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DETERMINATION OF UNDISSOLVED SLUDGE IN USED OILS Harry Levin and Charles C. Towne	181	DETERMINATION OF COPPER IN PARIS GREEN AND ORES J. P. Mehlig and T. P. Marsh	213
DETERMINATION OF DISSOLVED SLUDGE IN USED OILS Frank W. Hall, Harry Levin, and Wallace A. McMillan	183	DETERMINATION OF STRONTIUM IN THE PRESENCE OF CALCIUM R. Norris Shreve, C. H. Watkins, and J. C. Browning	215
TETRAPHENYLARSONIUM CHLORIDE AS ANALYTICAL REAGENT Hobart H. Willard and George M. Smith	186	ELECTROMETRIC INDICATORS WITH DEAD-STOP END-POINT SYSTEM. APPLICATIONS TO NEUTRALIZATION AND PRECIPITATION REACTIONS D. R. Clippinger with C. W. Foulk	216
DUPLICATING PIPETS Frederic E. Holmes	188	PREPARATION OF CARBON ELECTRODES FOR SPECTROGRAPHIC ANALYSIS A. T. Myers and B. C. Brunstetter	218
SPECTROPHOTOMETRIC DETERMINATION OF NITRITE AND OF NITRIC OXIDE IN FURNACE ATMOSPHERES Herman A. Liebhafsky and Earl H. Winslow	189	SINTERED-GLASS FILTERS AND BUBBLERS OF PYREX Hosmer W. Stone and Louis C. Weiss	220
IDENTIFICATION OF LINES IN QUALITATIVE SPECTROGRAPHIC ANALYSIS W. C. Pierce, O. Ramirez Torres, and W. W. Marshall	191	THERMOSTATIC BATH FOR LOW-TEMPERATURE VISCOSITY DETERMINATIONS E. L. Baldeschwieler and L. Z. Wilcox	221
DETERMINATION OF HYDROGEN PEROXIDE AND SOME RELATED PEROXYGEN COMPOUNDS J. S. Reichert, S. A. McNeight, and H. W. Rudel	194	HIGH-PERFORMANCE ELECTRONIC RELAY Roland C. Hawes	222
STANDARDIZATION OF SODIUM THIOSULFATE BY COPPER, USING PERCHLORIC ACID Joseph J. Kolb	197	CORRESPONDENCE: DETERMINING GOLD IN CYANIDE PLATING SOLUTIONS Louis Weisberg; J. B. Kushner	223
QUANTITATIVE DETERMINATION OF SELENIUM IN TISSUES AND FECES Ross A. Gortner, Jr., and Howard B. Lewis	198	MICROCHEMISTRY:	
IDENTIFICATION OF ALDEHYDES AND KETONES BY ESTIMATION OF HYDRAZINE NITROGEN ACCORDING TO JAMIESON METHOD G. B. L. Smith and Thomas G. Wheat	200	DETERMINATION OF ANTIMONY IN WHITE METALS C. W. Anderson	224
COLORIMETRIC DETERMINATION OF CHLORINE WITH <i>p</i> -AMINODIMETHYLANILINE D. H. Byers with M. G. Mellon	202	ANALYTICAL BALANCES IN QUANTITATIVE MICROANALYSIS A. A. Benedetti-Pichler	226
SEPARATION OF WOOD EXTRACTIVES INTO SIMPLER COMPONENTS E. F. Kurth	203	MODIFIED PREGL SPIRAL TUBE Charles W. Beazley	229
FACTORS INFLUENCING QUANTITATIVE DETERMINATION OF SULFATE AS BARIUM SULFATE Harold A. Fales and Will S. Thompson	206	APPARATUS FOR MICROANALYSIS OF GAS C. H. Prescott, Jr., and James Morrison	230
		MODERN LABORATORIES:	
		CHEMICAL ENGINEERING BUILDING AT VIRGINIA POLYTECHNIC INSTITUTE Frank C. Vilbrandt	234

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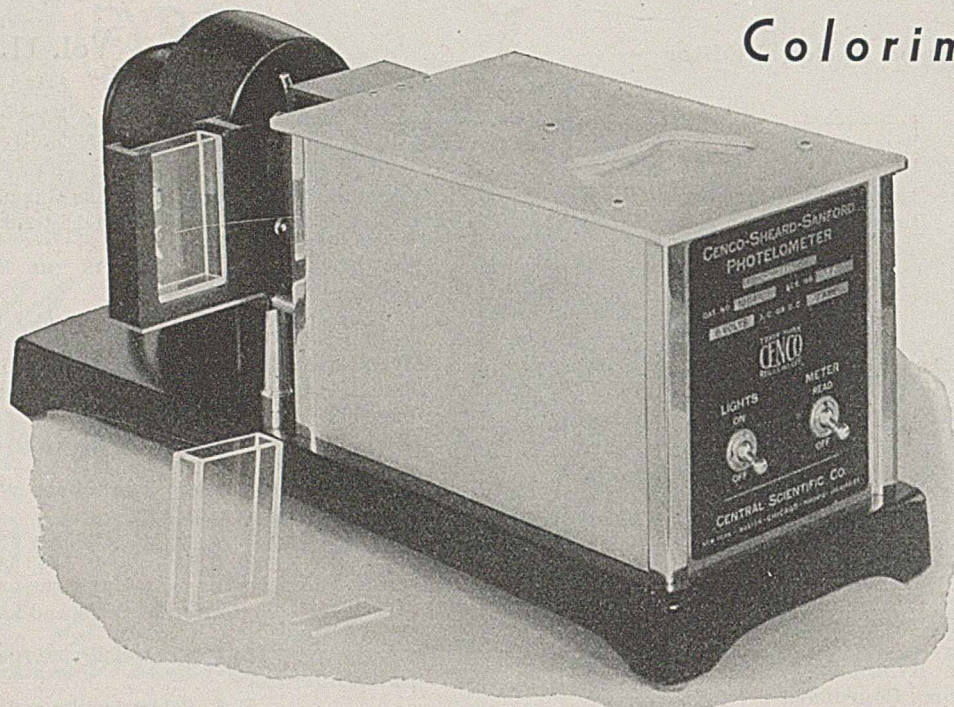
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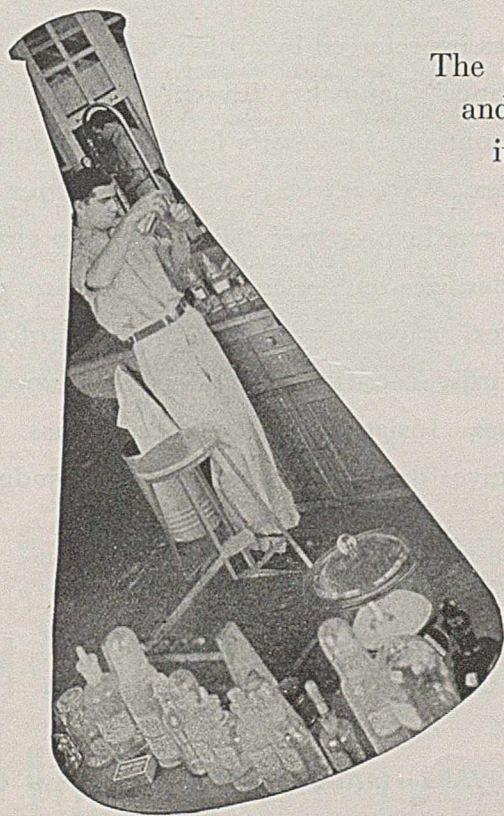
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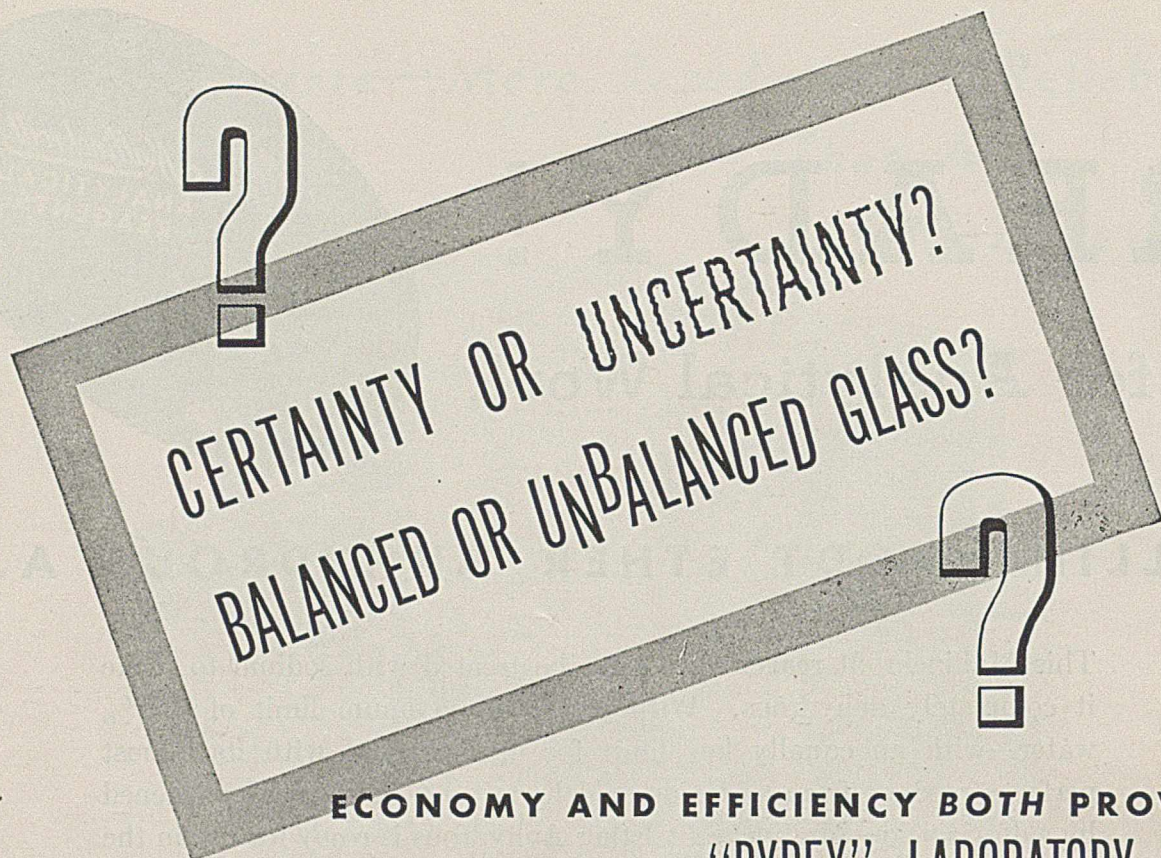


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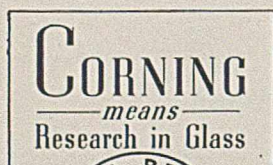
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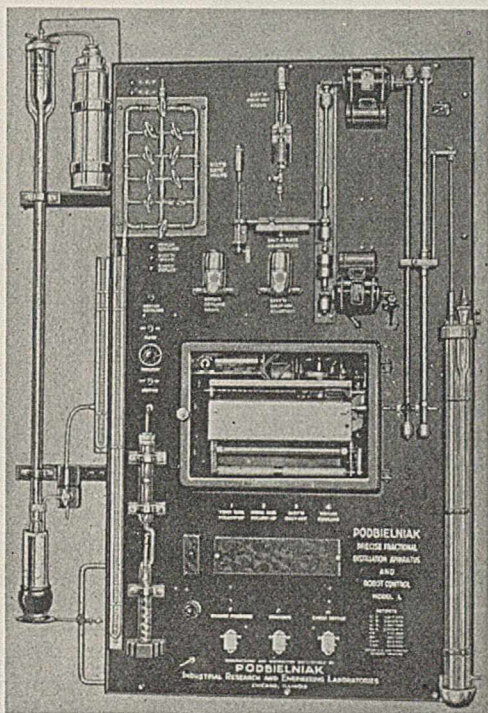
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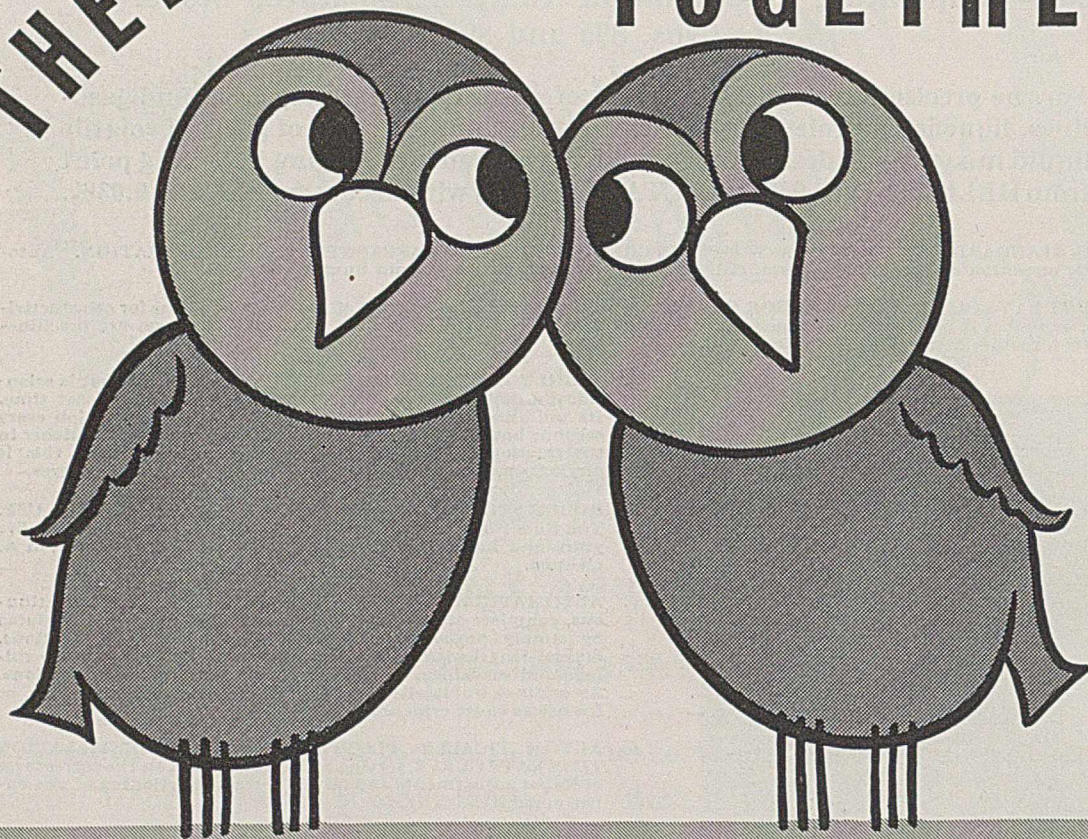
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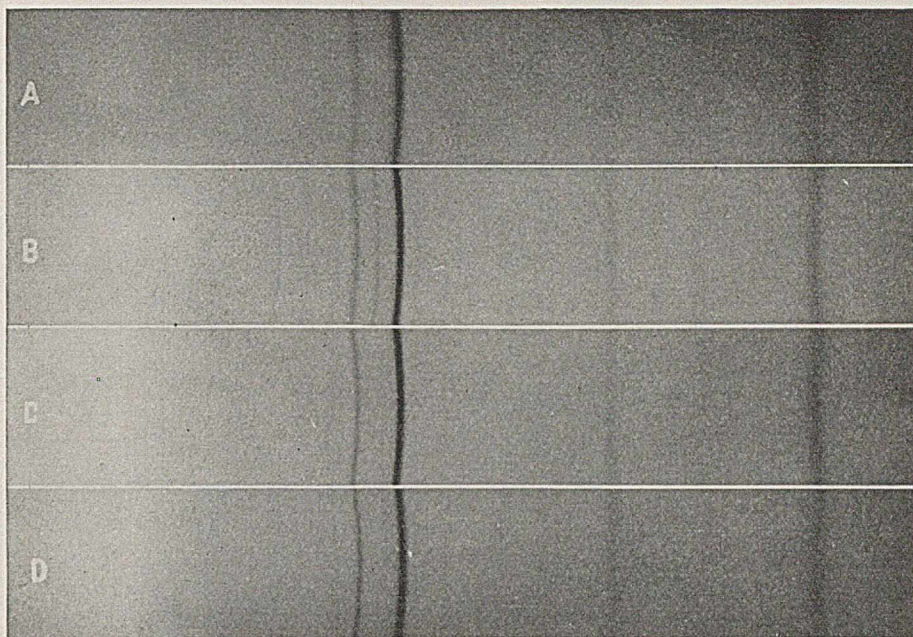
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These four patterns represent four forged bars of a permanent-magnet alloy steel. Coming originally from the same section of the parent ingot, and presumably receiving the same forging and heating treatment, the magnetic properties, nevertheless, were different. Bar A produced a magnet whose high coercivity and remanence were a maximum for the alloy. Bars C and D were of only average quality. In contrast, Bar B was practically worthless as a permanent magnet.

Chemical and spectrographic analysis showed all four to be identical in elementary composition. All four showed identical micro-structures at all magnifications. X-ray diffraction, however, produced three distinctly different patterns, showing definite structural differences.

Pattern A shows the particularly good bar to have the structure of tetragonal martensite, in which all of the alloying constituents are in solid solution. The high residual stresses resulting are indicated by the diffuseness of the diffraction lines. In pattern B are seen several lines in addition to the strong lines in A. Here tetragonal martensite structure is replaced by alpha-iron, the extra lines being from a complex metallic carbide with a cementite structure. This structure indicates that practically all of the alloying constituents have been precipitated, leaving a nearly stress-free alpha-iron bar. The crystallites of the carbide held in the iron matrix are evidently submicroscopic, since they could not be seen under the microscope, and it was for x-ray to reveal the structure indicating magnetic properties in bar B approaching those of soft iron.

Patterns C and D show some lines in addition to those due to alpha-iron or cubic martensite, which were identified as coming from a trace of retained austenite and from a metallic carbide, the latter having a different structure and therefore a composition different from cementite. Thus it



is shown that some of the alloying constituents are not in solution in the martensitic lattice and that decomposition of austenite has not been complete. This accounts satisfactorily for the difference in magnetic properties between bars C and D and bar A.

