suitable connections are made in one flange for a liquid and catalyst inlet, *G*, and in the other for a hydrogen inlet, *I*, a blow-off valve, *J*, and a thermocouple, *H*. This latter is made of pure iron tubing containing an insulated constantan wire. No sheath is used, so that there is no lag in reading the temperature of the liquid. The fitting of the thermocouple through the flange is illustrated in the insert in Figure 1.

The autoclave is rocked 20 times per minute over a 30° arc. The axis, *K*, is horizontal and perpendicular to the longitudinal axis of the autoclave and at its middle. The hydrogen inlet coil, *L*, consists of 5 meters of hard-drawn copper tubing 6.5 mm. in outside diameter and 3.5 mm. in inside diameter wound into a coil about 30 cm. in diameter. The water connections to the reflux condenser are brought back near the axis of rotation and connected to the stationary pipes by means of rubber tubing.

The entire autoclave is heavily lagged with magnesia lagging, *M*, including two large caps which are held over the ends of the tube by means of hooks, *N*. A 6-meter length of ordinary copper tubing, 5 mm. outside diameter, is coiled around the pressure tube within the jacket. The purpose of this coil, *O*, is to permit rapid cooling of the thermostatic liquid at the end of a run, since the heavy lagging would otherwise make it necessary to wait several hours before the charge was cooled down to room temperature. The thermostatic liquid is put in the jacket through a plug opening, *P*, leveled at cock *Q*, and drained off through cock *R*. Its temperature is taken with the thermometer, *S*.

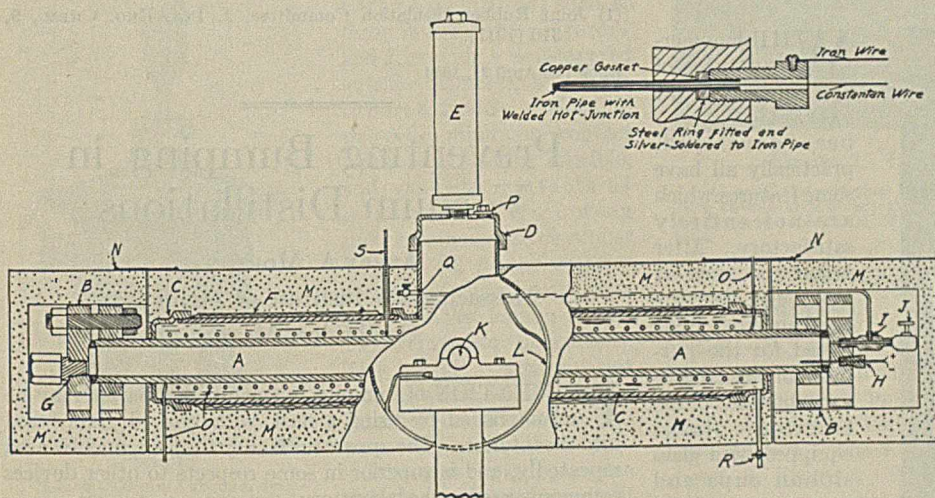


FIGURE 1. CONSTANT-TEMPERATURE AUTOCLAVE

lysts. Whenever the reaction is sufficiently exothermic and sufficiently fast, the amount of heat given off will raise the temperature considerably and accurate data cannot be readily obtained regarding the activity of the catalyst. Furthermore, in cases where either the compound being hydrogenated or the hydrogenation product is subject to thermal decomposition, and in cases where the reaction may take alternative courses at different temperatures, much better temperature control is desirable than can be achieved with this type of autoclave.

The autoclave described below retains all the advantages of the Peters and Stanger design, at the same time permitting accurate control of the temperature, practically independently of the heat evolved during the reaction. This is accomplished simply by surrounding the reaction tube with a jacket filled with a suitably chosen liquid, which is kept at its boiling point.

DESCRIPTION OF APPARATUS

The autoclave (Figure 1) is made of a 122-cm. length of seamless steel tubing 50 mm. in inside diameter and 75 mm. in outside diameter, *A*. This tube is closed at both ends by means of a steel flange, *B*, and a lens connection of the classical type. A jacket, *C*, made of standard 5-inch (12.5-cm.) pipe and fittings, is welded to this tube. The jacket is surmounted in the middle by a dome,

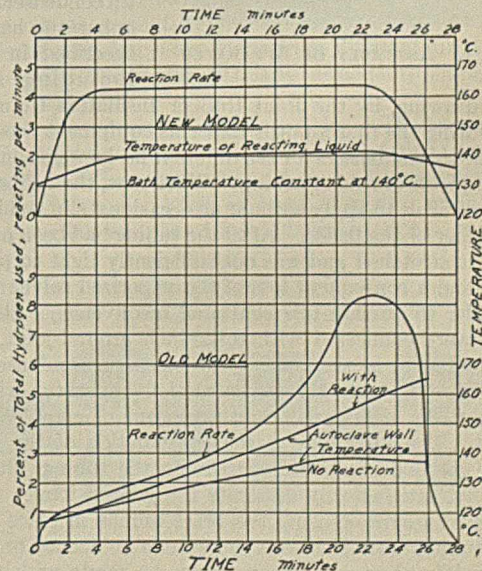


FIGURE 2. COMPARISON BETWEEN NEW AND OLD MODELS OF AUTOCLAVES

This unit has been used at temperatures up to 280° C. and pressures up to 218 atmospheres. Most of the work was done at 150° C. and 68 atmospheres pressure using a mixture of ethylene glycol and water as the thermostatic liquid. Under those conditions 1 liter of furfural in the presence of 40 grams of copper chromite catalyst, regardless of activity, can be hydrogenated, maintaining the temperature of the reacting liquid constant within 2° C. at an equilibrium temperature just above the temperature of the thermostatic bath. The equilibrium temperature is maintained for approximately 70 per cent of the time for the run.

Figure 2 demonstrates the difference between the old and

the modified models of the Peters and Stanger type of autoclave. Since no temperature equilibrium was obtained with the old type, comparison between various batches of catalyst was very difficult and of little value when applied to large-scale operation in a well controlled autoclave of a different type. The long equilibrium period obtained in the new model makes comparison between various catalysts easy and reliable.

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RECEIVED March 19, 1934.

An Improved Fat-Extraction Apparatus

ARTHUR D. HOLMES AND MADELEINE G. PIGOTT

The E. L. Patch Co., Boston, Mass.

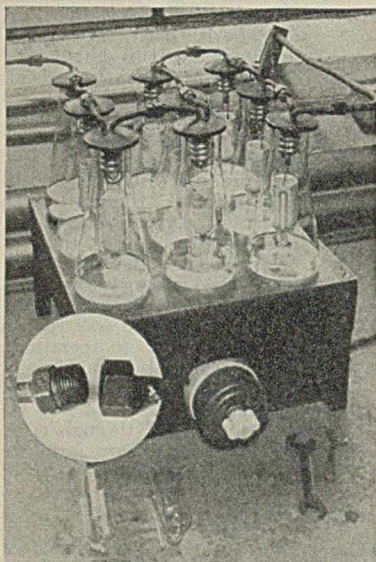


FIGURE 1. ASSEMBLY OF APPARATUS

WHILE numerous types of apparatus for fat extraction have been developed, practically all have some features which are not entirely satisfactory. After numerous tests it was found that the equipment best suited for the purposes of this laboratory consisted of extraction flasks equipped with glass siphon cups and copper covers fitted with a coiled block-tin condenser. This apparatus has been described in detail, including an assembly drawing, by the Joint Rubber Insulation Committee

(1). During the first months that this equipment was in use the block-tin condensers for the different flasks were connected by short pieces of rubber tubing. When new, the rubber tubing was difficult to apply without an occasional slip and knocking together of the flasks. After the tubing had been used for a time, it stretched and was not sufficiently tight to prevent leakage and a consequent loss of the vaporized solvent.

In order to obviate this continual inconvenience the condensers were connected with 0.125-inch ground-joint, brass unions, soldered to the ends of the block-tin condenser tubing. Figure 1 shows the fat-extraction apparatus with extraction flasks, condensers, and brass unions completely assembled. The insert shows the construction of the unions and the method of attaching them to the tubing, although it does not satisfactorily illustrate the ground joint.

The advantages of using the brass unions in place of the rubber tubing are: The brass unions can be opened or closed more rapidly than a connection can be made with rubber tubing. There is practically no wear on the unions and hence no need for replacement as in the case of rubber tubing.

The joints will stand greater water pressure; therefore a greater volume of water can flow through the condenser, thus increasing the efficiency of the condensing surface. The ground joints make a close connection and there is no leakage of water. The brass unions are rigid and individual flasks have no tendency to tip.

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RECEIVED April 21, 1934.

Preventing Bumping in Vacuum Distillations

AVERY A. MORTON

Massachusetts Institute of Technology,
Cambridge, Mass.

PREVENTION of bumping in vacuum distillation may be accomplished by using a flask with ground glass fused into the interior. The apparatus is easy to clean, may be used repeatedly, and is superior in some respects to other devices commonly used in the laboratory.

Pyrex glass is powdered in a mortar so that the largest sizes are not more than 1 to 1.5 mm. No attempt is made to separate the powder from the larger particles. Enough of the ground glass is put into a flask to cover thoroughly the lower half of its interior surface. The flask is then rotated in a flame and the desired portion heated high enough to soften the glass and cause the particles to become attached firmly. It is usually necessary to blow the flask a little to correct major deformations. After annealing, the flask is ready for use. Best results in distillation are secured when the coating of powdered glass is as thick as possible.

Distillation is carried out in the ordinary manner using an oil bath. In place of the usual bumping a little foaming occurs which fills the upper half of the flask. After this initial activity the surface subsides at once and remains relatively quiet during the remainder of the distillation. After use the flask is cleaned in the ordinary manner with acids or organic solvents and dried. Repeated use in this manner showed no diminution in its effectiveness in preventing bumping. Re-use without cleaning is possible, but prevention of bumping is not so effective.

These flasks are especially serviceable in the distillation of liquids which are sensitive to oxidation from the current of air which is frequently used. They are far superior to the common ebullator tubes.

RECEIVED June 20, 1934.