Bars B, C, and D, evidently, had not been heated to a sufficiently high temperature, or had not been held long enough at the proper temperature for complete solution of the carbides to take place before quenching. The difficulty was traced to unequal temperatures in the heat-treating furnace, and was soon eliminated by an adjustment of furnace operating conditions. RESULTS were: an improvement in uniformity of product; decreased losses from rejected material; and elimination of a perennial quarrel between the steel maker and the magnet manufacturer.

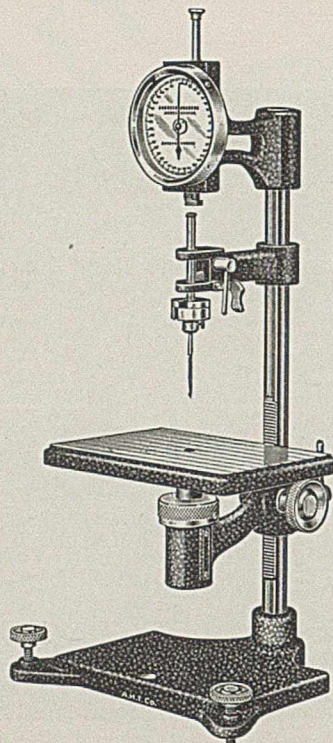
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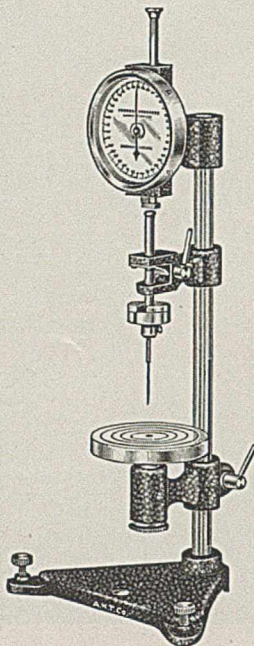
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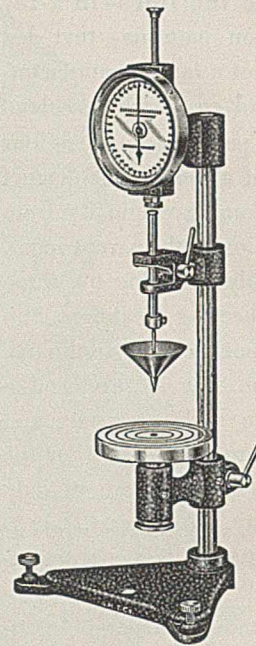
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1200-F



1202-K



7642-F

PENETROMETERS, KREBS. For measuring the distance of vertical penetration of a standard needle into a sample of bituminous material under known conditions of loading, time and temperature, in accordance with specifications for A.S.T.M. standard method D-5-25, A.S.A. method 1, A37.1-1930 and A.A.S.H.O. method T-49-38.

A new construction of Stainless steel and Duralumin, which offers the following advantages:

Adjustable platform for sample, permitting operation at convenient height so that the reflection of the image of the needle on the surface of the sample can be viewed without a mirror. Final setting is controlled by a micrometer screw.

Stationary head mounted at top of a solid Stainless steel column, which construction eliminates possible slippage of the needle from continual manipulation of a movable head assembly.

Weights mounted directly above the needle at lower end of needle bar, resulting in operation with minimum friction. The weights are slotted for ready attachment and are provided with a spring ball locking device.

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1200-F.	Penetrometer, Krebs Laboratory Model, as above described, with Duralumin platform $9\frac{1}{4} \times 6\frac{1}{2}$ inches. A rack and pinion provides for raising and lowering the sample for coarse adjustment and final setting is made by fine micrometer screw. Needle bar release clutch is operated by a lever pressed toward a finger grip. Over-all height $24\frac{1}{2}$ inches. Complete with one each 50 and 100 gram slotted weights and two A.S.T.M. standard needles.	Code Word Afdj
1202-K.	Ditto, Simplified Model, for field or laboratory use, with circular stage $4\frac{1}{2}$ inches diameter. Final setting of the needle is controlled by fine micrometer screw but the rack and pinion of the larger model is omitted and the clutch for needle release is simplified. Over-all height 21 inches, weight without case 8 lbs. With one each 50 and 100 gram slotted weights and one A.S.T.M. standard needle.	50.00 Affak
7642-D.	Consistometer, consisting of 1200-F Penetrometer, Laboratory Model, with needle replaced by a special cone (as shown in above illustration of 7642-F) for use with lubricating greases, etc., in accordance with specifications for A.S.T.M. test D-217-38T and A.S.A. method Z-11.3	138.00 Lerpu
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INDUSTRIAL and ENGINEERING CHEMISTRY

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Harrison E. Howe, Editor

Determination of Undissolved Sludge in Used Oils

HARRY LEVIN AND CHARLES C. TOWNE
The Texas Company, Beacon, N. Y.

THE standard dictionaries—Webster's New International Dictionary, Hackh's Chemical Dictionary, and Van Nostrand's Scientific Encyclopedia—give a variety of definitions for sludge, but the common thought running through most of them is that sludge is a muddy or slimy deposit that settles or is deposited on sedimentation. This fits very well the undissolved sludge encountered in used oils.

TABLE I. INSOLUBLE MATTER IN FILTERED USED DIESEL ENGINE OILS

Solvent	Oil 1 ^a Mg./10 g.	Oil 2 ^a Mg./10 g.	Oil 3 ^a Mg./10 g.
Isopentane, c. p.	32	26	66
Pentane, commercial	31	21	62
n-Heptane	15	13	41
Isooctane, commercial	14	15	44
Precipitation naphtha	9	12	37

^a Milligrams of precipitate per 10 grams of oil, the solvent to sample ratio being 10 to 1.

The sludge is muddy or slimy, instead of dry or solid, because it occludes oil. Since the amount of oil occluded continually decreases as the period of settling increases, it is impractical and of little significance to determine the mud or slime accurately. Therefore the proposed method for the determination of undissolved sludge measures only the non-oily component—that is, the characteristic constituent.

A knowledge of the amount of sludge which exists undissolved in samples of used, oxidized, or other unclarified motor oil is of special interest to the research worker who is concerned with the effect of refining processes and modifiers on the performance of lubricating oil, as well as with the impression the customer gets when he sees his drained crank-case oil.

The methods which are commonly applied for the determination of sludge are similar to those used to determine solubilities of bituminous materials. Among the solvents so employed are 86° (A. P. I. gravity) naphtha, A. S. T. M. precipitation naphtha, special light petroleum naphthas, and various pure hydrocarbons. The general procedure involves the hot or cold digestion of a weighed amount of sample with a measured amount of the particular solvent, followed by a period of settling, filtration through paper, asbestos, porous glass, or Alundum, washing with the solvent, drying, and weighing.

Such direct solubility methods are unreliable for determining undissolved sludge because the so-called solvent may

have a complex effect and not only dissolve the oil which is to be removed but also precipitate material which was actually in solution in the oil alone, the oil being commonly a better solvent than the analytical solvent employed in the analysis. Such a procedure measures not merely the undissolved sludge, but at best the sum of the undissolved plus an indeterminate amount of "dissolved sludge."

That ordinary paraffinic solvents may precipitate material which is in solution in the oil alone is illustrated by Table I. These data were obtained by filtering the undiluted used lubricating oil through cotton and running solubility tests on the filtrate with each of the solvents shown. Frequently the precipitable "dissolved sludge" is greater than the truly undissolved sludge (Table II), so that a true measure of the undissolved sludge is not reliably obtained by a simple solubility test on the used oil.

TABLE II. INSOLUBLE MATTER IN USED OILS

Oil Used in	c. p. Isopentane Solvent			Commercial Pentane Solvent		
	Unfil-tered sample	Fil-tered ^a sample	Undis-solved sludge	Unfil-tered sample	Fil-tered ^a sample	Undis-solved sludge
	Mg. per 10 grams of oil					
Automobile	22	12	10	19	7	12
	315	133	182	284	100	184
	53	1	52	52	0	52
	47	1	46	44	1	43
Automobile truck	20	2	18	19	5	14
	25	7	18	29	6	23
	10	5	5	8	1	7
Automobile bus	238	19	219	230	16	214
	34	4	30	32	3	29
1-Cylinder Diesel CFR engine	334	15	319	327	10	317
6-Cylinder Diesel truck Diesel	581	59	522	580	49	531
	64	32	32	59	31	28
	82	10	72	82	11	71
	206	26	180	205	21	184
	59	6	53	56	4	52
	158	10	148	141	3	138

^a Note that the insoluble matter in the filtered sample is occasionally greater than the undissolved sludge, so that a simple solubility test on the unfiltered sample is unsuitable as a means of determining undissolved sludge.

Furthermore, such solubility tests are influenced by the ratio of solvent to sample. There is an optimum solvent-to-sample ratio which yields the greatest amount of insoluble matter. It is commonly found that a large ratio will show a greater amount of undissolved matter in a particular sample than will a lower ratio, and this anomaly is explained by the fact that the amount of "dissolved sludge" precipitated by the solvent varies with the solvent-to-sample ratio.

Details of Method

The method which the authors use comprises the determination of the pentane-insoluble matter in the sample and in the filtrate obtained by passing the undiluted sample through absorbent cotton. From the difference in the two values the undissolved sludge is calculated. This is the sludge undissolved by the oil itself; it does not include water, which may be separately determined. The method is theoretically sound and its laboratory manipulations are practical.

SOLVENT. Commercial pentane.

APPARATUS. The only special apparatus is a simple filter consisting of a glass tube, 508 mm. long \times 17 mm. in inside diameter, containing a depth of 101 to 127 mm. of surgical absorbent cotton dry-packed at one end, a gauze cap supporting the cotton.

PROCEDURE. A representative portion of the sample is gravity-filtered through the cotton filter. This filtration is, for convenience, carried out overnight in a hot box at 65° to 75° C. On this clarified oil, as well as on a portion of the original sample, the matter insoluble in pentane is determined in the following manner:

Weigh 10 grams of sample into a suitable Erlenmeyer flask and to it add 100 ml. of pentane, agitating to maximum solution. Allow to stand stoppered overnight, then filter through well-packed asbestos in a Gooch crucible, using suction. Wash thoroughly with 100 ml. of pentane, suck dry, then heat in an oven at 110° C. for 1 hour and weigh.

CALCULATION. From the difference in the weights of insoluble matter the undissolved sludge is calculated as follows:

$$C = 1000 \left[A - \left(B \frac{10 - A}{10 - B} \right) \right]$$

where A = sludge undissolved by pentane, original sample (grams per 10 grams)

B = sludge undissolved by pentane, clarified sample (grams per 10 grams)

C = undissolved sludge (mg. per 10 grams)

When A is low (0.1), for practical purposes $C = 1000(A - B)$. The authors have found it convenient to report results in mg. per 10 grams of sample.

This method gave results reproducible within 5 per cent on the sludge basis when the sludge content was high, but duplicate tests within 4 mg. per 10 grams are considered its limit of reproducibility. Used oils from a variety of crankcase services varied in undissolved sludge content from a few to hundreds of milligrams per 10 grams of sample.

This method of analysis includes undissolved mineral matter in the value for undissolved sludge. Determine the mineral matter separately in the usual manner by solution in mineral acids or by ignition.

The sludge, which may become visible on settling, will of course include water that is present. Therefore, when desired, the water should be determined on another portion of the sample, and for this the A. S. T. M. method (1) is suitable.

The proposed method is free of the faults of the other methods—namely, the error due to coprecipitation of matter which was dissolved in the oil sample itself, and the effect of solvent-to-sample ratio—because the solvent in identical ratio is applied to the filtered sample and the quantity of insoluble matter so obtained is used to correct the test made on the unfiltered sample. The quantity of insoluble matter obtained in the filtered sample is in itself unimportant; it merely serves as a correction for the similar material coprecipitated with the undissolved sludge in the original unfiltered sample. The ratio of solvent to sample is therefore unimportant, except that the same ratio must be used on the original unfiltered sample and on the cotton-filtered sample.

Selection of Solvent

Of the common hydrocarbon series the paraffins are the poorest solvents for asphaltic and tarry matter, and the lower-boiling members are the poorest solvents of this series.

Since the undissolved sludge of a used oil may contain material of an asphaltic or tarry nature, besides carbon and mineral matter, the authors' efforts were concentrated on the pentanes. These are the lowest boiling liquid paraffin hydrocarbons that can be conveniently handled and experiments showed that they do not dissolve matter which exists undissolved in the used oil itself.

Much of the authors' original work had been done with *c. p.* isopentane because the use of this solvent was established practice at this laboratory for certain solubility tests. Subsequent work showed that results with commercial mixed pentanes checked those by isopentane. Since *c. p.* isopentane costs about five dollars and mixed pentanes less than one dollar per gallon, commercial pentane was adopted. Each has good solvent power for lubricating oil and neither dissolves sludge which is undissolved by the used oil itself. This latter point was shown by the fact that microscopical examination ($\times 320$) of the pentane-soluble matter from a large number of used crankcase oils, taken at random, showed no black nor dark undissolved particles. The microscopical examination was made at room temperature after the evaporation of the solvent. The absence of dark particles proves that the pentane did not dissolve anything which the oil itself could not hold in solution. Any other solvent can be used, provided it dissolves the oil of the sample but not the undissolved sludge.

Clarifying Used Oil

Various means were investigated for obtaining the clarified sample.

The filtering medium must be inert; hence active clays, etc., are to be avoided. A 15-cm. (6-inch) layer of sand was inadequate, permitting the passage of the fine sludge of used crankcase oils. A 5-cm. (2-inch) layer of Filter-Cel was too dense, requiring weeks for the recovery of a few grams of filtrate. A 10-cm. (4-inch) layer of sand over a 5-cm. (2-inch) layer of Filter-Cel was unsuitable for the same reason as the Filter-Cel alone. Filtration through filter paper (Whatman's No. 44) was unsatisfactory; a single paper allowed the sludge to pass through; three papers clarified the oil, but filtration required days and often weeks and creeping caused trouble. Absorbent cotton was the best filtering medium found, yielding a clear filtrate in a reasonable time. All these filtrations were of the gravity type.

Attempts at reduced-pressure filtration were unsuccessful, as the fine sludge of the samples soon came through the filter or clogged it completely. Centrifuging the undiluted sample at 75° C. for 4 hours at 6000 r. p. m. was also tried, but it did not ensure complete sludge removal as judged by the appearance of the spot made on filter paper by a drop of the centrifuged oil.

TABLE III. UNDISSOLVED SLUDGE IN USED OILS

Clarification Procedure	Motor Oil	Airplane Oil		Diesel Lubricating Oil
		1	2	
<i>Mg. per 10 grams</i>				
Centrifuging	3	63	59	57
Filtration through cotton	5	62	56	56

For the authors' purpose it is necessary that the filtering medium, used to obtain the clarified sample, be one which neither reacts with nor selectively adsorbs material components of the sample being filtered through it. That absorbent cotton is such an inert filtering medium was shown by the fact that results obtained with its use satisfactorily checked results obtained using clarified oil which was prepared by prolonged high-speed high-temperature (70° C.) centrifuging without the use of any filtration medium. A comparison of typical results obtained with oils clarified by cotton and by centrifuging is given in Table III.

Some viscous oils which contain large amounts of undissolved sludge do not yield as much as 10 grams of filtrate through cotton overnight. Such samples should first be centrifuged to remove the bulk of sludge and then filtered through cotton in the usual manner.

Microscopic examination ($\times 320$) at room temperature of the "filtrates through cotton at 65° to 75° C." from numerous used crankcase oils, taken at random, showed no dark particles in most of them; a small percentage showed a few isolated particles estimated to be not more than 2 per cent of the amount visible in the samples before the filtration. The absence of the dark particles proves that the oils while filtering at the elevated temperature did not dissolve sludge which they could not retain in solution at room temperature. Since crankcase oils in use are commonly at these and even higher temperatures and hence have the opportunity to act on the sludge, the additional warm period during filtration should not materially influence the solution of the sludge in the oil.

Attempts at determining undissolved sludge by filtering the undiluted sample through a weighed filter, followed by wash-

ing the residue on the filter with a suitable solvent, failed completely. The fine sludge of the sample soon came through the filter or clogged it completely.

Acknowledgment

The authors acknowledge their appreciation of the assistance of A. J. Millendorf, S. K. Williams, and F. P. Farrell, who did most of the analytical work. They also wish to acknowledge the unpublished contributions of C. G. Ludeman of this laboratory on this general subject.

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Determination of Dissolved Sludge in Used Oils

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IN THE present terminology of the petroleum industry the word "sludge," when considered in connection with used oils, usually refers to material thrown out of oil by the chemical and physical changes resulting from use in an engine. Some definitions include the mineral and metallic particles resulting from wear, abrasion, and contamination, while others particularly exclude these inorganic products and include only insoluble materials of hydrocarbon origin. However, most neglect those other degradation, polymerization, or oxidation products which may be dissolved in the used oil, but which may properly be considered dissolved sludge, since they are not present in the original oil but are formed during use. Such dissolved materials are probably an indication of what may come out of solution on further use or dilution and contribute to lacquer- or gumlike deposits on engine parts. As separated in the proposed method, the dissolved sludge precipitates in forms varying from finely divided particles almost microscopic in size to large agglutinated particles, but in all cases on evaporation from benzene solution it is obtained as a lustrous, brittle, continuous, adherent lacquer-like film, varying from pale yellow to dark red-brown in color—very similar to lacquerlike engine deposits.

TABLE I. EFFECT OF PROPANE DESLUDGING TEMPERATURE ON SLUDGE VALUES OF USED OILS

Desludging temperature, ° C.	22	66
Dissolved sludge, mg. per 10 grams	30	31
	148	167
	148	185
	157	177
	640	750

Using the method for the determination of undissolved sludge previously presented (1) and the method for determining dissolved sludge described here, the quantity and distribution of sludge present in used motor oils can be determined.

To arrive at a measure of the dissolved sludge, the material insoluble in propane is determined on the clarified sample obtained by passing it undiluted through a filter tube packed with cotton (1). The determination is carried out at room temperature. Employing liquid propane at higher temperatures commonly gives larger quantities of insoluble matter (Table I), but since well-made lubricating oils may have

components which are insoluble in hot liquid propane, calling such matter sludge is unjustified. On the other hand, that which is thrown out by liquid propane at ordinary temperatures is asphaltic, generally absent from well-made motor oils, and considered undesirable.

The amount of insoluble matter found in an oil commonly increases as the boiling point of the paraffin hydrocarbon used as a solvent decreases. Though more insoluble matter may be found by using liquid ethane or methane than by using propane, their low critical temperatures would greatly complicate the apparatus and method and the same objection would apply as to the use of hot propane.

Classifying as dissolved sludge only that portion (of a clarified used motor oil) which is insoluble in liquid propane is obviously empirical. However, it has been found useful in the study of motor oils to know not only the undissolved sludge which may be visually observed and is objectionable from the customer's point of view, but also the dissolved sludge which may be just as objectionable from the engineer's standpoint, since it represents alteration products of the oil and may be considered as potential sludge.

On residual oils it is desirable to determine the dissolved sludge on the unused oil also, in order to evaluate better the change brought about by service or engine tests.

Method

The following method has been in use in this laboratory for several years:

The sample is clarified by filtration, undiluted, through absorbent cotton, using the apparatus previously described (1).

APPARATUS. The desludging apparatus is shown in Figures 1 and 2. It consists of a 184 \pm 1 mm. section of Pyrex "high-pressure" gage glass tubing 32 mm. (+0.5 to -1.5 mm.) in outside diameter with a wall thickness of approximately 3 mm., having one end sealed, closed, and rounded to a radius of approximately 16 mm., and the open end fire-polished flat at right angles to the axis of the cylinder. The tubes were made on order by the Corning Glass Works.

The pressure assembly for the test tube is shown in Figures 1 and 2. The outside tube is made of seamless brass tubing and should fit the glass tube snugly. The rubber cushion is made from a rubber stopper of good grade, hollowed to fit the bottom of the tube.

FIGURE 1. LABORATORY PROPANE
DESLUDGING APPARATUS

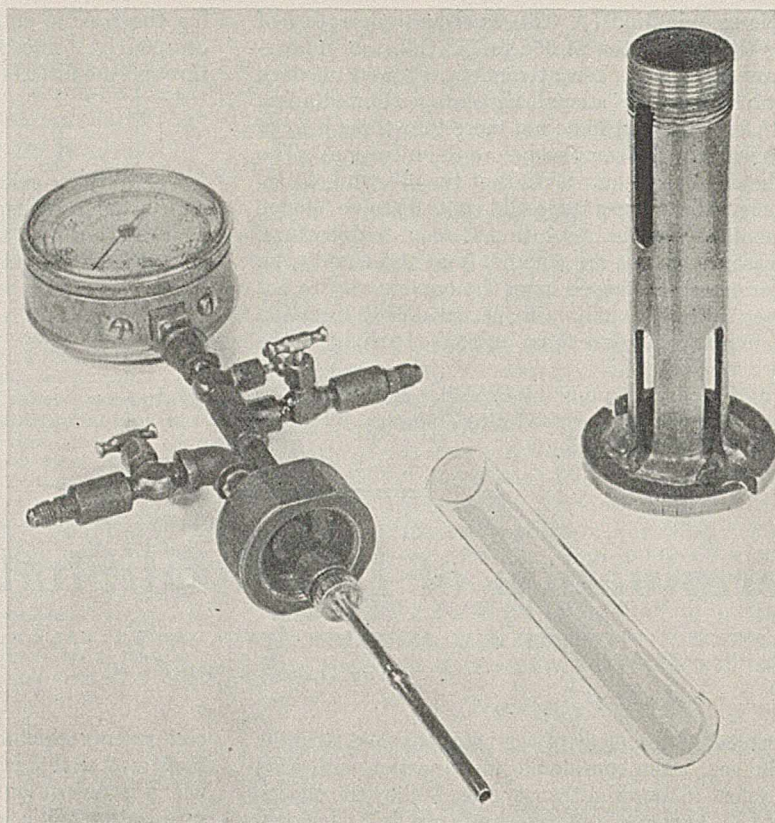
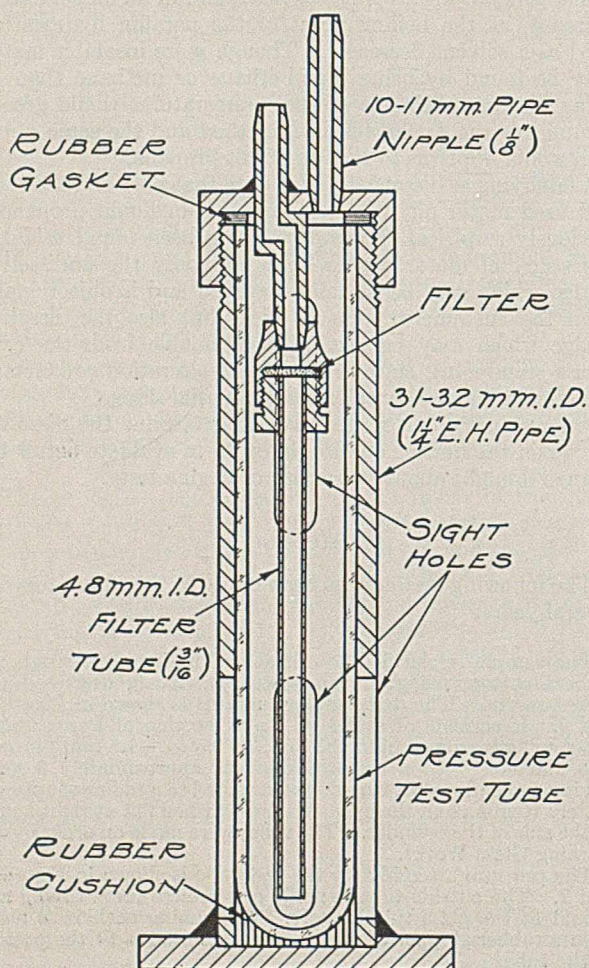


FIGURE 2. SECTIONAL ELEVATION OF
DESLUDGING APPARATUS



As a safety precaution a reinforced glass shield should be used around the pressure assembly, as shown in Figure 3.

PROCEDURE. The filter which must be placed in the filter cap (Figure 2) is made by cutting a disk from blotter press paper with the aid of a cork borer of the proper size. A suitable paper is the Eaton and Dikeman Co.'s filter paper No. 625 (0.66 mm., 0.026 inch). This disk serves both as filter and gasket. To prevent a large sludge from clogging this filter, the tube is packed with absorbent cotton from the filter downward for a distance of about 76 mm.

Four grams of the clear sample are weighed into the pressure test tube and the apparatus is assembled. The metal cap, with valves 1 and 2 closed (Figure 3), is screwed on hand-tight, finishing by holding the cap in a vise. During assembly, the apparatus should be held in an inclined position so as to keep the sample from rising to the filter, valve 1 being kept closed for the same reason and valve 2 being closed to protect the gage.

The assembly is now rotated in an inclined position so as to distribute the sample over a large surface and is then placed in the wired glass frame. For safety, stout goggles should be worn when working with propane in this test, since at room temperature the pressure within the test tube is of the order of 10.5 kg. per sq. cm. (150 pounds per square inch). Liquid propane (commercial, 98 per cent purity, free from odorants and nonhydrocarbon substances, has been used for all tests) from an inverted cylinder is introduced through valve 1, valve 3 being left open for a few moments to allow air to be displaced. Valve 3 is now closed, the apparatus set upright, valve 2 opened, and the introduction of liquid propane continued until the liquid level is at the mark on the pressure test tube. By means of a sticker the test tube is marked at a level so that the liquid volume assembled will be 64 ml. Valve 1 is closed and the adjacent union disconnected from the propane supply. Valve 2 is closed to protect the gage and the entire assembly (Figure 3) gently agitated until all the liquid dissolves. The assembly is returned to an upright position and allowed to remain that way for 20 minutes or until the sludge has settled, valve 2 being opened each time the assembly is left in an upright position.

A short length of copper tubing is connected to the nipple off valve 1 and the propane solution pressure-decanted through valve 1, which is opened slightly so as to maintain the pressure on the liquid substantially beyond the discharge end of the valve.

The sediment is washed by refilling the test tube with propane in a similar manner but this time the propane is introduced

through valve 3, though pressure-decanted through valve 1. The washing is similarly repeated twice more.

Care should at all times be taken to vent the propane slowly, so as to avoid chilling the apparatus. When the pressure is down to atmospheric the apparatus is dismantled and the sediment is dissolved by means of warm benzene from the test tube, filters, gasket, and other parts where it could have been deposited during the test. The benzene solution is then filtered through a rapid paper (Whatman's No. 41 H, 9 cm.) into a small tared beaker, the filtrate is evaporated on a steam bath, and the residue is dried in an oven at 110° C. and weighed.

The weight of dissolved sludge multiplied by the decimal fraction of "dissolved sludge plus oil" in the sample gives the dissolved sludge on the basis of the original unfiltered sample.

Dissolved sludge is reported in terms of milligrams per 10 grams.

Experimental

Results obtained on used oils have shown that frequently the dissolved sludge is greater than the undissolved. Typical results are shown in Table II.

TABLE II. TYPICAL VALUES FOR DISSOLVED AND UNDISSOLVED SLUDGE

Sample	Used Motor Oil	Dissolved Sludge ^a Mg./10 g.	Undissolved Sludge Mg./10 g.
1	From laboratory test car	151	112
2	From road test car A	17	9
3	From road test car B	7	2
4	From road test car C	36	45
5	From road test car D	20	28
6	From Diesel truck E	67	392
7	From Diesel truck F	42	391
8	Used airplane oil, from laboratory test engine	153	7

^a Note that dissolved sludge is frequently greater than undissolved.

The method has yielded results reproducible within 5 per cent on samples containing large amounts of dissolved sludge, and within 5 mg. per 10 grams on samples containing small amounts.

For work with hot propane, the authors employed a brass assembly similar to Figure 1 except that the brass bomb had no sight holes, the pressure test tube was not used, a higher pressure gage was used, and a transfer case was employed to introduce the propane. Hot propane was not deemed desirable for dissolved sludge determinations.

TABLE III. EFFECT OF RATIO OF SOLVENT TO SAMPLE ON SLUDGE VALUES OF USED OIL

Ratio of Solvent to Sample	Dissolved Sludge				
	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5 ^a
	Mg. per 10 grams of oil				
30:1	100	134	156	20	2180
15:1	152	153	150	34	2300
10:1	141	158	134	18	2330
7:1	136	136	110	..	2260

^a Samples 1 to 4 were used engine oils; sample 5 was a white medicinal oil after oxidation at 171.7° C. (341° F.) under conditions of the German tar-forming number test. Desludging with propane was done at room temperature (22° C.).

This work has also shown that the amount of dissolved sludge thrown out by propane varies on some samples with the solvent-to-sample ratio (Table III) and the maximum

sludge precipitated does not occur at a uniform ratio for different samples. The ratio which has been adopted was selected as being of most general utility and it is hoped that the method will find use as a tool in the complicated task of used oil analysis.

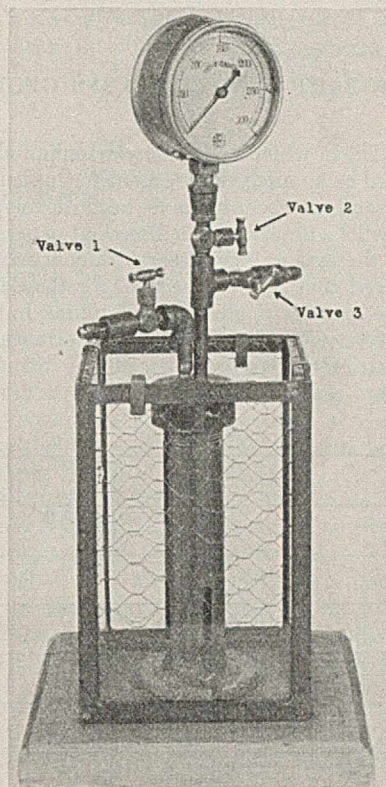


FIGURE 3. DESLUDGING APPARATUS ASSEMBLED

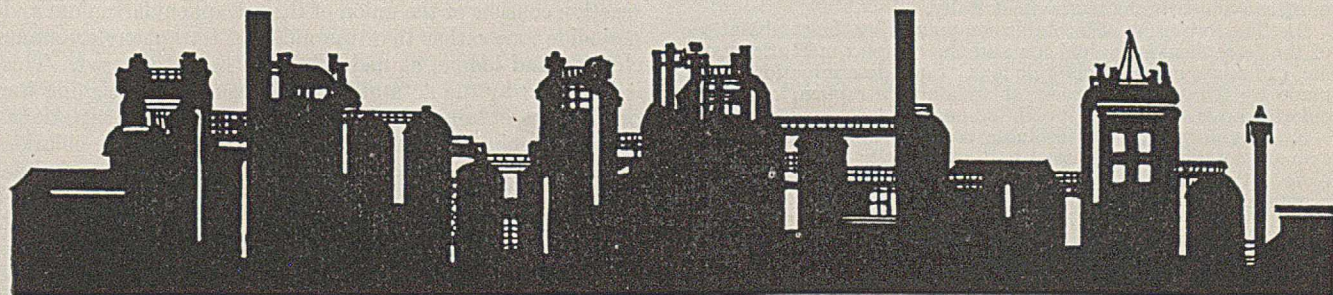
Unsatisfactory results are obtained when one attempts to determine undissolved sludge by means of propane tests on the original and filtered samples of a used oil. This is due to the fact that fine hard particles of the original sample are forced through the filter in the pressure decantations and small particles of dirt or bearing metal constitute a large proportion of the sludge.

Acknowledgment

The authors wish to acknowledge the assistance of J. R. McDowell, H. C. Becker, and A. J. Millendorf, who did most of the analytical work involved in the development of this method.

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Tetraphenylarsonium Chloride as an Analytical Reagent

Titration by Iodine

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METHODS in which tetraphenylarsonium chloride may be used as an analytical reagent for mercury, tin, cadmium, zinc, and perchlorate have been developed by the authors and will be described in subsequent papers. Lamprey (3), who did the exploratory research in connection with the reagent, showed that it could be used for the determination of perchlorate, periodate, gold, and platinum, but his studies were not exhaustive. He showed that the reagent could be used gravimetrically, or volumetrically by titrating the excess of standard reagent potentiometrically with iodine.

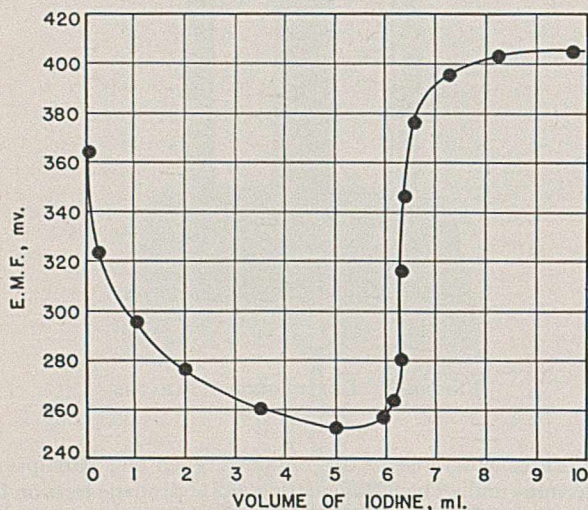


FIGURE 1. TETRAPHENYLARSONIUM CHLORIDE TITRATED WITH IODINE
Solution saturated with sodium chloride

Tetraphenylarsonium chloride (obtainable from Merck & Co.) was prepared according to the method of Blicke and Marzano (1), with slight modifications developed by the authors and others. According to Blicke and Monroe (2) the aqueous solution is a strong electrolyte which yields tetraphenylarsonium, $(C_6H_5)_4As^+$, and chloride ions.

Three types of reactions have been noted in which the reagent is serviceable:

1. The formation of insoluble salts by the combination of the tetraphenylarsonium ion with such ions as perchlorate, permanganate, periodate, and perchlorate. Such determinations were most conveniently made gravimetrically.
2. The formation of insoluble compounds by the combination of the tetraphenylarsonium ion and the complex mercuric, stannic, cadmium, and zinc chloride ions. Such determinations were made by titrating the excess of standard tetraphenylarsonium chloride potentiometrically with iodine.
3. The formation of insoluble compounds with such thiocyanate complexes as those of iron and cobalt. These reactions have not yet been thoroughly investigated, but they appear to present analytical possibilities.

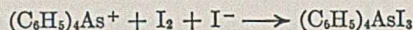
The analytical behavior of several other arsonium ions was studied. Although all gave precipitates resembling those ob-

tained with tetraphenylarsonium ion, none reacted quantitatively with iodine or with perchlorate, perchlorate, or chlorocadmiate ions. The compounds were similar to tetraphenylarsonium chloride with one of the phenyl groups replaced by an alkyl or substituted alkyl group. The compounds tried were iodomethyltriphenylarsonium chloride, triphenylarsinehydroxy chloride, phenacyltriphenylarsonium chloride, allyltriphenylarsonium bromide, β -hydroxyethyltriphenylarsonium chloride, methyltriphenylarsonium chloride, and carboxymethyltriphenylarsonium chloride. The effect of the substitution of an alkyl group for the phenyl group is to increase the solubility of the compounds.

Since the determinations of the mercuric, stannic, cadmium, and zinc ions depend upon the potentiometric titration of the excess of standard tetraphenylarsonium chloride by means of standard iodine solution, this titration is discussed in this paper. Applications of the reagent will be presented in subsequent papers.

Potentiometric Titration of Tetraphenylarsonium Chloride with Iodine

This titration, by means of which the tetraphenylarsonium chloride solution is standardized, depends upon the reaction



and the fact that there is a sudden large increase in the oxidation potential when an equivalent quantity of iodine containing iodide has been added to the tetraphenylarsonium chloride solution (Figure 1). It is seen from the equation that one molecular weight of tetraphenylarsonium chloride requires two atomic weights of iodine and one of iodide.