Rubber Stopper Remolding for Reduced Pressure Filtration

G. FREDERICK SMITH AND J. L. GRING, University of Illinois, Urbana, Ill.

THE many forms of Gooch-type filtering crucibles with their multiplicity of sizes, wall tapers, and heights introduce the problem of providing rubber adapters for inserting the crucible into holder for use in vacuum filtration (1-3). Fritted glass, quartz, or porous-bottomed porcelain crucibles as well as platinum Gooch Monroe crucibles are examples in question. The inverted perforated stoppers here described are substitutes for stock apparatus (1-3), but have the advantage that the dimensions obtainable are variable over a much wider range than is possible using special molded rubber forms.

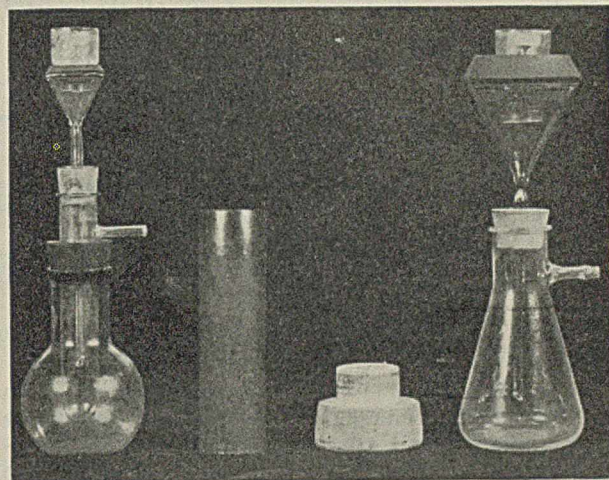


FIGURE 2. REMOLDED RUBBER STOPPERS

Left, small sintered-glass filtering crucible, 25 × 37 mm.; No. 7 stopper using 25-mm. cork borer; glass funnel, 37 mm. diameter at top; side-arm filtering test tube, 25 × 37 mm.; 250-ml. Soxhlet flask to support filter tube.

Center, 43-mm. cork borer and wooden handle.

Right, large sintered-glass filtering crucible, 37 × 60 mm.; No. 13 stopper, using 35-mm. cork borer; glass funnel, 75-mm. diameter at top; 250-ml. filtering flask.

and 4.4-cm.) outside diameter are made from brass tubing having a 1-mm. wall thickness, sharpened at one end by making a tapering cut in the lathe on the outside, and tapered inside at the other end to provide a snug fit for the wooden hand support. The 1.75-inch (4.4-cm.) cork borer parts are shown in Figure 2. The wooden handle is turned in the lathe as shown, starting with a wooden roll paper end, which has a center hole already supplied for use in removing the rubber core cut from a stopper. A No. 13 rubber stopper is shown cut as desired in the top center object in Figure 3. The remaining forms are made from different sized stoppers and hole dimensions and are finally formed into shape by being turned inside out.

Large stoppers must have large holes. The minimum hole in a No. 13 stopper which will permit of its being turned inside out is 35 mm. [approximately 1.5-inch (3.1-cm.) cork borer]. To provide smaller holes in large stoppers, small stoppers after inversion are placed inside larger stoppers, as shown in

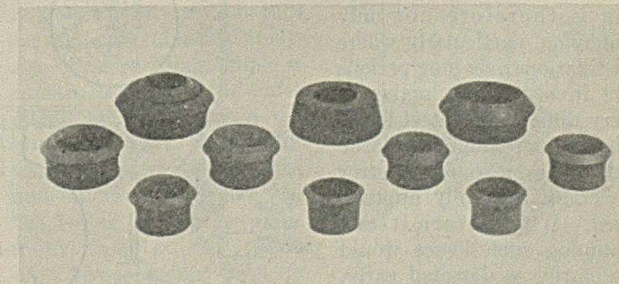


FIGURE 3. FINISHED STOPPERS
Stoppers in Table I after inversion



FIGURE 1. FILTERING ASSEMBLY

8-inch (200-mm.) vacuum desiccator, 250-ml. beaker, and 25 × 37 mm. sintered glass crucible supported in a special filtering tube, using No. 7 stopper with 28-mm. hole.

midsection flange prevents the troublesome cone deformation under pressure which causes the ordinary stopper form to pull through.

TABLE I. DIMENSIONS OF STOPPERS, CORK BORER, AND INVERTED FINISHED STOPPERS

RUBBER STOPPER No.	STOPPER DIAMETER		CORK BORER DIAMETER	INVERTED-STOPPER MEASUREMENTS			Hole ^d
	Top	Bottom		Top ^a	Middle ^b	Bottom ^c	
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
13	70	60	43	57	75	63	42
13	70	60	35	60	76	59	34
12	64	58	35	53	70	53	34
11	56	50	35	45	60	53	35
10	50	42	35	44	52	45	34
10	50	42	28	42	55	43	25
9	45	37	28	35	47	39	27
9	45	37	25	35	47	40	23
8	40	32	25	35	44	37	23
8	40	32	28	32	43	36	27
7	37	30	25	31	40	33	23
7	37	30	28	32	40	32	33

^a Diameter of circle made by sharp edge at top of stopper.

^b Largest diameter at extreme midsection edge.

^c Diameter of outside edge of bottom.

^d Diameter at small end of curving tapered conical center hole.