TABLE I. GRAVIMETRIC DETERMINATION OF TETRAPHENYLARSONIUM ION

I_2 Used Mg.	$(C_6H_5)_4AsI_3$ Calcd. Mg.	$(C_6H_5)_4AsI_3$ Found Mg.
13.83	41.6	41.8
13.83	41.6	41.6
13.80	41.5	41.7
13.87	41.7	41.8
13.83	41.6	41.6

The reaction is carried out in volumes less than 150 ml. in saturated sodium chloride solution. Since the product, a rusty-orange precipitate, does not form unless the iodine solution contains potassium iodide, it is evident that the reaction consists of the union of the tetraphenylarsonium and periodide ions rather than the union of tetraphenylarsonium chloride and iodine, as had originally been supposed. This is indicated by the data of Table I, secured by weighing the precipitates obtained from several potentiometric titrations. Measured volumes of standard tetraphenylarsonium chloride solution were titrated potentiometrically with standard iodine solution. The precipitates were filtered through Gooch crucibles, washed with water, dried at 105° C., and weighed. Within the limits of experimental error the observed weights of the precipitates are the same as the weights of tetraphenylarsonium periodide calculated from the volume of standard

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iodine used. However, the gravimetric standardization of the reagent with excess iodine is not as convenient nor as precise as the potentiometric method.

The potentiometric standardization is carried out as follows:

Five to 10 ml. of the aqueous tetraphenylarsonium solution, 0.01 to 0.03 *M*, are measured and diluted to nearly 100 ml. with water or saturated sodium chloride solution. The reference and indicator electrodes are immersed in this solution while standard iodine solution of about the same concentration, containing 6 to 8 grams of potassium iodide per liter, is added slowly with constant stirring. As the iodine is added the potential of the system steadily decreases to a minimum value. When this minimum is reached, the iodine is added dropwise and time allowed for the system to reach equilibrium. When an equivalent quantity of iodine has been added there is a sudden increase in potential amounting to 25 to 35 millivolts per 0.01 ml. of 0.02 *N* iodine. Near the end point the solution must be completely saturated with salt before the titration is completed.

Any type of potentiometer system may be used. The indicator electrode was a smooth platinum wire and the reference electrode a calomel half-cell.

By the above procedure 4 to 100 mg. of tetraphenylarsonium chloride can be determined conveniently, and successive titrations duplicated within 0.02 to 0.03 ml. of 0.02 *N* iodine solution. The optimum concentration is 10 to 50 mg. of the reagent in about 100 ml. of solution, although acceptable results are obtained in 200 ml. It is best to saturate with sodium chloride just before the end point is reached. The time required is 20 to 30 minutes.

TABLE II. EFFECT OF SODIUM CHLORIDE CONCENTRATION ON TITRATION

[1 ml. of reagent solution contains 4.086 mg. of (C ₆ H ₅) ₄ AsCl]		
NaCl	(C ₆ H ₅) ₄ AsCl	(C ₆ H ₅) ₄ AsCl
Moles/l.	Ml.	Mg./ml.
0	20	4.10
0	10	4.12
0	5	4.18
0	1	4.39
1.00	5	4.14
2.50	5	4.11
4.00	5	4.084
4.50	5	4.090
5.00	20	4.080
5.00	10	4.080
5.00	5	4.082
5.00	2	4.087

For best results the temperature of the solution being titrated should be 20° to 30° C., and never above 40° to 45° C., because of the volatility of the iodine and the increased solubility of the periodide precipitate.

TABLE III. SOLUBILITY OF TETRAPHENYLARSONIUM CHLORIDE IN AQUEOUS SODIUM CHLORIDE SOLUTIONS

(60-Ml. volume. Temperature, 30° C.)		
NaCl	(C ₆ H ₅) ₄ AsCl	(C ₆ H ₅) ₄ AsCl
Moles/l.	G./100 ml.	Mole/l.
0	32.50	0.776
1.0	10.43	0.240
2.0	1.27	0.038
2.5	0.459	0.011
3.0	0.205	0.0049
3.5	0.101	0.0024
4.5	0.034	0.00081
Satd.	0.011	0.00026

The influence of the sodium chloride concentration is shown by Table II. Equilibrium is attained very slowly in low salt concentrations, thus making the titration very slow and uncertain. However, when the solution is almost saturated with sodium chloride, equilibrium is reached in a short time, and constant and easily reproducible results are obtained. A small amount of potassium iodide produces similar results but may form insoluble tetraphenylarsonium iodide.

Although the tetraphenylarsonium chloride precipitates slowly, it is insoluble in concentrated sodium chloride solution, as Table III shows. Since the conversion of solid

tetraphenylarsonium chloride to the periodide is very slow, it is best to avoid formation of the solid by beginning the titration with a moderate salt concentration and completing the saturation just before the end point is reached. The standard iodine solution should not contain more than 6 to 8 grams of potassium iodide per liter of 0.01 to 0.02 *N* solution; otherwise insoluble tetraphenylarsonium iodide will form.

The solubilities in water of other tetraphenylarsonium halides at 25° C. were investigated, and are presented in Table IV.

TABLE IV. SOLUBILITIES OF TETRAPHENYLARSONIUM HALIDES (Temperature, 25° C.)

Compound	Solubility	
	G./100 ml.	Mole/l.
Tetraphenylarsonium fluoride	17.45	0.434
Tetraphenylarsonium chloride (30° C.)	32.50	0.776
Tetraphenylarsonium bromide	1.29	0.0279
Tetraphenylarsonium iodide	0.14	0.0028

A typical titration curve is shown in Figure 1. The first portion of the curve, in which the potential falls rather sharply as the iodine is added, probably corresponds to the removal of tetraphenylarsonium ion. The potential rises abruptly with the first slight excess of iodine, and the addition of a further excess causes a negligible change.

The direct titration of the reagent with iodine, or the titration of the excess of iodine with standard thiosulfate in the presence of the periodide precipitate with starch as the indicator is impossible, since the color of the precipitate obscures the color of the starch-iodide complex. The potentiometric titration of excess iodine with thiosulfate in the presence of the precipitate is impossible because of the uncertainty of the end point.

TABLE V. EFFECT OF ACIDITY AND NITRATES ON TITRATION

[5 ml. of (C ₆ H ₅) ₄ AsCl in 100 ml. of solution saturated with salt]	
Iodine Required	Substances Present besides Sodium Chloride
Ml.	
4.58	None
4.58	Concd. HCl, 2.0 ml.
4.56	Concd. HCl, 3.0 ml.
4.57	NaNO ₃ (neutral), 2.0 grams
4.58	NaNO ₃ , 2.0 grams
	Concd. HCl, 0.2 ml.
4.58	NaNO ₃ (neutral), 10.0 grams
	80% salt satn.
4.50	NaNO ₃ , 10.0 grams
	Concd. HCl, 1.0 ml.
	80% salt satn.
4.35	NaNO ₃ , 10.0 grams
	Concd. HCl, 1.0 ml.
	80% salt satn.
	More time allowed than in preceding titration

The presence of free acid, except nitric acid, in moderate amounts is not objectionable, as shown by Table V. Nitric acid, and nitrates in the presence of acid, oxidize the iodide in the standard iodine solution to free iodine, causing the end point to be premature. When nitrates are present, the solution is neutralized to methyl red with sodium bicarbonate before titrating. Large quantities of nitrate cause the precipitation of tetraphenylarsonium nitrate.

Other chlorides, except those capable of oxidizing iodide or reducing iodine and those that form complex halide ions, may be substituted for sodium chloride. Other salts, such as sulfates, are not as effective in coagulating the precipitate. The alkalis and alkaline earths, nickel, cobalt (ous), chromium, manganese, borate, bicarbonate, acetate, phosphate, sulfate, citrate, and tartrate even in fairly high concentration do not interfere. The solution must be neutral or slightly acid. All anions that form fairly insoluble compounds with the reagent—e. g., tungstate, molybdate, chromate, perrhenate, permanganate, periodate, perchlorate, iodide (except in the iodine solution), bromide and fluoride—and all cations that form complex halide ions—e. g., zinc, cadmium, mercuric,

thallic, stannic, bismuth, ferric, platinum, and auric—interfere.

Ferrous ion (100 mg. or less) may be present. When ferric ion is present the addition of about 2 ml. of sirupy phosphoric acid and 2 grams of disodium phosphate will eliminate interference up to 200 mg. of iron, but results are not ideal with

TABLE VI. EFFECT OF CERTAIN CATIONS ON TITRATION

[5 ml. of $(C_6H_5)_4AsCl$ in 100 ml. of solution saturated with sodium chloride. 5 ml. of $(C_6H_5)_4AsCl$ are equivalent to 7.17 ml. of iodine solution]

Iodine Required Ml.	Substances Present besides Sodium Chloride
7.18	$MnCl_2 \cdot 2H_2O$, 1 gram
7.17	$CrCl_3 \cdot 6H_2O$, 1 gram
7.17	Sodium citrate, 8.8 grams
7.23	Sodium citrate, 17.5 grams
7.17	Cu^{++} , 400 mg.
	Sodium citrate, 4 grams
7.16	Cd^{++} , 88 mg.
	Sodium citrate, 4.5 grams
7.20	Zn^{++} , 10 mg.
	Sodium citrate, 4.5 grams
7.28	Bi^{+++} , 33 mg.
	Sodium citrate, 4.5 grams
7.33	Sn^{++++} , 16 mg.
	Sodium citrate, 4.5 grams
7.16	Fe^{+++} , 200 mg.
	Disodium phosphate, 2 grams
7.22	$FeSO_4 \cdot 7H_2O$, 500 mg.

amounts beyond 100 mg. Citrate and tartrate are not effective in this respect, but citrate prevents interference by rather large amounts of cupric ion and by very small amounts (a very few milligrams) of tin, bismuth, zinc, and cadmium. A few grams of sodium citrate and enough citric acid to make the solution acid to methyl red are added before titrating. Table VI shows the effect of various cations on the titration.

All common organic solvents interfere either by preventing precipitation or by obscuring the end point.

Summary

Tetraphenylarsonium chloride is useful as a reagent for determining mercuric, stannic, cadmium, zinc, perrhenate, periodate, perchlorate, and other ions.

Periodate, perchlorate, permanganate, perrhenate, fluoride, bromide, iodide, thiocyanate, molybdate, chromate, tungstate, and large amounts of nitrate interfere by forming insoluble salts with the reagent.

Mercury, tin, cadmium, zinc, platinum, gold, bismuth, and iron, the complex halide ions of which form insoluble compounds with the reagent, and all ions that can oxidize iodide or reduce iodine interfere.

Interference by copper, iron, cadmium, zinc, bismuth, and tin may be eliminated to some extent.

The reagent may be standardized potentiometrically with standard iodine, the reaction producing a rusty-orange precipitate of tetraphenylarsonium periodide.

The total volume to be titrated should be about 100 ml. of neutral or slightly acid solution saturated with sodium chloride just before the end point is reached.

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FROM a thesis presented by G. M. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

Duplicating Pipets

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PIPETTS similar to Ostwald-Van Slyke "between marks" pipets, but having two bulbs, offer many advantages.

1. The amount of solution required to fill the uncalibrated part of the pipet below the lower mark is half as great for the two samples as for samples taken in two fillings of a single-bulb pipet. This small saving of the specimen is often important where a number of different analyses are required on a limited sample of blood or serum or where capillary blood samples are used. Pipet A, Figure 1, has been used where economy of sample is important—for instance, routinely in taking samples of serum or plasma for cholesterol determinations by the author's method.

2. When duplicate samples of a supernatant solution are to be drawn off from above a precipitate which is easily disturbed, the use of the duplicating pipet avoids stirring up this precipitate between samples. Pipet B has been used for taking samples of supernatant fluid for ascorbic acid determinations after precipitation of proteins. Its greater length of tip is convenient in removing samples from or delivering to narrow tubes, etc.

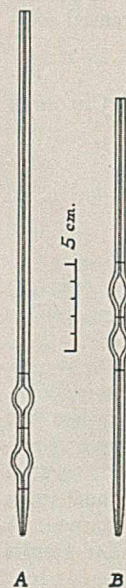


FIGURE 1.
DUPLICATING PIPETS

3. Whenever it is undesirable to use the same single bulb pipet for a second sample—for example, in avoiding exposure of a thin film of sample to air on the walls of the pipet or the trapping of persistent bubbles in a viscous solution—the use of a single duplicating pipet in place of two single pipets effects a saving in cost of pipets, and in time consumed in washing the pipets.

4. Even though a single pipet could be used, the duplicating pipet saves the analyst's time, and, what is more important, speeds up the handling of unstable solutions.

5. The average of duplicates involves errors at only two calibration marks instead of four.

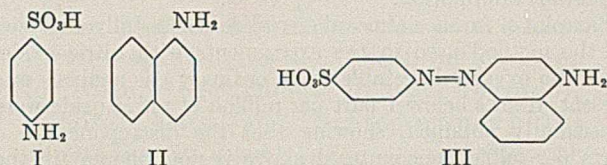
Specifications are purposely omitted from Figure 1, since these are type forms which can be modified to adapt them to particular uses.

FROM The Children's Hospital Research Foundation and the Department of Pediatrics, College of Medicine, University of Cincinnati.

Spectrophotometric Determination of Nitrite And of Nitric Oxide in Furnace Atmospheres

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GRIESS (6) first discovered that nitrous acid could be detected by reacting it with sulfanilic acid (I), coupling the resulting diazonium compound with α -naphthylamine (II) to form a highly absorbing pink azo dye (III):



Perhaps the most sensitive method of detecting nitrite or nitrous acid as such (5, 7, 8), the formation of this dye can also be used to measure amounts of any substance that will yield nitrite in known proportion—for example, traces of oxygen could be determined by the use of nitric oxide in large excess. Over a year ago, the problem of estimating the small amounts of nitric oxide in certain furnace atmospheres arose in this laboratory, and the authors were led to investigate the usefulness of Griess's reagent for this purpose. Recently they discovered that Bennett (2) had already completed a similar investigation, employing visual methods where they used a recording spectrophotometer (15), and that their results in general confirm his earlier findings.

Griess's reagent, as modified by Ilovsay and Lunge, was prepared approximately according to the directions of Dennis (4).

Sulfanilic acid (0.5 gram) was dissolved in 150 cc. of 5 *N* acetic acid; 0.1 gram of α -naphthylamine was boiled with 20 cc. of water, filtered while hot, and the filtrate added to 150 cc. of 5 *N* acetic acid. The two solutions were mixed and kept in a glass-stoppered bottle that stood in the dark. A known aqueous potassium nitrite solution containing 10 micrograms per cc. was prepared from the c. p. salt (84.5 per cent KNO_2). Standard nitrite solutions for colorimetric work were prepared by adding the proper volume of this stock solution to 20 cc. of 0.5 *N* sodium hydroxide, and shaking after the mixture had been acidified with 1.6 cc. of glacial acetic acid. After the further addition of 4 cc. of the Griess reagent, dilution to 27 cc., and thorough mixing, the solutions were allowed to stand 20 minutes before their transmissions were measured on the spectrophotometer in a cylindrical quartz cell (inside length, 5.15 cm.; inside diameter, 2.40 cm.).

TABLE I. CONCORDANCE OF CURVES

After 20 Minutes' Standing. $I_B = 76.2\%$						
m	0.50	1.00	2.00	4.00	6.00	10.00
Δ	0.049	0.0785	0.1488	0.3115	0.4620	0.7816
k	0.098	0.0785	0.0744	0.0779	0.0770	0.0782
m (calcd.)	0.63	1.02	1.93	4.03	5.99	10.1
Av. $k = 0.0772$						
After 50 Minutes' Standing. $I_B = 75.7\%$						
m	0.50	1.00	2.00	4.00	6.00	10.00
Δ	0.050	0.0777	0.1483	0.3074	0.4591	0.7753
k	0.101	0.0777	0.0742	0.0769	0.0765	0.0775
m (calcd.)	0.65	1.01	1.94	4.02	5.99	10.1
Av. $k = 0.0766$						

The standard solutions were prepared in this way mainly because aqueous sodium hydroxide was used as absorbent in the nitric oxide determinations; thus the troublesome purification of the reagents could be circumvented. Also, the sodium acetate, by decreasing the acidity, may speed up the reactions involved in the formation of the azo dye. The transmission curves for the standard nitrite solutions are shown in Figure 1.

The maximum absorption of visible light by the azo dye evidently occurs at 5200 Å., and this wave length was accordingly chosen for quantitative colorimetric work. Beer's law in the form

$$\Delta = \log I_B/I = k(m) \quad (1)$$

where I_B is the intensity of transmitted light at 5200 Å. for the reagent blank, I is the corresponding intensity for the sample, and m is the micrograms of added potassium nitrite, will be used to show the concordance of the curves at the absorption maximum.

The average k , which is used in computing m (calculated), is the arithmetical mean of all values except that for 0.5 microgram. The data show: (1) that above $m = 0.5$, m and m (calculated) are in excellent agreement: Beer's law is obeyed within the experimental error (usually less than 2 per cent); (2) that, after the first 20 minutes, standing up to 30 minutes more has little or no effect on the results. This concordance, which might be increased even further, establishes this as one of the more accurate colorimetric methods; it shows that Bennett (2) was correct in attributing his larger (5 to 10 per cent) errors to the personal factors associated with visual comparisons. It suggests that the conversion of nitrite into azo dye, a relatively complex process, is virtually complete even at these very low concentrations of nitrite. The colorimetric method might be a valuable tool for investigating the mechanism of the reactions involved in the conversion.