The ordinary cork borer set does not extend to sizes sufficiently large to make the stoppers as shown in Figure 3. Cork borers of 1-, 1.25-, 1.5-, and 1.75-inch (2.5-, 3.1-, 3.7-,

the upper left-hand object in Figure 3. The hole must be cut exactly in the center of the stopper. Failure to do this results in an inverted stopper having a flange of unequal width and an oval shape. A little 3-in-1 Oil is used to lubricate the cork borer. With large cork borers, cutting straight through the stopper is easier than with small borers. The cork borer can be withdrawn from a partially cut stopper for application of additional lubricant. The lower outside surface of the inverted stopper can be sandpapered to smooth out slight imperfections as a result of an imperfect cut. If the inverted stopper is too tall it is slipped over the cork borer and a razor blade is passed around and through the stopper to shorten it

to the desired extent. The sanding of the lower outside edge is carried out with the stopper held as for shortening.

The apparatus and materials described and illustrated in this work are all standard laboratory equipment, with the exception of the large cork borers which should be made available as standard laboratory apparatus.

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RECEIVED July 2, 1934.

A Differential Pressure Control Mechanism for Vacuum Distillation

S. PALKIN AND O. A. NELSON, Bureau of Chemistry and Soils, Washington, D. C.

THE advantages of pressure-regulating devices which require only intermittent operation of the pump over those requiring continuous pumping have only recently been appreciated. In a review of the literature on the subject by Hershberg and Huntress (1) only five of some thirty publications cited relate to the intermittent pumping type, and these, with but one exception, have all appeared within the past two years. To these may be added one more recent publication (4).

A decided advance in pressure-control technic was contributed by Hershberg and Huntress (2) in their publication describing a novel manostat in which sulfuric acid constitutes the manostatic liquid. The latter, with an appropriate thermionic relay and flutter valve, is claimed to permit pressure control within ± 0.015 mm. of mercury. To use this device, however, they found it necessary to make the pump operation continuous and to use three valves to bleed in air at atmospheric pressure for the adjustment.

In a distillation system intended for precision work, which should be reasonably tight to begin with, any unavoidable minor leaks should require but very infrequent pumping for adjustment. The use of continuous pumping is therefore not only annoying, particularly where distillations over long periods are involved, but makes it very difficult to detect losses of the more highly volatile substances, a source of error generally not fully appreciated. With intermittent pumping such losses would ordinarily be detected early, as any increase in frequency of pumping over that occasionally necessary for com-

pensation becomes at once an audible warning of leaks and inadequacies in the condensing system. It is thus particularly valuable as a safeguard against the loss of important volatile constituents.

The pressure-control scheme described in this paper takes advantage of the sensitive Hershberg-Huntress (2) sulfuric acid manostat, so adapted as to make possible accurate pressure control with the pump operating intermittently. Sulfuric acid is used as a manometric liquid, and a convenient simple U-type manometer of high sensitivity is included as a part of the system. A manometer of this kind, in view of its simplicity, and high sensitivity, should prove a generally useful device for laboratory purposes. As a rule, lighter liquids, such as dibutylphthalate and oils, cannot be used in U-type manometers, except in open-arm forms such as the Hickman mercury vapor pump gage, as it is virtually impossible to dislodge the liquid from the closed end even at very low pressures, owing probably to surface tension. For similar reasons inclined mercury manometers (4), although they provide magnified movement of the mercury thread, are not sufficiently rapid in response to gradual pressure change to be useful for accurate readings. McLeod gages require tedious calibration, provide very limited range, and do not permit of continuous observation.

The sulfuric acid manometer, while it does not possess quite the degree of accuracy of the Hickman gage, is relatively simple in construction. It provides a convenient and ready means, particularly with pressure-control devices, for setting and maintaining fixed pressures.

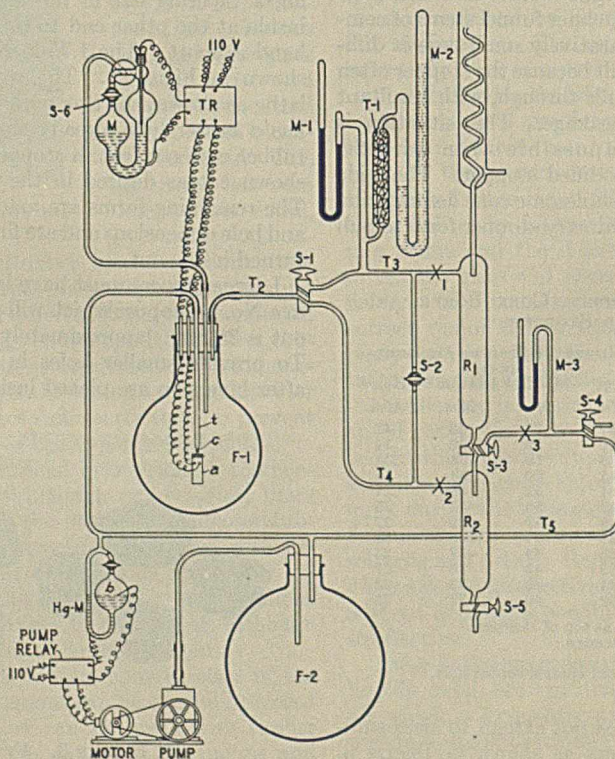


FIGURE 1. DIAGRAM OF APPARATUS

APPARATUS

Two distinct pressure systems are maintained with a pressure difference of from 4 to 30 mm. These are in intermittent communication with one another by way of a valve operated by a magnet, controlled in turn by a Hershberg-

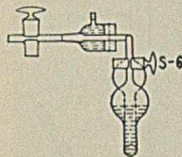


FIGURE 2

Huntress (2) sulfuric acid manostat and thermionic relay. In the low-pressure system, pressure is maintained only approximately constant by means of a mercury manostat relay, and may be from 4 to 30 mm. lower than the pressure in the distillation system. The flask containing the valve which is in direct communication with the distillation apparatus represents the other system, in which the pressure is accurately controlled.