The molar extinction coefficient of the azo dye can be calculated from k if complete conversion of the added nitrite is

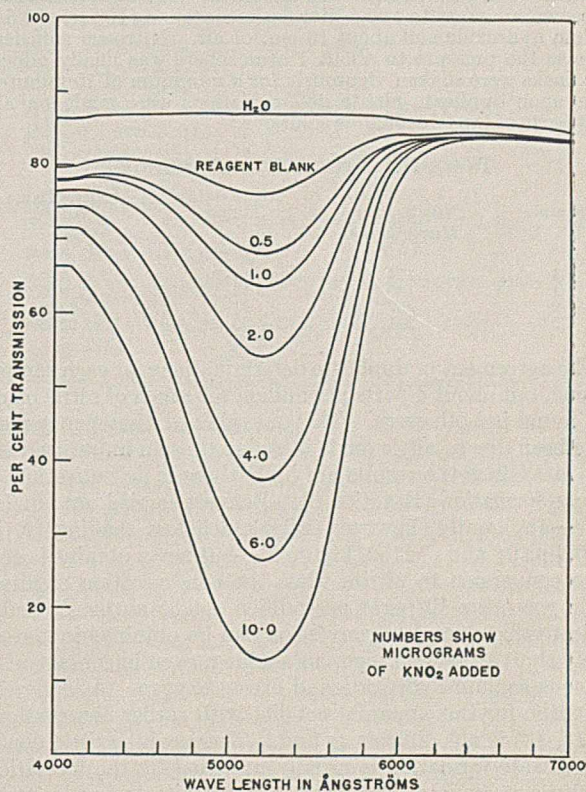
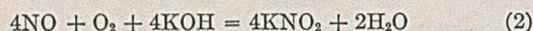


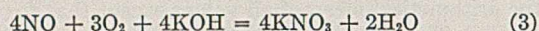
FIGURE 1. TRANSMISSION CURVES OBTAINED WITH THE POTASSIUM NITRITE STANDARD SOLUTIONS

assumed. The result, $\epsilon = 34,400$ for 5200 \AA. , is in close agreement with the maximum coefficients for dithizone ($30,400$ at 6200 \AA.) and copper dithizonate ($35,600$ at 5080 \AA.) (13); since the magnitude of ϵ is an index of the sensitivity of a colorimetric method, it may be that $35,000$ or thereabouts is an upper limit that maximum extinction coefficients in colorimetric methods may be expected to approach; ϵ of the zirconium-quinalizarin lake, for example, is only $10,000$ (14).

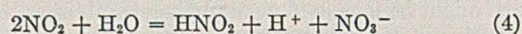
An extensive literature testifies that the stoichiometry of the reaction between nitric oxide and oxygen is a complex and somewhat controversial subject; no complete discussion can be given here. Baudisch and Klinger (1) first proved that the reaction



could be used for the determination of nitric oxide; stoichiometric conversion into nitrite occurs, provided the hydroxide is sufficiently dry (12) and the oxygen is admitted to nitric oxide that is already in contact with the alkali. If these conditions are not carefully observed, the reaction



also occurs. Reaction 3 is known to involve the intermediate formation of nitrogen dioxide, which can react with water (perhaps also with the alkali) to give nitrate and nitrite, for example:



This earlier work would indicate that nitric oxide can never be completely converted to nitrite if it is mixed with an excess of oxygen and permitted to stand in contact with dilute alkali.

It was accordingly necessary to test the stoichiometry of the reaction between nitric oxide and oxygen.

Pure nitric oxide was prepared by reacting potassium nitrite, potassium iodide, and sulfuric acid (9); and was passed through 90 per cent sulfuric acid, then through 50 per cent potassium hydroxide. The resulting gas was diluted with nitrogen and added in known amounts to two 4-liter flasks containing 100 cc. of 0.5 *N* sodium hydroxide and about 10 cm. of air. Nitrogen sufficient to raise the pressure to about 1 atmosphere was finally added. The flasks were shaken vigorously for a minimum of 10 minutes, whereupon duplicate nitrite determinations were made on aliquot parts of the two alkaline solutions.

TABLE II. NITRITE DETERMINATIONS

Sample	Nitrite Found	Nitric Oxide Found	Nitric Oxide Added
	Micrograms of KNO_2	<i>P. p. m.</i>	<i>P. p. m.</i>
1	171	12.7	8.0
1	168	12.5	8.0
2	367	27.2	22.8
2	351	26.0	22.8

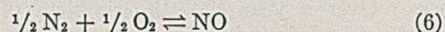
The agreement of duplicate determinations for each sample is good, but about 4 parts per million too much of nitric oxide was found in both cases. This unexplained discrepancy may have been due to nitric oxide introduced as an impurity. At any rate, since the results are high, there is no indication of nitrate formation (Reaction 3). Bennett carried out similar tests—apparently, however, with much less shaking (2, p. 1150, line 9; and p. 1152, Figure 9)—but never obtained complete conversion to nitrite when the concentration of nitric oxide was near 10 parts per million. The authors' results indicate that complete conversion can be obtained in a relatively short time with vigorous shaking, even in contact with aqueous sodium hydroxide and excess oxygen. A likely explanation for this apparent conflict with earlier observations (1, 11, 12) is not difficult to find. There can be little doubt that nitrate formation is usually preceded by the formation of nitrogen dioxide (Reaction 4), since nitrate formation is enhanced by the presence of water or of excess oxygen. The

gaseous reaction by which nitrogen dioxide is formed from nitric oxide and oxygen follows the law (10)

$$-d(\text{O}_2)/dt = k(\text{NO})^2(\text{O}_2) \quad (5)$$

Equation 5 predicts that nitrogen dioxide formation will be retarded by reducing the nitric oxide pressure; consequently no nitrate may have formed in the authors' experiments because the nitric oxide pressure was too low. But the whole subject deserves further attention—a kinetic investigation, using the colorimetric method, of the oxidation of nitric oxide at very low pressures by oxygen in the presence and absence of aqueous sodium hydroxide should yield interesting and important information.

Samples of furnace atmospheres were successfully analyzed by the method used in the experiments with nitric oxide. When no oxygen detectable in an ordinary gas analysis was present, results below 1 part per million of nitric oxide were consistently obtained, showing that the discrepancy of 4 parts per million encountered above is not inherent in the analytical method. When a gas containing 0.7 per cent oxygen, 9.7 per cent carbon dioxide, no carbon monoxide, and 89.6 per cent nitrogen issued from a furnace in which the maximum temperature was 1390°C. , about 80 parts per million of nitric oxide were found. This concentration is about one seventh the equilibrium concentration for the reaction



at 1390°C. and far above the concentration for room temperature (3), indicating that the mixture of gases cooled rapidly enough to slow up the dissociation of nitric oxide (of course, equilibrium at 1390°C. may never have been established). The colorimetric method might be used to study the rate of the reverse, and perhaps of the forward, reaction in the important Equilibrium 6.

Attempts to collect the nitric oxide by passing the furnace gas mixed with air through liquid air and then through a bubbler containing dilute sodium hydroxide were unsuccessful, probably because there was insufficient time for the conversion of nitric oxide to nitrite.

Summary

The determination of very small amounts of nitrite with Griess's reagent (sulfanilic acid and α -naphthylamine in acetic acid solution) has been studied with a recording spectrophotometer and found to be one of the more accurate colorimetric methods.

The same reagent has been used successfully for the determination of nitric oxide in concentrations well below 10 parts per million.

The possible use of the colorimetric method in several other connections has been pointed out.

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Identification of Lines in Qualitative Spectrographic Analysis

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Charts giving a wave-length scale, an iron arc reference spectrum, and analysis lines for 47 elements are constructed for the region 2500 to 5150 Å. by use of a quartz Littrow spectrograph. Directions are given for using the charts in spectrographic qualitative analysis. Reproductions of the charts may be used as accurate wave-length and analysis scales for any quartz spectrograph.

A COMPLETE spectrographic analysis for fifty or more elements is a tedious procedure, usually done by comparing the analysis spectrum with standard plates or by using enlargements of standard spectra. A method of identification has been used in this laboratory that has materially shortened the labor of an analysis, and is believed to be fully as reliable as other methods. The procedure is to project an enlarged image of the analysis spectrum onto a chart which contains a standard spectrum map, an iron arc reference spectrum, and a wave-length scale. The standard map gives the important analysis lines of all elements sought. Instead of identifying all lines or looking for specific lines of various elements, it is necessary only to note coincidences of projected lines with lines of the map.

The complete set of charts is shown in Figure 1. There are nine charts, each inked on a stiff card measuring 15 × 62.5 cm. (6 × 25 inches). Each card corresponds to a plate region of 3.8 to 4.4 cm. (1.5 to 1.75 inches), five cards being required for examination of a completely filled 10 × 25 cm. (4 × 10 inch) plate. There is some overlapping of the spectral regions covered by successive cards, so that a line may be identified in one section and then be used as a reference point for beginning the examination of the following section.

Construction of Charts

The wave-length or dispersion scale was first constructed by use of an iron arc spectrum. Selected lines, at convenient intervals, were identified by use of a standard grating spectrum and the wave lengths of these lines were ascertained by reference to Kayser's (2) tables. The spectrum was now projected, at a magnification of 13×, onto the *x*-axis of a large sheet of coordinate paper and the positions of the selected lines were carefully marked. A wave-length curve was next plotted on the same sheet and selected values at 10 or 20 Å. intervals were projected from the curve onto the *x*-axis. These integral wave-length values were transferred to cardboard sheets and each interval was subdivided into equal portions for the unit values shown in the charts. The positions of the selected iron lines were also transferred to the cardboard and these lines were inked just below the scale, to serve as a guide for projection at exactly the same magnification as that employed in the original construction. Finally, the analysis lines of the more important elements were marked on the charts.

The spectrum of each element was photographed separately, each accompanied by an iron arc reference spectrum placed directly above the sample spectrum by means of a slit diaphragm. (The diaphragm has an opening 1 mm. in height for the iron spectrum and 1.5 mm. in height for the spectrum of the sample. The projected iron lines are the same height as the lines of the chart.) The spectra were projected onto the cardboard, the iron lines exactly matched to those of the iron map, and the

positions of the most important lines of the sample marked. The selection of analysis lines was made by inspection of the plate and was confirmed by reference to the tables of Gerlach and Riedl (1) and of Ryde and Jenkins (3).

Table of Analysis Lines

In order to facilitate use of the charts the analysis lines shown have been listed in Tables I and II, which cover, respectively, the two regions for which the spectrograph is usually set. The ultimate test for the identification of an

TABLE I. ANALYSIS LINES IN REGION 2490 TO 3280 Å.

(More important lines for each element in bold-face type. Important lines in other regions designated by parentheses)

Ag	3281a
Al	2568b, 2575b, 3082b, 3093a
As	2493b, 2745b, 2780a , 2860a, 2899b, (2350)
Au	2676a , (2428)
B	2497a , 2498a
Be	3130a , (2349)
Bi	2898b, 2938b, 3024b, 3068a
Cd	2881b, 2980b, 3261a , (2288)
Co	3044a, 3062b, 3072b, 3087b, 3121b, (3454)
Cr	2836b, 2843b, 2850b, 2986-7a, 3015a, 3017a, 3021a, (4254 , 4275 , 4290)
Cu	3248a , 3274a
Fe	See iron map
Ga	2660a, 2720a, 2874a, 2944a , (4172)
Ge	2593b, 2651a , 2691b, 2710b, 2754a, 3039a, 3269a
Hg	2537a
In	3039b, 3256a , (4511)
Ir	2544b, 2640b, 2665b, 2694b, 2824b, 2850a, 2925a, 3133a, 3221a
Mg	2776-83(5 lines)b, 2796a , 2803a , 2852a
Mn	2576a , 2594a, 2606a, 2795a , 2798a, 2801a
Mo	3133a , 3158b, 3170a, 3194a, 3208b, (3798)
Ni	3002a , 3051a , 3054b, 3058b, 3102b, (3415 , 3525)
Os	2637b, 2838a, 2909a , 3018a, 3031b, 3059a
P	2534b, 2536a , 2553a , 2555b
Pb	2577b, 2614a, 2663b, 2823b, 2833a , 2873b
Pt	2651b, 2659a , 2707a, 2734b, 2830b, 2998a, 3043a, 3065a
Sb	2528a(Si), 2598a , 2718b, 2770b, 2878a
Si	2507b, 2514b, 2516a, 2519b, 2524b, 2528b, 2882a
Sn	2547b, 2707a, 2840a , 2863a, 3009b, 3034a, 3175a , 3262a
Ta	2648a, 2653a , 2715a
Th	2837a , (3741 , 4019)
Ti	2611a, 2641a, 2644a, 2647a, 2942a, 2949a, 2956a, 3079a, 3088a, 3200a, 3235-37-39-42a
Tl	2768a , 2918b, 3230b, (3776)
V	2908b, 2924b, 3051a, 3054a, 3056a, 3061a, 3066a, 3093a, 3102a , 3110a, 3118a, 3125a, 3183-4-6a
W	2589a, 2658a, 2724a, 2832a, 2896a, 2944a , 2947a (4009)
Zn	3076b, 3282a

element is based on the important lines, shown in bold-face type. The symbols "a" and "b" denote the stronger and weaker lines, respectively, both in charts and in the tables. No attempt has been made to separate arc and spark lines, but all classifications are based on the apparent intensities in spectra taken with a direct-current carbon arc operated at 10 amperes from a 220-volt source (the drop across the arc is about 45 volts). Because of the use of a carbon arc, certain of the strong lines listed by Gerlach and Riedl have not been included when these lines fall in a region in which the CN bands have high intensity; rather an attempt has been made to choose lines which fall in a region of low background intensity. For example, the identification of chromium is based on the lines at 4254, 4275, and 4290 Å. rather than on the stronger lines at 3579 and 3594 Å., because the latter lines fall in a region of high band intensity.

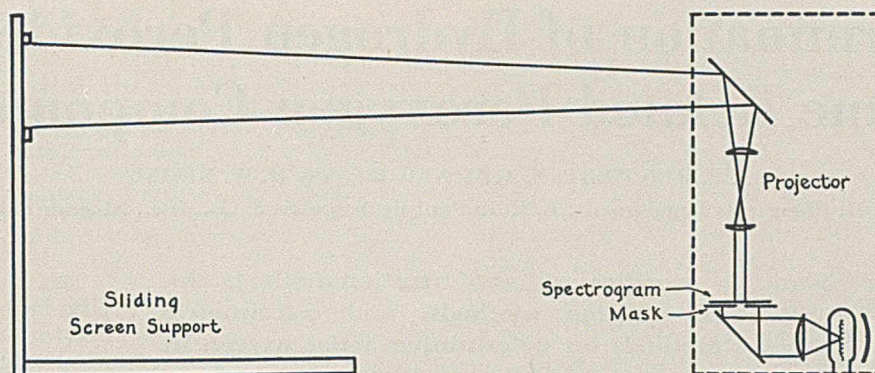


FIGURE 2. ARRANGEMENT FOR PROJECTION OF SPECTRA

TABLE II. ANALYSIS LINES IN REGION 3230 to 5150 Å.

(Important lines in other regions designated by parentheses)

Ag	3281a, 3383a
Al	3944a, 3962a
Ba	3501b, 4554a, 4934a
Ca	3350b, 3361b, 3631b, 3644b, 3934a, 3968a, 4227a
Cd	3261a, 3404b, 3466-7a, 3611a, 4800a, 5086a, (2288)
Co	3405a, 3412a, 3444b, 3449b, 3453a, 3502a, 3894b, 3995b
Cr	3379a, 3593a, 3605a, 4254a, 4275a, 4290a
Cs	4559a, 4593a
Cu	3248a, 3274a
Ga	4033a, 4172a
In	3256a, 3259b, 4102a, 4511a
K	4044a, 4047a
Li	3233b, 4603a
Mo	3194a, 3209a, 3358b, 3903a
Na	3302-3a (Zn), (5890-6)
Ni	3415a, 3446a, 3458a, 3462a
Pd	3243a, 3405a, 3421a, 3609b, 3634a
Rb	4202a, 4216a(Sr)
Rh	3397b, 3435a, 4375a
Ru	3437a, 3499a, 3635a, 3661a, 3727-8a
Sn	3262a
Sr	4078a, 4216a, 4607a
Th	3188a, 3741a, 4019a, 4276b, 4281b, 4381a, 4392a, 4863a, 4920a
Ti	3200a, 3235-37-39-42a, 3342a, 3370-1-3a, 4301a
Tl	3230b, 3519a, 3529a, 3776a, (5351)
U	4090a, 4242a
V	3184-5a, 4379a, 4385a, 4408a
W	4009a, 4074b, 4295a, (2944)
Zn	3282a, 3303a, 3345a, 4680a, 4722a, 4811a
Zr	3392a, 3438a, 3496a

must be made to coincide with the chart before this is used for analyses.

Use of Charts in Analysis

Each sample spectrum is accompanied by an iron arc reference spectrum, placed directly above that of the sample. The two spectra are projected onto the chart and the magnification is adjusted to bring the iron spectrum into exact coincidence with the iron lines of the chart. It is not necessary to bring an entire section into exact coincidence, but the examination is made in successive small regions by sliding the chart so that it coincides in the desired region. When the iron lines are in coincidence the presence of any element of the chart is shown by coincidence of projected lines with map lines, provided there has been no displacement of the plate holder between the exposures for the iron arc and the sample. (If the sample contains iron, as is often the case, an inspection of the iron doublet near 2600 Å. shows whether or not there has been any displacement of the plate holder during the exposures.)

A single coincidence with the chart does not usually establish an analysis, but in most cases an analysis can be considered positive if all the "a" lines are observed. If the analysis seems doubtful, the tables of Gerlach and Riedl (1) are next consulted and the possibilities of interfering substances are examined. The final test, seldom needed except in the case of very complex spectra, is to prepare a spectrum of a sample of known purity and to identify from the charts the lines of the sample not found in the sample of known purity.

In certain analyses it is desirable to determine the wave length of some lines and to consult Kayser's tables. To determine the wave length of a line the adjacent iron lines are first adjusted to their exact scale positions, as given in Kayser's tables. Then the wave length of the sought line is read directly from the scale. At the magnification usually employed an accuracy of 0.1 Å. is readily attainable in the region below 2700 Å.