The valve-operating mechanism enclosed in flask *F-1* consists of a small simple magnet (old type of telephone bell-ringing magnet), the movable part (hinged lid) of which is covered with a strip of smooth rubber. The magnet and a long 0.125-inch (0.32-cm.) tube, *t*, the end of which has a capillary opening, *c*, are securely fastened to a base as indicated. The movable part of the magnet effects intermittent closure of the capillary.

The sulfuric acid manostat and thermionic relay, *M* and *TR*, are essentially as described by Hershberg and Huntress (2), a mercury-sealed ground-glass joint (Figure 2) being substituted for the ground-steel joint used in their apparatus.

The mercury manostat (*Hg-M*) is similar to the sulfuric acid manostat in construction and provides for a wide range of pressures. It is rendered less sensitive than the ordinary U-type mercury manostat by making bulb *b* relatively large.

The manometer, *M-2*, is a simple U-type made from Pyrex glass tubing at least 2 cm. in inside diameter, to compensate for the high viscosity of the acid (2). Sulfuric acid, of the concentration used in the sulfuric acid manostat (sp. gr. 1.71), may be used as a manometer liquid, the apparatus being properly trapped to prevent diffusion of gases or vapors to or from the acid. Melville (3) mentions the use of sulfuric acid for such a purpose. After filling, it was carefully boiled out by gentle heating, the pressure having been reduced to 1 to 2 mm. of mercury; 7.9 mm. difference in acid level corresponded to 1 mm. pressure of mercury.

Flasks *F-1* and *F-2* are used to eliminate possible pressure fluctuations when the valve opens. It was noticed that with a pressure difference of 5 to 6 mm. in the two systems and with flask *F-1* of 2-liter capacity, there was a movement of about 1 mm. in the sulfuric acid levels on opening and closing the valve. Substituting a 5-liter flask eliminated this difficulty entirely, with a pressure difference of 32 mm. of mercury in the two systems. Flask *F-2* may be of any convenient size; 2-, 5-, and 12-liter flasks and a 20-gallon (75.7-liter) tank gave equally good results, the only difference being somewhat more frequent starting and stopping of the vacuum pump with the smaller vessels.

*T*₁ is a trap filled with quicklime. Other traps may be used at *T*₂, *T*₃, etc.

The entire apparatus with the exception of the pump was made portable as in the case of the Hershberg-Huntress scheme (1), by mounting it on an instrument board with a fixed base, connections with distillation apparatus being made with rubber tubing at *X*₁, *X*₂, and *X*₃.

The general principle of dual pressure control described above can be applied to some advantage even with the pump (mechanical or water-aspirator type) continuously operated. When so used the mercury manostat, *Hg-M*, and pump relay are eliminated.

Leakage or an inadequate condensing system would manifest itself by too frequent operation of the thermionic relay, *TR*, and valve.

OPERATION

For use with a fractionating column the following sequence has been found desirable and permits the taking of fractions during the distillation without disturbing the pressure:

To evacuate the system the manostat stopcock, *S-6*, is opened and stopcocks *S-1*, *S-3*, and *S-4* are turned so as to connect *F-1* with *F-2*, and the by-pass between receivers *R*₁ and *R*₂ is opened

through *S-2*, so that the entire system is now connected directly with *F-2* and the vacuum pump. When the required pressure is reached, *S-2* is closed and *S-3* is turned so as to connect *R*₁ and *R*₂. At the same time the sulfuric acid manostat is adjusted so that capillary tip *c* of tube *t* inside *F-1* is closed by the rubber pad as discussed above and the manostat stopcock is closed. *S-1* is turned so as to connect *F-1* with *R*₁. Evacuation of *F-2* is continued until the desired pressure difference between the two systems is reached, as observed on manometers *M-1* and *M-3*, when the mercury manostat, *Hg-M*, is adjusted.

To remove a fraction of the distillate from the receiver *R*₂, the following procedure is recommended:

S-3 is turned to shut off *R*₁ from *R*₂, and *S-4* is opened to the atmosphere. Through *S-3*, *R*₂ is brought to atmospheric pressure, and the fraction is run out through *S-5*. During this operation, the pressure in the distillation apparatus as a whole is being-maintained constant. After the fraction has been taken, the pressure in *R*₂ is reduced to that which prevails in the still, in two stages as follows: *R*₂ is connected with *F-2* through *S-4*, and evacuation continued until the pressure recorded on *M-3* has practically reached that of *M*, and *S-4* is promptly turned off. Final adjustment of the pressure in *R*₂ is accomplished by establishing communication between it and *F-1* through *S-1*, after which all stopcocks are turned to their original positions.

SUMMARY

In the pressure-control assembly here described, a dual pressure system is maintained with the two systems about 4 to 30 mm. apart. One vessel, in continuous communication with the distillation system, constitutes the higher pressure system, the pressure being maintained constant by means of a valve operated by a magnet controlled by a Hershberg-Huntress sulfuric acid manostat and thermionic relay. Another vessel, in continuous communication with the pump but in intermittent communication with the first vessel, constitutes the lower pressure system, the pressure being maintained only approximately constant.

The pump operates only occasionally and is controlled in turn by a mercury manostat and relay.

The sulfuric acid U-type manometer described is about eight times as sensitive as the ordinary mercury manometer.

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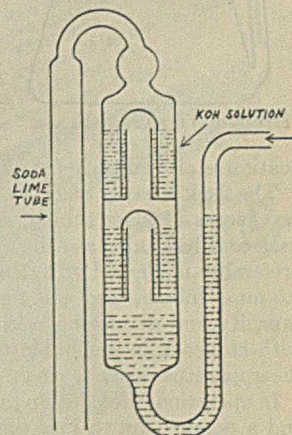
RECEIVED May 18, 1934.

A Simple Absorption Pipet

ELDON A. MEANES AND EDWARD L. NEWMAN

Wichita Testing Laboratories, Wichita, Kans.

THE accompanying diagram illustrates a carbon dioxide absorption tube for organic combustion analysis. Besides being simple in construction, it has the added advantages of being in one compact unit, easy to fill, easily hung on the balance, and much more rugged than the Liebig or Geissler bulbs. Very satisfactory results have been obtained from the use of this pipet.



RECEIVED July 7, 1934.

Agitator for Lamp-Method Sulfur Titrations

LYLE DOLAN

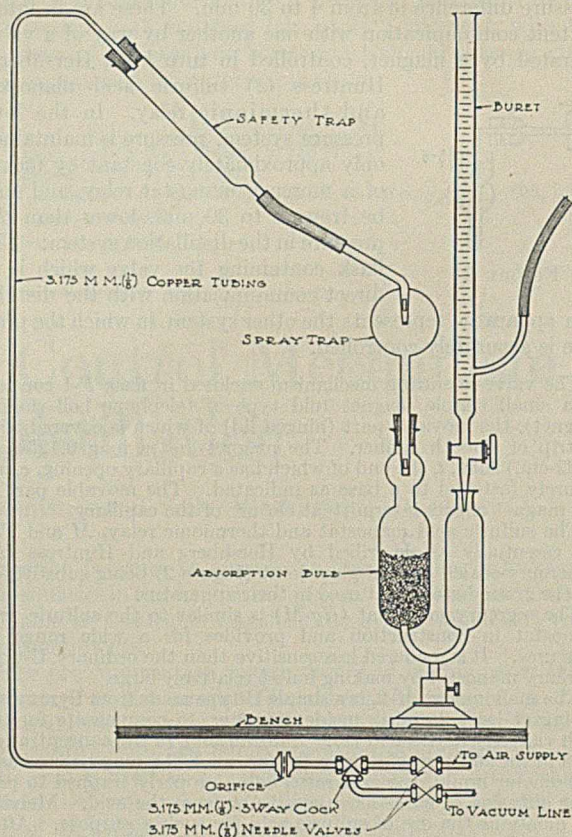
The Texas Company Laboratory, Wilmington, Calif.

IN THE usual procedure for the determination of sulfur in petroleum products by the lamp method (A. S. T. M., D90-30T), it is specified that the carbonate solution in the absorption bulb be agitated during titration by alternately blowing and sucking by mouth on the exit side of the bulb. Considerable pressure is required to force the liquid backward and forward through the packing and, when running a large number of such analyses during a day, this operation becomes rather fatiguing and inefficient, particularly when, as is often the case, the connecting tube becomes partly obstructed by the packing.

This tedious and rather unsanitary procedure is obviated by the use of a simple arrangement, shown in the figure, which has been in continual and successful use in this laboratory for about 14 months. By simple manipulation of the conveniently located three-way stopcock a continuous and uniform agitation may be secured during titration and, when near the end point, the carbonate solution may be transferred rapidly backward and forward between the two bulbs.

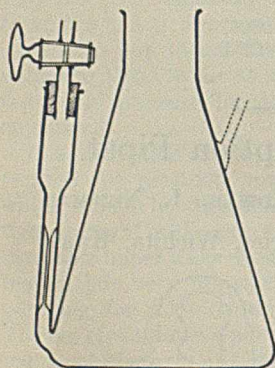
The orifice shown in the line to the bulb is of the correct size to prevent any reagent being blown from the bulb when the three-way cock is wide open. Where the air pressure supply is high compared to the vacuum obtainable, more uniform operation can be secured by plugging the openings in the three-way cock and drilling suitably small holes to the air and vacuum sides of the cock.

RECEIVED March 12, 1934.



A Divided Titration Flask

J. W. YOUNG, Glenmore Laboratory, Calgary, Canada



DIVIDED TITRATION FLASK

THE simple and convenient divided-titration stirring rod recently described by Richardson (3) has been used by the writer for some time. Richardson has pointed out the advantages of speed, accuracy, and convenience offered in titrations. In many cases, particularly in the Kjeldahl nitrogen determination, titration is preferably made in a flask and the stirring rod is inconvenient. The flask here described is a simple device for extending the method and with slight modification is also suitable for differential electrometric titration.