Use of Charts for Other Spectrographs

The charts were constructed for use with a Hilger E1 quartz spectrograph, and it was not anticipated that they would be generally useful for spectra taken with other instruments. It has been found, however, that spectra from other quartz Littrow spectrographs will fit the charts closely enough to enable these charts to be used for analysis. In some cases the spectra cannot be made to coincide over the entire length of a section, but it is sufficient to have coincidence over a space of a few inches at each setting. Smaller copies of the charts have even been used successfully for examination of spectra from a medium quartz spectrograph.

At present photostatic copies of the charts¹ are used in this laboratory. These are of slightly reduced size, each section being 52.5 cm. (21 inches) in length, but no detail is lost in this reduction. For use with a medium quartz spectrograph it has been found advantageous to construct a chart with the sections 25 to 30 cm. (10 to 12 inches) in length, using copies of the wave-length scale but redrawing the iron and analysis lines so that they are 1.25 cm. (0.5 inch) in length.

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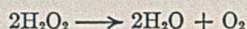
Determination of Hydrogen Peroxide and Some Related Peroxygen Compounds

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BOOKS recently published in German by Machu (16) and by Kausch (11) include a review of methods for the determination of peroxygen compounds. This paper, which presents a critical discussion of the chief methods for the determination of peroxygen compounds, places special emphasis on the methods which have been used or tested in this laboratory.

The inorganic peroxygen compounds of commerce, hydrogen peroxide, sodium peroxide, sodium perborate, and the peroxides of calcium, barium, strontium, magnesium, and zinc behave similarly from an analytical point of view. These peroxygen compounds may be considered as variations of hydrogen peroxide, since in solution they all display the properties of H_2O_2 , probably owing to the presence of the common HO_2^- ion (3). Analysis of these products consists in a determination of their active oxygen content—i. e., the oxygen given up when they revert to the oxide. For example,



This may be determined in three basically different ways: by titration, by measuring the volume of oxygen evolved on complete decomposition, and by a colorimetric method. The results may be expressed as per cent of active oxygen, or as per cent of hydrogen peroxide (or other peroxide). The most commonly used term for expressing the active oxygen content of peroxide solutions is volume concentration. This is defined as the number of cubic centimeters of oxygen gas, measured at 0° C. and 760 mm. pressure, liberated from 1 cc. of the solution (measured at 20° C.) when the peroxide is completely decomposed. This may be converted into per cent of hydrogen peroxide by use of the expression

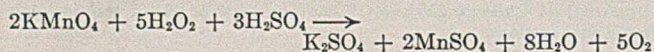
$$\text{Per cent of } H_2O_2 \text{ by weight} = \frac{\text{volume concentration} \times 0.30385}{\text{density}}$$

where the volume concentration and density (grams per cc.) are both measured at 20° C., and the factor 0.30385 is based on a molar volume of 22.3927 liters for oxygen gas. The density of solutions of hydrogen peroxide in water has been determined by Maass and Hatcher (15). From their density values the volume concentration may be calculated with an accuracy of 1 per cent from the expression

$$\text{Volume concentration} = 1000 (\text{density} - 1)$$

Titration Methods

POTASSIUM PERMANGANATE TITRATIONS. The simplest and most commonly used method for determining hydrogen peroxide is by titration with potassium permanganate. This titration is based on the reaction



A critical review of titration methods, decomposition methods, and colorimetric methods for determining active oxygen in the commercial peroxygen compounds is presented in this paper. The principal analytical procedures are outlined and their advantages and limitations are discussed. A new potentiometric method is presented for determining active oxygen in highly colored peroxide solutions containing organic matter.

This method cannot be applied in the presence of organic matter or other substances which reduce permanganate, but in their absence it gives accurate results. In this laboratory the following two procedures have been found satisfactory for titrating samples of 10-volume (3 per cent) hydrogen peroxide or stronger.

A 1-cc. sample of the solution to be tested is measured out with an Ostwald-Van Slyke capillary pipet and to this are added 50 cc. of 20 per cent sulfuric acid. It is then titrated with 0.1786 *N* potassium permanganate until a permanent rose color is obtained. The volume concentration of the solution is equal to the number of cubic centimeters of potassium permanganate used in titration.

As an alternative procedure a 10-cc. sample of the solution under test is diluted to 250 cc. and a 10-cc. aliquot of this is taken for titration. This procedure involves more manipulation than the previous method, but does not require a 100-cc. buret nor an accurately calibrated 1-cc. pipet.

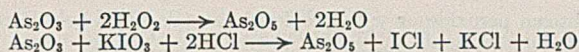
If the concentration of the sample to be tested is less than about 10 volumes, larger samples must be used in both methods.

A fading end point in this reaction is indicative of the presence of organic matter or other reducing agents, and if fading persists and high accuracy is desired, the permanganate titration cannot be relied upon. In colored solutions where the end point is difficult to observe, the addition of one or two drops of an oxidation-reduction indicator will be found helpful. The ferrous sulfate complex of *o*-phenanthroline, which has been recommended by Willard and Young (22) for use in ceric sulfate titrations, has been found to be an aid in the potassium permanganate titration of colored solutions.

POTASSIUM IODIDE-THIOSULFATE TITRATIONS. The method which comes next to the permanganate titration in utility is the potassium iodide-sodium thiosulfate titration, which depends upon release of iodine from potassium iodide by the hydrogen peroxide and subsequent titration of the liberated iodine with standard sodium thiosulfate. This method was described by Kingzett (12) and on the suggestions of Kolthoff (14) and of Rothmund and Burgstaller (19) has been improved by the use of ammonium molybdate as a catalyst for accelerating the liberation of the iodine. As used in this laboratory the procedure is to acidify the sample with 20 per cent sulfuric acid, then add 1 cc. of 10 per cent ammonium molybdate solution and an excess of potassium iodide, and titrate with 0.1 *N* sodium thiosulfate, using starch as an indicator. For the analysis of materials which are not water- or acid-soluble, a modification of this method described by Greenbank and Holm (6) is used, using chloroform as solvent and acetic acid instead of sulfuric acid.

The potassium iodide method is of general utility, particularly when the permanganate method fails, but it cannot be used in the presence of other oxidizing agents or unsaturated compounds which react with the free iodine.

SODIUM ARSENITE TITRATIONS. A method has been described by Jamieson (9) which employs the oxidation of arsenite solutions according to the equations:



According to the recommended procedure, 10 cc. of 10 per cent sodium hydroxide are added to a quantity of 0.2 *N* arsenic trioxide sufficient to provide an excess beyond that required to react with the hydrogen peroxide in the sample. The sample is then added and the mixture allowed to stand for 2 minutes, after which 40 cc. of concentrated hydrochloric acid are added, followed by 6 to 7 cc. of chloroform. The residual arsenic trioxide is titrated with 0.2 *N* potassium iodate solution. Rupp and Siebler (20) have described a somewhat similar method in which the solution is made alkaline, diluted with water, and titrated to a colorless end point with standard potassium bromate, using methyl orange as an indicator.

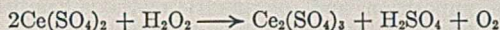
Arsenite titrations are claimed to be affected less by organic matter than the permanganate method, but they obviously cannot be used in the presence of other compounds which are oxidizing towards arsenite solutions.

TITANIUM TRICHLORIDE TITRATIONS. One of the oldest methods for the determination of hydrogen peroxide in the presence of organic matter is that of Knecht and Hibbert (13) who made use of the oxidation of titanium trichloride solutions by hydrogen peroxide. When an acid solution of hydrogen peroxide is titrated with titanium trichloride, the color is at first yellow which changes to a deep orange and finally to a colorless end point. The over-all equation is



The titanium trichloride is standardized against a ferric chloride solution using potassium thiocyanate as an indicator. This method has the disadvantages that the end point is difficult to determine and the titanium trichloride solution requires frequent standardization.

CERIC SULFATE TITRATIONS. A more recently developed method for hydrogen peroxide in the presence of organic matter is titration with ceric sulfate solutions:



This was first carried out potentiometrically in sulfuric acid solution by Atanasiu and Stefanescu (2). A further potentiometric investigation by Furman and Wallace (5) showed that the titration is also satisfactory in the presence of hydrochloric, nitric, and acetic acids. The use of the previously mentioned *o*-phenanthroline indicator in the ceric sulfate titration makes the end point sufficiently pronounced for visual detection. This method is well adapted for use with solutions containing organic matter or hydrochloric acid, either of which may prevent the use of potassium permanganate.

POTENTIOMETRIC TITRATIONS. Potentiometric titrations for hydrogen peroxide have been used chiefly for determining it in mixtures with permonosulfuric acid and persulfuric acid.

Rius (18) described the analysis of such a mixture using a potentiometric titration with sodium sulfite as the reducing agent. The total oxidizing power—i. e., the sum of hydrogen peroxide, Caro's acid (H_2SO_5), and persulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$)—was determined by adding an excess of ferrous sulfate and titrating the excess with potassium permanganate. The sum of hydrogen peroxide and permonosulfuric acid was then determined potentiometrically with sodium sulfite, using a normal calomel cell and a platinum electrode. The hydrogen peroxide was determined by a modified permanganate method which consists in instantaneous mixing of approximately the total titer of potassium permanganate with the sample and proceeding then by trial and error to determine the correct titer.

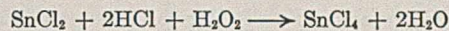
The analysis of mixtures of hydrogen peroxide and permonosulfuric acid was carried out potentiometrically by Müller and Holder (17), who titrated the permonosulfuric acid with potassium iodide, adding benzene to prevent precipitation of iodine on the platinum electrode, then adding sodium acetate as a buffer, and titrating the hydrogen peroxide with bromine in potassium bromide solution.

A convenient and reliable method for determining hydrogen peroxide, permonosulfuric acid, and persulfuric acid when all three are present, is the subject of a current investigation in this laboratory.

With the object of developing an accurate and convenient analytical method for determining hydrogen peroxide in highly colored solutions containing organic matter, the authors have investigated a number of potentiometric titrations, using a mercurous sulfate half-cell and a gold electrode. The following reagents were included in this study: potassium permanganate, ferrous ammonium sulfate, sodium thiosulfate, sodium arsenite, stannous chloride, titanium trichloride, sodium sulfite, and sodium nitrite. The most suitable titrating agent found was sodium nitrite.

Acid solutions of hydrogen peroxide can be accurately titrated potentiometrically with a standard potassium permanganate solution. The potentiometric end point checks exactly with the colorimetric end point and shows a change in e. m. f. of over 400 millivolts for one drop of the reagent. However, potassium permanganate cannot be used for potentiometrically determining active oxygen in solutions containing organic matter, since in that case no sudden change in e. m. f. occurs to indicate the end point.

Ferrous ammonium sulfate, sodium thiosulfate, and arsenious oxide solutions are likewise not satisfactory for the potentiometric titration of hydrogen peroxide, since no sudden change of e. m. f. occurs with either cold or hot solutions even in the absence of organic matter. According to Jellinek and Krebs (10) stannous chloride reacts quantitatively with hydrogen peroxide.



The authors' investigations have confirmed this at temperatures of 75° to 90° C. but the reaction is slow and takes several minutes to come to equilibrium after each addition of the titrating agent. The addition of a catalyst (copper, iron, chromium, and manganese) accelerates the reaction but even under these conditions the titration is still much too slow to be of practical use.

The titration of hydrogen peroxide solutions with titanium trichloride can be followed potentiometrically. The maximum break in the e. m. f. is in the order of 150 to 200 millivolts per drop of 0.1 *N* reagent, but this occurs about 0.3 cc. beyond the colorimetric end point. However, in the presence of organic matter the potentiometric titration is not satisfactory, since there is a rapid change in potential throughout the titration, and there is no evidence of a pronounced break at the equivalent point.

Acid solutions of hydrogen peroxide have been potentiometrically titrated with sodium sulfite (10), the change in e. m. f. at the end point being about 150 millivolts. However, this titration is not satisfactory; the sulfite solution is unstable, the gold electrode loses its sensitivity, and the potential drifts on approaching the end point of the reaction.

Hydrogen peroxide in acid solution can be accurately titrated with sodium nitrite solutions, either in the presence or absence of colored organic matter. The change in e. m. f. at the equivalent point is 150 to 200 millivolts at 90° C. The titration can best be carried out by adding a nearly equivalent amount of the nitrite solution to the acidified hydrogen peroxide, heating to 90° C., and continuing the titration. By this procedure only low concentrations of hydrogen peroxide are heated and hydrogen peroxide decomposition losses are negligible. In titrating the active oxygen in the presence of organic matter it is necessary to add a small concentration of nitric acid, since in its absence determinations of low hydrogen peroxide concentrations are inaccurate.

The following procedure has been found satisfactory for this titration:

Pipet 50 cc. of the hydrogen peroxide solution which has been diluted to about one volume concentration into a 250-cc. beaker and add 50 cc. of distilled water. Acidify the solution with 50 cc. of 20 per cent sulfuric acid and add 5 cc. of *N* nitric acid. Connect the solution to the mercurous sulfate cell by means of a saturated potassium sulfate bridge and titrate potentiometrically with 0.1786 *N* sodium nitrite as follows: (a) Heat the mixture to 90° C. and titrate to the nearest cubic centimeter with the standard sodium nitrite solution; (b) prepare another sample, add nearly an equivalent amount of sodium nitrite as determined in (a), heat the mixture to 90° C., and continue the titration to the nearest 0.1 cc. The change in e. m. f. at the equivalent point is 150 to 200 millivolts. The standard nitrite solution is stable and this method is satisfactory for the determination of hydrogen peroxide in highly colored solutions.

Decomposition Methods

The fact that hydrogen peroxide decomposes to yield oxygen gas can be made the basis of its analytical determination by measuring the volume of gas which is given off upon complete decomposition. This decomposition may be brought about by a reaction with compounds such as potassium permanganate or sodium hypochlorite (4), or by catalytic decomposition with platinum, manganese, or copper; platinum is the preferred catalyst. These methods are valuable for use with highly colored solutions or in the presence of other oxidizing agents which interfere with titrations but which do not liberate a gas under the conditions of the peroxide decomposition.

Colorimetric Methods

POTASSIUM PERMANGANATE. For the determination of small amounts of peroxide, colorimetric methods can be used. Allen (1) has described a method for the determination of small amounts of hydrogen peroxide by a colorimetric permanganate method. An acid solution of potassium permanganate containing a small amount of magnesium sulfate is treated with the unknown solution and the color is then compared with that of similar solutions containing known amounts of hydrogen peroxide. It is claimed that this method will detect 1 part of hydrogen peroxide in ten million parts of water, but the same limitations must apply to its use as applied in the case of permanganate titrations.

TITANIUM TRICHLORIDE. The titanium method finds its chief use colorimetrically and in this laboratory has given good results on solutions containing less than 5 p. p. m. of hydrogen peroxide. It is carried out by adding 3 cc. of a titanium sulfate solution to 100 cc. of the unknown and then matching it against solutions containing known amounts of hydrogen peroxide. The titanium sulfate solution is prepared by treating 1 gram of titanium dioxide with 100 cc. of concentrated sulfuric acid for 15 to 20 hours at about 150° C. and filtering off any undissolved material before using.

FERRIC THIOCYANATE. Another valuable method depends upon the formation of the deep red ferric thiocyanate by reaction of hydrogen peroxide in a solution containing ferrous iron and potassium thiocyanate. As described by Horst (?) the method consists of completely reducing a 10 per cent ferric sulfate solution with hydrogen sulfide, flushing out the hydrogen sulfide with carbon dioxide, then adding the unknown and the thiocyanate, and comparing with a standard. The procedure in this laboratory is as follows: Ten grams of the unknown are dissolved in 175 cc. of 20 per cent sulfuric acid and diluted to exactly 200 cc. with water. Half of this serves as a blank and to the other half is added 0.5 cc. of an indicator solution prepared by dissolving 78.4 grams of ferrous ammonium sulfate hexahydrate and 58.3 grams of potassium thiocyanate in 20 per cent sulfuric acid and diluting to 1 liter. This is compared with a solution prepared from a basic standard made up by dissolving 1.7140 grams of potassium thiocyanate and 3.0 grams of ferric ammonium sulfate in 100 cc. of 20 per cent sulfuric acid and then diluting to exactly 1 liter with water. With proper blank corrections it is possible by this method to determine hydrogen peroxide in concentrations up to 0.02 per cent with a high degree of accuracy.

MISCELLANEOUS COLORIMETRIC METHODS. The yellow color of permolybdic acid is the basis of a method described by Isaacs (8). The indicated procedure is to add 1 cc. of the unknown to 10 cc. of 5 per cent citric acid in 30 cc. of water; 1 cc. of a 10 per cent solution of ammonium molybdate is then added and the color is compared with solutions containing known amounts of

hydrogen peroxide or with previously standardized solutions of potassium chromate.

Mention should also be made of the recent suggestions of Schales (21) who has discussed the use of Stamm's reagent, fluorescein, and luminol. Many other color reactions have been suggested for use in the analysis of hydrogen peroxide; references to these methods may be found in Kausch's (11) text.

Related Peroxygen Compounds

SODIUM PEROXIDE. Sodium peroxide, Na_2O_2 , forms alkaline solutions which behave like alkaline solutions of hydrogen peroxide and may, therefore, be analyzed by the same methods. Solid sodium peroxide is best dissolved for analysis by adding it slowly and with vigorous stirring to an excess of dilute sulfuric acid.

SODIUM PERBORATE. Sodium perborate solutions behave like buffered alkaline solutions of hydrogen peroxide and hence may be determined by the methods described for hydrogen peroxide. Solutions for analysis should be prepared from crystalline sodium perborate by dissolving the solid in an excess of dilute sulfuric acid.

MAGNESIUM AND ZINC PEROXIDES. The peroxides of zinc and magnesium present no difficulty in analysis, since, although they are not soluble in water, they dissolve readily in sulfuric acid to yield solutions which may be analyzed by the methods given for hydrogen peroxide.

CALCIUM AND BARIUM PEROXIDES. The peroxides of barium and calcium are not soluble in water and cannot be dissolved in sulfuric acid. They can, however, be dissolved in dilute hydrochloric acid and if a small sample is used the active oxygen content may be determined by titration with potassium permanganate after the addition of sulfuric acid.