The flask is easily made by sealing a capillary tube between two pieces of glass tubing, and attaching to an Erlenmeyer flask and test tube, as shown in the figure. The apparatus is preferably made of Pyrex, the capillary being about 3 cm. of 0.5-mm. tubing, and the test tube being of about 15 ml. capacity and diameter less than 1 cm. The rubber stopper with stopcock is preferable to a sealed-in stopcock, making the apparatus easier to clean.

In operation, the solution to be titrated is placed in the flask and a portion drawn into the side tube. Titration is made

rapidly until the end point is passed, and part of the solution in the side tube run in. A more careful titration to the end point, with a final rinse of the side tube, completes the titration. With a buret having a time of over 1 minute, it is almost impossible to pass the end point, the liquid in the side tube always serving as a reserve and obviating annoying back-titration. With normal swirling for mixing during titration, there is very little disturbance of the liquid in the side tube and it will not splash onto the stopper.

The flask can be modified to make a very satisfactory arrangement for differential electrometric titration as described by Cox (1) and modified by MacInnes and Jones (2). A two-holed rubber stopper, carrying stopcock and a glass tube with platinum foil electrode, replaces the stopper and stopcock on the side tube. The second electrode may be placed in the solution through the mouth of the flask but is preferably inserted through a side tube, as shown by dotted lines. This second electrode has a rather narrow strip of foil and is easily attached by slip-on rubber tubing. Mechanical agitation is unnecessary in this titration, swirling by the hand being sufficient for thorough mixing.

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- (3) Richardson, *Ibid.*, 55, 2794 (1933).

RECEIVED April 20, 1934.

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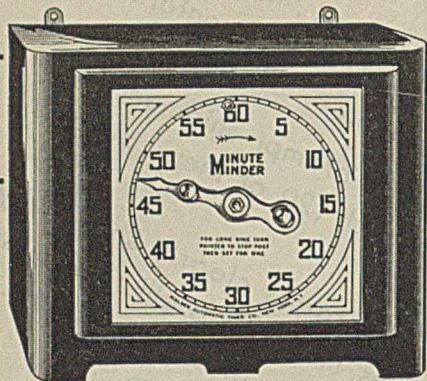
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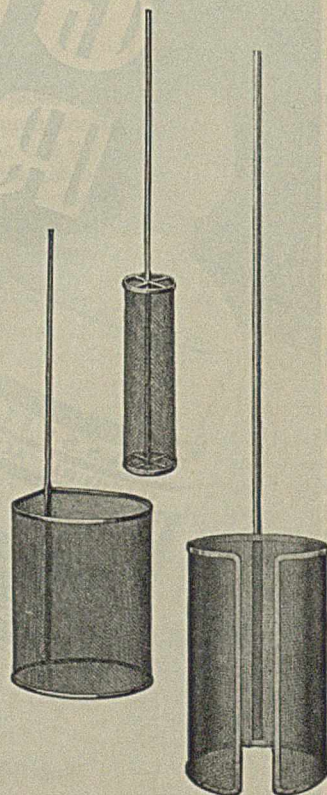
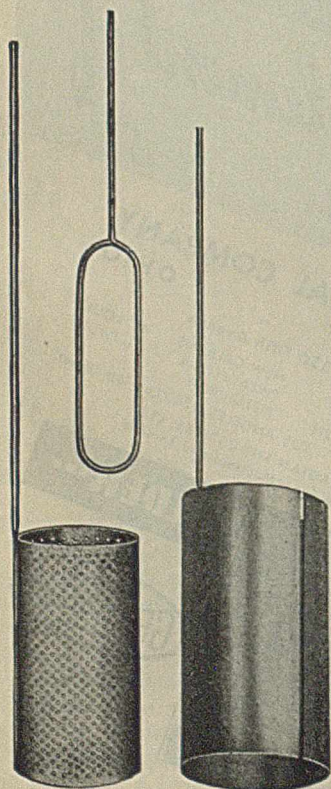
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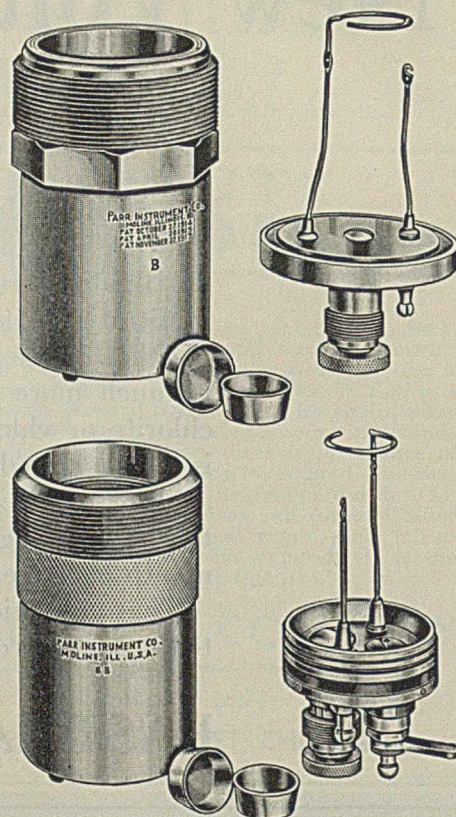
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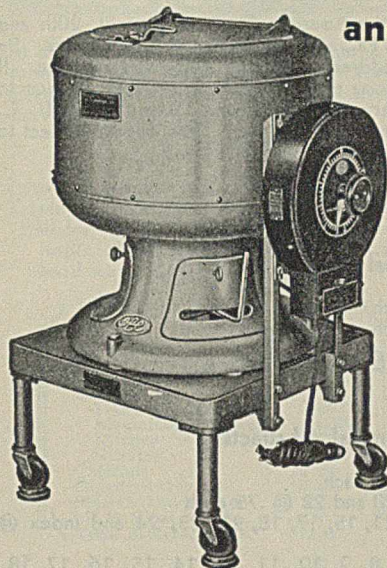
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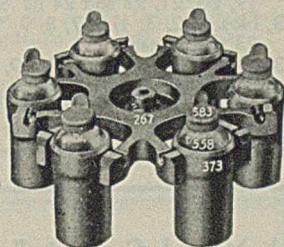