Summary

The analysis of solutions of peroxygen compounds by titration, decomposition, and colorimetric methods has been discussed.

The permanganate titration is recommended for determining active oxygen in solutions containing neither organic matter nor other reducing substances.

The ceric sulfate titration should be used for solutions containing organic matter or other reducing substances, although some analysts will prefer the iodine-thiosulfate titration which is satisfactory if the organic matter does not contain unsaturated compounds.

A colorimetric method should be used for determining traces of peroxides. The titanium trichloride method is recommended.

A decomposition method may be used for determining active oxygen in highly colored solutions where color changes cannot be detected accurately. A simpler method for use under these conditions, based on potentiometric titration with sodium nitrite, has been developed.

The methods recommended for hydrogen peroxide can also be used for determining the active oxygen in solutions of sodium peroxide, sodium perborate, barium peroxide, calcium peroxide, magnesium peroxide, and zinc peroxide.

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Standardization of Sodium Thiosulfate by Copper, Using Perchloric Acid

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IN THE available methods for standardizing thiosulfate iodometrically against copper, the copper is dissolved by the oxidizing action of concentrated nitric acid, and various means are used subsequently to eliminate oxides of nitrogen that would interfere in the titration. Among the expedients used, all of them somewhat cumbersome, are the following: addition of sodium hypochlorite and phenol (3); addition of sulfuric acid, evaporation, then addition of hydrochloric acid and further evaporation (1); addition of bromine water and boiling until the excess is removed (8); and the use of urea and boiling (2). Such treatment is followed by the addition of ammonia in slight excess, boiling off the excess, then addition of acetic acid to adjust the acidity.

The method described here consists simply of dissolving copper in concentrated boiling perchloric acid, adding an equal volume of water, boiling for 2 minutes, and diluting to volume. Aliquots are titrated with thiosulfate after addition of potassium iodide using starch and a soluble thiocyanate as described by Foote (1).

Perchloric acid is a good reagent for dissolving copper since solution is fairly rapid on boiling; all the by-products are instantly and completely removed by volatilization (6), while the dilute cold perchloric acid itself does not interfere in the titration (5). No chloride could be detected in solution.

Reagents

Copper, 99.96 per cent pure (4).
 Perchloric acid, concentrated (68 to 70 per cent), technical.
 Potassium iodide, iodate-free, 1 *N* solution.
 Sodium thiosulfate solution standardized against potassium iodate, the purity of which had been checked against iodine.
 Starch solution prepared according to Sutton (7).
 Potassium thiocyanate, reagent grade.

Procedure

The following procedure applies to the standardization of an approximately 0.025 *N* thiosulfate solution.

To a 0.60- to 0.65-gram sample of copper in a 100-cc. volumetric flask add 6 to 8 cc. of concentrated perchloric acid (about 11 *M*); heat to boiling (hood!). Boil gently until solution is complete, continue boiling for a few minutes, then cool slightly. Add an equal volume of water and boil for 2 minutes to drive off any chlorine that may be still present. After cooling dilute to volume. To 10-cc. portions add 5 cc. of 1 *N* potassium iodide. Let stand for 2 minutes and titrate with sodium thiosulfate until the yellow color is nearly discharged. Add 5 cc. of starch solution

and titrate to near the end point. Add 1.5 to 2.0 grams of potassium thiocyanate (1) and titrate to the disappearance of the blue color. The end point should be checked by the addition of 0.025 *N* iodine, since at the end point the titration mixture is not white but flesh-colored.

TABLE I. STANDARDIZATION OF THIOSULFATE

Normality	Average Error	Number of Titrations
	Against KIO ₃	
0.02484	±0.00002	3
0.02488	±0.00001	3
	Against Cu(ClO ₄) ₂	
0.02483	±0.00003	6
0.02484	±0.00001	3
0.02486	±0.00002	9
0.02490	±0.00001	3

If 10 to 12 cc. of 5.5 *M* perchloric acid are used, solution will be much slower. Eight cubic centimeters of acid of this concentration will not completely dissolve the copper. Variation of the acid concentration in the copper solution from 0.3 *N* to 0.7 *N* has no apparent effect on the titration value. Greater acidity than this should be avoided, since the amount of thiosulfate consumed tends to become slightly too high (about 0.30 per cent). Titrating under artificial light, the end point tended to appear too early (about 0.25 per cent). No blank correction was necessary.

The mean value against copper as well as against iodate is 0.02486 ± 0.00002.

Acknowledgment

The copper used in this work was kindly supplied by W. M. McNabb, University of Pennsylvania. The writer wishes to thank G. Toennies of this institute for his suggestions and criticisms.

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Quantitative Determination of Selenium in Tissues and Feces

A Photometric Method

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THE recent interest in the toxicology of selenium compounds has resulted in the development of new and exact methods for determining traces of this element in soils and biological material.

Robinson (5), in a search for a quantitative method for determining selenium in plants and soils, acted upon the assumption that selenium might be expected to behave in a general way like sulfur. Accordingly, he developed a method by which selenium could be separated from all elements except arsenic and germanium. This procedure was improved upon shortly thereafter by Robinson, Dudley, Williams, and Byers (6), who made it applicable for amounts of selenium as small as 0.01 mg. Dudley and Byers (1) made it even more suitable for biological materials. The principle involved initial hydrolysis and oxidation of the material, conversion of selenium to the bromide, distillation of the bromide, and reduction to the free element. The selenium precipitate was then filtered off, dried, and weighed, or, in the case of minute amounts reprecipitated in the presence of gum arabic solution, so that the red color of the colloidal selenium could be estimated colorimetrically.

Horn (3) modified an earlier procedure proposed by Schmidt (7) for detecting small amounts of selenious acid in sulfuric acid. Plant materials were digested as in the regular Kjeldahl method with added mercuric oxide, which served to prevent loss of selenium through vaporization. When a few drops of saturated aqueous codeine sulfate were added to aliquot portions of the clear digests, blue colors developed in those tubes containing selenium. By comparing these colors with those of similar standards, a roughly quantitative estimation of the amount of selenium could be made. Vanadium alone interfered in the test. This method was later used by Franke and Painter (2) in the rough determination of the selenium content of toxic grains, but it has not heretofore been applied to the more exact determination of small amounts of selenium in animal tissues and products.

In the course of experiments concerned with chronic selenium intoxication in rats, it was necessary to determine the selenium content of the feces and certain tissues. None of the existing methods proved to be very satisfactory for determining the minute amounts of selenium present in rat tissues; the results were inconsistent and the procedure of Robinson, Dudley, Williams, and Byers (6) as modified by Dudley and Byers (1) involved many steps which required considerable time to complete and increased the chances for loss of selenium. Accordingly, the colorimetric method of Horn (3) was adopted and modified. It is believed that the photometric application of this color reaction is capable of extensive application to the analyses of biological products for selenium.

Experimental

The samples of dried feces were prepared for analysis by first grinding them in a mortar to ensure uniform mixing. One-gram samples were then weighed out for analysis. In the analysis of tissues, particularly of liver, it was found necessary to effect a preliminary removal of most of the fat, since fat is digested in the Kjeldahl procedure only with great difficulty. Fatty degeneration

of the liver is commonly associated with selenium poisoning in rats. Attempts to analyze livers that had not been defatted resulted in very black and lumpy digests, even after 10 to 15 hours of digestion, despite the fact that during the period of digestion, at intervals of 60 to 90 minutes, small amounts of hydrogen peroxide were added to facilitate oxidation. A preliminary extraction with chloroform was, accordingly, carried out. Since in most cases it was not possible to analyze the tissues immediately after removal from the animal, they were preserved in 10 per cent formalin solution until analyses could be undertaken. The formalin served also to harden the tissues so that they could easily be ground for extraction. Analyses of the formalin in which the organs had been preserved showed that no selenium had been removed.

The fat extractions were carried out as follows: The organs were removed from the preserving fluid, pressed between filter papers to remove most of the liquid, and ground in a small porcelain mortar. The ground tissue was then transferred to a 250-cc. Erlenmeyer flask, 100 cc. of chloroform were added, the flask was connected to a water condenser, and the mixture was refluxed on the steam bath for 3 to 4 hours. The chloroform was then removed from the extracted tissue by filtration, and the residual tissue was washed twice with small portions of hot chloroform, and dried in air at room temperature. Weighed amounts of this dry material were analyzed.

The digestion of a dry sample was carried out in a 100-cc. Kjeldahl flask. Yellow mercuric oxide (0.20 gram) was added and any particles adhering to the neck of the flask were washed down into the flask with 5 to 10 cc. of water, which served also to prevent foaming at the beginning of the digestion. Thirty to 40 cc. of concentrated sulfuric acid were added, with two glass beads to prevent bumping. Digestions were continued for 6 to 9 hours, at the end of which time only a light yellow tinge remained in the solution. The occasional addition of 5 to 10 drops of 30 per cent hydrogen peroxide served to accelerate the oxidation. Upon cooling, the solution became colorless and a white precipitate of mercuric sulfate formed. The cooled digest was trans-

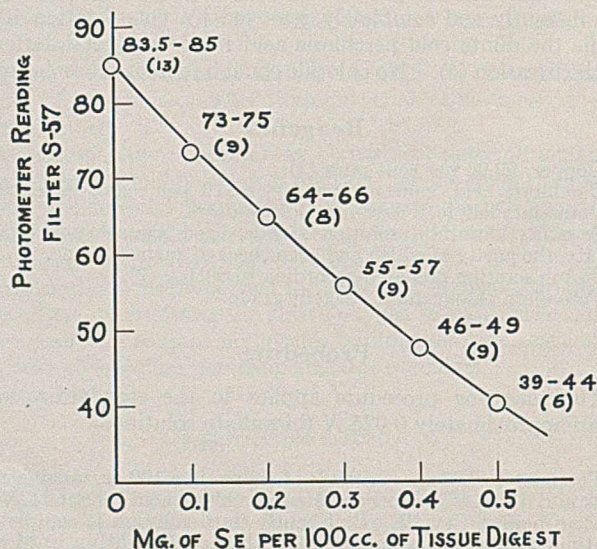


FIGURE 1. STANDARD PHOTOMETRIC CURVE FOR ANALYSIS OF SELENIUM IN TISSUE DIGESTS

Plotted from data in Table II. Figures at each point on curve indicate range of photometric readings; those in parentheses indicate number of determinations for each concentration of selenium.

ferred quantitatively to a 50-cc. volumetric flask, diluted to volume with concentrated sulfuric acid, mixed, and centrifuged for 15 to 20 minutes at approximately 1800 r. p. m. A 10-cc. portion of the clear colorless centrifugate was pipetted into a clean dry test tube and 3 drops of a saturated aqueous solution (3 per cent) of codeine sulfate were added. The tubes were stoppered tightly and placed in a dark cupboard for 7 hours to permit the development of the blue color. The percentage transmission of light of the solution was then determined in a Zeiss-Pulfrich photometer (4), used in the vertical position. A 10-mm. cell containing approximately 5 cc. of solution and the yellow filter S-57 were found most convenient.

TABLE I. INFLUENCE OF TIME OF COLOR DEVELOPMENT ON PHOTOMETER READINGS OF NORMAL FECAL DIGESTS CONTAINING ADDED SODIUM SELENITE

(All readings are for separate determinations)

Time of Color Development Hours	Concentration of Se, Mg. per 100 Cc. of Fecal Digest						
	0	0.05	0.1	0.2	0.3	0.4	0.5
		Photometer Readings ^a					
4	81	72	61	58	48
5	85	..	81	72.5	60	57	44
	90	..	79.5	66.5	58	51	43
	80.5	67	59	47.5	41.5
6	91.5	..	80	68	60	57.5	43
	91.5	..	84	69	57	49.5	40
	90	85	76.5	65.5	56.5	50	39
	91	88	81	69	58	56.5	49
	91.5	69	..	56	..
7	92	85	78	67	57	46	..
	90	..	79	67.5	58	52	42.5
	92	..	79	69	56	50	42
8	90	..	78	66	55	47	..

^a Expressed as percentage transmission (D per cent).

Standard curves were constructed by measuring the percentage light transmission of the blue solutions obtained with digests to which known amounts of selenium had been added. These standard curves differed slightly for tissues and feces. Digests of known selenium concentration were most simply prepared from a digest of the feces or tissues of normal animals, assumed to be free from selenium, and a similar digest to which sodium selenite had been added to give a selenium content of 0.5 mg. per cent. By appropriate admixture of the two, it was easy to obtain solutions containing from 0.0 to 0.5 mg. per cent of selenium. A typical curve is presented in Figure 1.

Various factors which might influence color development were studied. Horn (3) reported that when the digests took up moisture the blue color faded; accordingly, care was taken to prevent access of air to the acid solutions after the digests cooled. Light was also found to affect the color development. When the tubes were exposed to daylight for a day or more, the blue color turned to purple, while in other tubes kept in the dark for a similar period the change to purple was not noted.

The effect of time on the development of the blue color is shown in Table I. After 4 hours the colors were incompletely developed, while after 6 to 8 hours the photometric readings were consistent. An interval of 7 hours between addition of the codeine sulfate and the photometric estimation was arbitrarily selected.

Since in the analyses of tissues of rats it was not always possible to obtain as much as 1 gram of the dry powdered organs, a study was made to determine the effect of different amounts of tissue in the sulfuric acid digests on color development. As is shown in Table II, reproducible readings were obtained when the amount of dry tissue used for analysis varied from 0.6 to 2.0 grams. The fact that the recovery of added selenium, when digests of 1.5 to 2.0 grams of tissue were used, was no greater than the recovery when 0.6 gram was used in the preparation of the digest is indicative of the absence of any significant amounts of selenium in normal rat tissues.

From the typical data given in Tables I and II, smooth standard curves (Figure 1) were easily constructed. When known amounts of selenium were added to normal rat feces and the analytical procedure was carried out using color-development periods of 6 to 8 hours, the selenium determined was in 75 per cent of the cases within 10 per cent and in 88 per cent of the cases within 15 per cent of the theoretical amount. All the remaining discrepant values were obtained with digests in which the color had been allowed to develop only 6 hours. The values for the tissue digests in Table II, in which a standard time interval of 7 hours was employed, were even more consistent, 98 per cent of the determinations checking to within 10 per cent of the amount of selenium added. In most cases the photometer readings ranged well within the limits of accuracy of the instrument. The results of the application of this method will be presented elsewhere.

TABLE II. EFFECT OF VARYING THE AMOUNT OF TISSUE IN DIGESTS CONTAINING KNOWN AMOUNTS OF SELENIUM

(Seven hours allowed for development of colors)

Dry Fat-Extracted Tissue Grams	Se Added Mg./100 cc.	Range of Photometer Readings ^a	No. of Determinations	Se Found		Maximum Error %
				Mg./100 cc.	%	
0.6	0.0	83.5-85	3	0.0-0.01
	0.10	73.0-73.5	2	0.1-0.105	5	3
	0.20	65	2	0.195	3	3
	0.30	56	2	0.30	0	0
	0.40	47	2	0.41	3	3
0.8	0.50	40	1	0.505	1	..
	0.0	84.5-85	2	0.0-0.005
	0.10	73	1	0.11	10	3
	0.20	64	1	0.205	3	3
	0.30	56	1	0.30	0	0
1.0	0.40	47	1	0.41	3	3
	0.0	85	3	0.0
	0.10	73-75	2	0.09-0.11	10	8
	0.20	65-66	2	0.185-0.195	10	2
	0.30	56-56.5	2	0.295-0.30	2	6
1.5	0.40	46-48	2	0.40-0.425	6	10
	0.50	44	1	0.45
	0.0	85	4	0.0	3	3
	0.10	73.5-74	3	0.095-0.10	10	10
	0.20	65-66	3	0.185-0.195	10	3
2.0	0.30	55-57	3	0.29-0.310	3	3
	0.40	48-49	3	0.39-0.40	3	3
	0.50	40-42	3	0.48-0.505	4	..
	0.0	84	1	0.01	5	20
	0.10	73	1	0.105	0	0
	0.20	61	1	0.24	0	0
	0.30	56	1	0.30	0	0
	0.40	48	1	0.40	0	0
	0.50	39	1	0.515	3	..

^a Expressed as percentage transmission (D per cent).

Williams and Lakin (3) have emphasized the possibility of losses of selenium by volatilization during the period of digestion with acid. This must be considered particularly when large amounts of a sample, rich in materials difficult of digestion, are used in the analyses. The authors have employed the procedure described for the analyses of animal tissues or excreta only. Under these conditions, the method has given consistent and reproducible results which are believed to be reliable.

Summary

Horn's modification of the codeine sulfate reaction for the detection of selenium has been applied to the quantitative determination of minute amounts of selenium in animal tissues and feces. The dry sample is digested with sulfuric acid and mercuric oxide, cooled, made to volume, and centrifuged. To a portion of the clear digest is added codeine sulfate solution and an interval of 7 hours in the absence of light is allowed for development of the blue color, after which time the transmission of light is determined in the Zeiss-Pulfrich photometer with the use of the yellow filter S-57 (4). The amount of selenium present is easily calculated from standard curves obtained in a similar manner, using digests of normal tissues or feces containing added sodium selenite.

The advantages of the method are the speed with which a given analysis can be carried out, the large number of determinations which can be done within a short time, and the simplicity of the procedure as compared to other existing methods. The use of the photometer makes it possible to obtain accurate readings on solutions in which the depth of color is too slight to be estimated in a colorimeter.

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Identification of Aldehydes and Ketones

By Estimation of Hydrazine Nitrogen According to the Jamieson Method

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ALDEHYDES and ketones are frequently identified by the derivatives which they form with hydrazine or one of its substitution products. Semicarbazones can be prepared and purified readily in most instances, and, accordingly, have found extensive application in systematic organic analysis. Analysts rely on the melting point and occasionally the crystal habit of the semicarbazone for the identification of the aldehyde or ketone.