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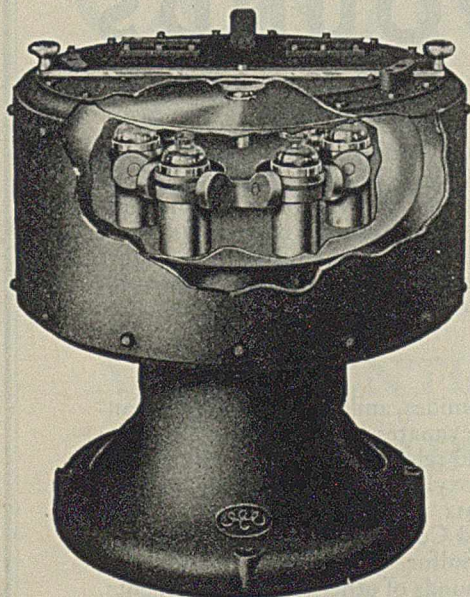
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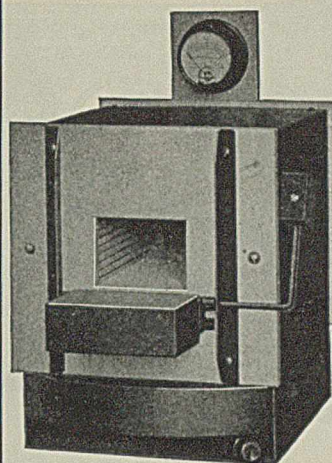
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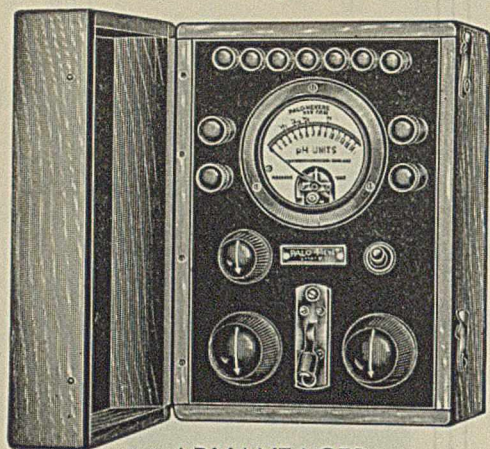
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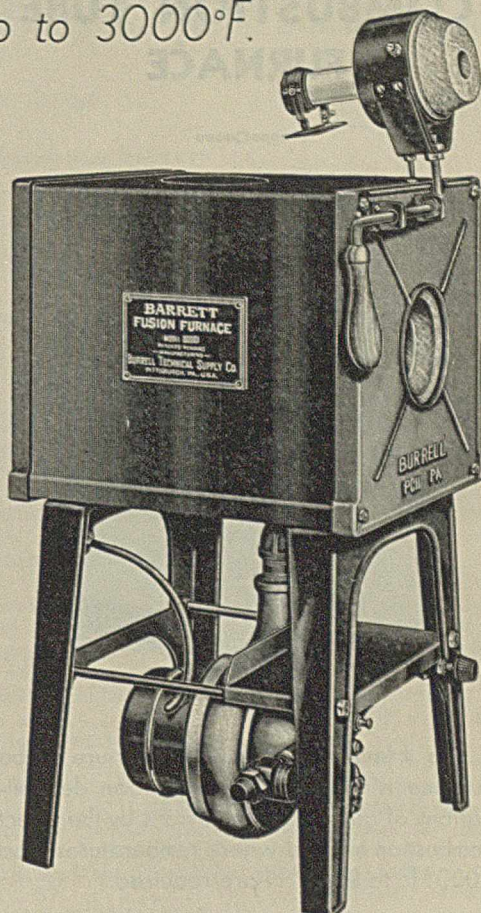
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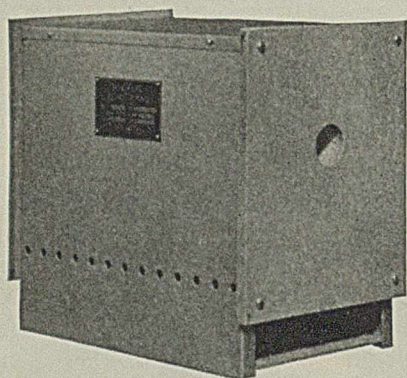
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