In spite of the importance and great utility of these derivatives, certain limitations are inherent in the methods employed. Difficulties may be encountered in characterizing carbonyl components in complex mixtures from natural sources, or indeed even in mixtures of synthetic solvents. Physical constants of the components and melting points of their derivatives are sometimes changed markedly by the presence of small amounts of impurities. In the investigation of new substances, moreover, the physical properties of derivatives give no aid in the initial characterization of the compounds.

The determination of the hydrazine nitrogen content of a semicarbazone (or other hydrazone) will enable an analyst to compute the equivalent weight of the parent carbonyl compound. If the compound has been characterized previously, he may check its identity as determined by the classical method, or if the compound is new, the equivalent weight may be compared with the molecular weight as measured by one of the familiar physical methods. It has been found in these laboratories that hydrazine nitrogen can be determined in a number of derivatives of hydrazine by the method devised by Jamieson (16), and the experiments described in this paper were undertaken in order to investigate the applicability of the Jamieson method for the determination of hydrazine nitrogen in a series of semicarbazones of certain common aldehydes and ketones. The following semicarbazones were prepared and analyzed by this technique: acetophenone, cyclohexanone, diethyl ketone, acetone, benzophenone, benzaldehyde, cinnamic aldehyde, and furfural. The method is applicable for all semicarbazones studied except furfural semicarbazone. A few isolated experiments on other applications of the Jamieson method are also described.

Historical

The name hydrazine was applied by Emil Fischer to the hypothetical substance N_2H_4 , which he considered to be the parent substance of phenylhydrazine, isolated in 1875 (11, 14). Curtius isolated the first hydrazine salts in 1887

(5, 6). Piloty, Fischer, Baeyer, and other workers found that hydrazine, and more especially phenylhydrazine (9), *p*-bromophenylhydrazine (10), and semicarbazide (2, 3) were of value in preparing derivatives of carbonyl compounds. Curtius and Jay (7, 8) and others (1) similarly investigated the hydrazides and diacyl hydrazines of organic acids.

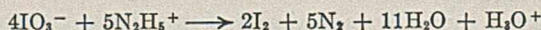
The reducing powers of hydrazine were also the subject of much study. Pechmann found that certain hydrazine compounds could be oxidized to tetrazines (17), and soon many workers were investigating the reduction of potassium iodate by hydrazine (18, 19, 20, 23). In 1912 Jamieson proposed the particular quantitative modification of these methods that now bears his name (15, 16).

In 1931 Botti analyzed cobalt complexes of hydrazine by this method (4). In 1936 and 1937 Fuller employed it for the detection and estimation of aminoguanidine and benzalaminoguanidine (12, 13). Lastly, Schaeffer and Weinberger have used the Jamieson method to determine the equivalent weights of the hydrazides of kerrolic, aleuritic, and isoaleuritic acids (21, 22, 24, 25). Their results in all cases agreed closely with the molecular weights determined by the Rast method.

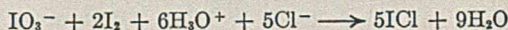
Experimental

ANALYTICAL METHOD. Samples of the hydrazine compound are transferred to 150-ml. glass-stoppered bottles, 20 ml. of water and 30 ml. of concentrated hydrochloric acid are added, and the sample is dissolved and hydrolyzed simultaneously. Chloroform or carbon tetrachloride is added and the mixture is titrated with an 0.1 *N* solution of potassium iodate. Between additions of the reagent the stoppered bottle is shaken vigorously.

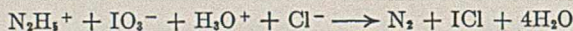
On the first addition of reagent free iodine appears in the chloroform layer and on further addition reaches a maximum. This stage of the reaction may be formulated as follows:



On further addition of reagent the iodine color is discharged and the final disappearance of the iodine color in the chloroform layer is taken as the end point. This end point may be located to within one drop of 0.1 *N* reagent. This second stage of the reaction may be represented as follows:



Hence the stoichiometrical equation for the complete reaction is written as follows:



The standard solution is prepared by dissolving 3.567 grams of potassium iodate in water and diluting to 1 liter. This 0.1 *N* solution should be standardized against recrystallized hydrazinium sulfate and 1 ml. of this solution is equivalent to 0.00217 gram of hydrazinium sulfate or 0.000534 gram of hydrazine.

PREPARATION OF MATERIALS. The semicarbazones are prepared by adding a warm aqueous solution containing equal amounts of semicarbazide hydrochloride and sodium acetate to the aldehyde or ketone, and agitating the mixture vigorously in a stoppered bottle or flask. The crystals of the semicarbazone are separated by filtration on a Büchner funnel, washed, and finally recrystallized from alcohol.

In the case of acetone, the following procedure is employed: Twenty-five grams of semicarbazide hydrochloride in saturated aqueous solution are added to 21.8 grams of sodium acetate in an alcoholic solution. The solution is cooled to 0°, 12.9 grams of acetone are added, and the mixture is warmed. After standing for approximately 16 hours, the crystals are separated. If more acetone is added to the mother solution more semicarbazone may be obtained.

Benzophenone semicarbazone is prepared in the following manner: A weighed portion of benzophenone is dissolved in alcohol and water is added until cloudiness appears, whereupon alcohol is added to clear the solution. An approximately equivalent quantity of semicarbazide hydrochloride is added together with the same weight of sodium acetate. The solution is heated under a reflux for several hours, cooled, and the benzophenone semicarbazone is separated on a Büchner funnel.

TABLE I. ANALYSES

Compound	Substance Taken	Weight Found	Error
	Gram	Gram	%
Pure hydrazine sulfate	0.0414	0.0416	+0.5
	0.0242	0.0245	+1.2
	0.0763	0.0769	+0.8
	0.0725	0.0724	-0.1
	0.0628	0.0629	+0.2
Semicarbazide hydrochloride	0.0523	0.0522	-0.2
	0.0476	0.0481	+0.8
	0.0593	0.0595	+0.3
	0.0532	0.0531	-0.2
Acetophenone semicarbazone M. p. found, 197-199° C. M. p. reported, 198° C.	0.0656	0.0661	+0.8
	0.0543	0.0545	+0.4
	0.0641	0.0639	-0.3
	0.0525	0.0527	+0.4
Crude cyclohexanone semicarbazone	0.0470	0.0489	+4.0
	0.0408	0.0427	+4.7
	0.0668	0.0713	+9.7
	0.0466	0.0478	+2.6
Purified cyclohexanone semicarbazone M. p. found, 165-167° C. M. p. reported, 166-167° C.	0.0214	0.0217	+1.4
	0.0115	0.0111	-3.5
Diethyl ketone semicarbazone M. p. found, 138° C. M. p. reported, 139° C.	0.0403	0.0403	0.0
	0.0370	0.0369	-0.3
	0.0540	0.0550	+1.9
	0.0364	0.0362	-0.6
Acetone semicarbazone M. p. found, 187.5-188.5° C. M. p. reported, 187° C.	0.0581	0.0606	+4.3
	0.0542	0.0543	+0.2
	0.0597	0.0604	+1.2
	0.0340	0.0338	-0.6
	0.0669	0.0678	+1.3
Benzophenone semicarbazone M. p. found, 154-164° C. M. p. reported, 167° C.	0.0814	0.0809	-0.6
	0.0442	0.0448	+1.4
	0.0575	0.0561	-2.4
	0.0466	0.0457	-1.9
Benzaldehyde semicarbazone M. p. found, 212-213° C. M. p. reported, 222° C.	0.0400	0.0394	-1.5
	0.0824	0.0821	-0.4
	0.0265	0.0262	-1.0
	0.0457	0.0447	-2.2
	0.0417	0.0413	-1.0
	0.0607	0.0603	-0.7
Cinnamic aldehyde semicarbazone M. p. found, 208° C. M. p. reported, 208° C.	0.0269	0.0276	+2.6
	0.0605	0.0593	-2.0
	0.0201	0.0197	-2.0
	0.0303	0.0298	-1.7

ANALYSES. The standard solution of potassium iodate was employed first for the determination of hydrazine nitrogen in pure hydrazine sulfate and then in semicarbazide hydrochloride. The hydrazine nitrogen in the following semicarbazones was determined by the unmodified Jamieson procedure: acetophenone semicarbazone, cyclohexanone semicarbazone, diethyl ketone semicarbazone, and acetone semicarbazone. This procedure was applicable also to semicarbazide hydrochloride. In the cases of the semicarbazones of

benzylphenone, benzaldehyde, and cinnamic aldehyde it was necessary to heat the hydrochloric acid solution to 100° C. in order to hydrolyze the semicarbazones.

Furfural semicarbazone was treated by both procedures described above, but on titration with the solution of potassium iodate no end point was reached. The hydrazine nitrogen in thiosemicarbazide could not be determined by the Jamieson technique. Hydrolysis was attempted by employing a 10 per cent solution of sodium hydroxide, digestion with concentrated sulfuric acid, and lastly evaporation to dryness from a concentrated solution of hydrochloric acid. In the last method values were obtained which corresponded to twice those expected.

p-Bromophenylhydrazine hydrochloride gave the following results:

Weight of sample taken: 0.0296, 0.0311, 0.0482 gram
Found: 0.0302, 0.0309, 0.0476, gram; % error, +2.0, -0.6, -1.2

Dextrose and lactose phenylosazones were analyzed by the Jamieson method and consistent values were obtained but they were between the values which would be expected if (1) one phenylhydrazine molecule had reacted and (2) two phenylhydrazine molecules had reacted with one molecule of the sugar. These results are not understood.

Conclusion

This work has demonstrated that the Jamieson method for hydrazine is applicable to the determination of hydrazine nitrogen in semicarbazide and the semicarbazones of a number of aldehydes and ketones. The method failed in the case of furfural semicarbazone. The method is successful for *p*-bromophenylhydrazine but not for thiosemicarbazide. Sugar osazones gave anomalous results.

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Colorimetric Determination of Chlorine with *p*-Aminodimethylaniline

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THE American Public Health Association recommends the *o*-tolidine method (2) for the determination of residual chlorine. A more recent colorimetric method is based upon the use of *p*-aminodimethylaniline as the color-forming reagent. Important papers dealing with the latter procedure are those of Kolthoff (7), Alfthan and Jarvis (1), and Haase and Gad (5).

Since a spectrophotometric study had revealed interesting facts concerning the *o*-tolidine method (4), it seemed worth while to investigate the *p*-aminodimethylaniline method in a similar manner. This paper presents a summary of what were considered the most significant results obtained. After a preliminary investigation of the earlier proposals for applying the method, the work was finally confined to the more promising modification of Haase and Gad.

Experimental Work

APPARATUS AND REAGENTS. The general technique followed, including the preparation and handling of standard solutions of chlorine, was reported previously (4). Most of the color measurements were made with a recording spectrophotometer, set for a spectral band width of 10 m μ , and the pH values were determined with a glass electrode.

The reagent was prepared by dissolving 0.10 gram of *p*-aminodimethylaniline hydrochloride (E. K. No. 492) in 10 ml. of water, to which were added first 25 ml. of 85 per cent orthophosphoric acid and then 15 ml. of water containing 1 gram of iron-free sodium dihydrogen phosphate dodecahydrate. This reagent showed no deterioration in 6 weeks. It was used by adding 0.40 ml. to 100 ml. of sample containing chlorine. Standard comparison solutions were made by diluting to 100 ml. the required volumes of an acidified solution of methyl red prepared according to the directions of Alfthan and Jarvis (1) except for making the concentration 0.00161 per cent.

THE COLOR REACTION. When the reagent is added to a dilute solution of chlorine, a purple hue develops. Presumably the color may be attributed to a meriquinone (3, 9, 11), known as Wurster's red, formed by the oxidizing action of chlorine on *p*-aminodimethylaniline. Excess chlorine decreases the color, probably through the formation of some quinone. Optimum color development for concentrations of chlorine up to 1.6 p. p. m. were obtained with 0.40 ml. of the reagent. The color developed immediately with chlorine in solution as such, but with chloramine 6 to 7 minutes were required for full color development. Although the colored system is not as stable as one would wish, making comparisons within 5 minutes after development of the color keeps the error from this source within the limit of visual matching errors. Beer's law was found not to hold for concentrations greater than 0.65 p. p. m.

Previous workers specified a pH range of 2.6 to 3.4 (1, 7). The optimum range found is 2.6 to 3.4 for concentrations up to 0.6 p. p. m. and 3.2 to 4.5 for higher concentrations. A change in hue from purple to yellow occurs in the range pH 8 to 9.

Figure 1 (solid curves) shows spectral transmission curves, for a cell thickness of 5 cm., for concentrations from 0.05 to 1.00 p. p. m. As the curves for 0.40, 0.60, and 1.00 p. p. m. were calculated from measurements for 1-cm. cells, they are probably not as reliable as the others. The small band at 530 m μ and the general symmetry of the curves are rather exceptional. The meriquinone system has a true purple hue.

COLORIMETRIC STANDARDS. As it is necessary, in using this method with the standard series or comparator technique, to employ permanent standards, the acidified methyl red solution previously recommended (1, 5) was studied. A 0.00161 per cent solution was finally selected. One milliliter of it, when diluted to 100 ml. in a Nessler tube, is colorimetrically equivalent to 0.10 p. p. m. of chlorine, treated with an excess of *p*-aminodimethylaniline, in a sample of 100 ml. The selection of this concentration was based upon the purity and brightness values calculated for I. C. I. illuminant C from the curves in Figure 1 (6, 10). Visually the match between the unknowns and standards is satisfactory, although the respective transmission curves do not check closely. Subsequent work in this laboratory indicates (8) the possibility of using as a standard a solution of potassium permanganate containing excess periodate. However, the methyl red

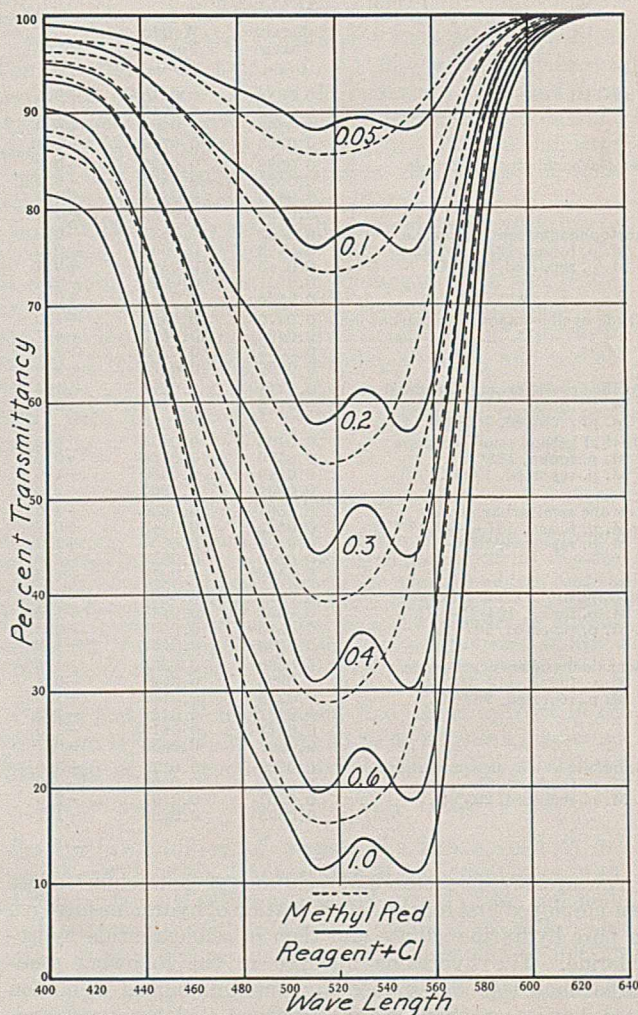


FIGURE 1. SPECTRAL TRANSMISSION CURVES
Solutions of chlorine plus *p*-aminodimethylaniline (solid curves) and for corresponding methyl red standards (broken curves)

standards were stable for several weeks and conform closely to Beer's law over the range used.

INTERFERING IONS. Since the color reaction rests on the oxidizing capacity of chlorine, interference may be expected with certain substances, such as the ferric and nitrite ions, just as with the *o*-tolidine method.

Iron increases the color intensity. For free chlorine the error for 0.1 p. p. m. of iron is equivalent to about 0.01 p. p. m. of chlorine. This error is doubled for 1.0 p. p. m. of iron. As the iron interference, at least at the beginning, is a function of time, larger errors may be expected with the slower acting chloramine. In this case, in the normal course of a determination, 0.1 p. p. m. of ferric iron will interfere to the extent of 0.02 p. p. m. of chlorine. Nitrites decrease the color intensity, the error being approximately of the same magnitude as that for iron. Chloramine gives a larger error than free chlorine.

Summary

A spectrophotometric study of the *p*-aminodimethylaniline method for the colorimetric determination of residual chlorine has shown the characteristics of the colored system and confirmed reports of others on certain factors affecting the appli-

cation of the method. A change in concentration of the methyl red solution for standards is recommended. The sensitivity varies from 0.01 p. p. m. at the lower limit to 0.03 at the higher concentrations. This method seems to have no advantage over the more familiar *o*-tolidine method unless one prefers matching purple rather than yellow hues.

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ABSTRACTED from a thesis presented by D. H. Byers to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of master of science.

Separation of Wood Extractives into Simpler Components

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WOOD is not uniform—that is, it is not chemically or structurally homogeneous. Its composition varies among species, in individual trees, and within the tree itself. In recent years, methods have been developed whereby wood can be quantitatively separated into its three major components: extractives, holocellulose, and lignin. Means for separating the carbohydrate fraction, holocellulose, into simpler components have been described elsewhere (4). Lignin, although amorphous, is relatively homogeneous when prepared from extractive-free wood taken from a single species. The extractive fraction contains by far the greatest variety of compounds. It is with the isolation, estimation, and characterization of the numerous components of this wood fraction that this paper deals.

Extractives are those substances which are removed from plant materials by inert solvents such as ether, alcohol, and water. They are not an organic part of the structural elements or of the wood substance. Materials removed from wood by the use of chemical reagents, such as alkalis, mineral acids, and bleaching agents, lie outside of the above definition, as these reagents attack the wood substance and remove portions of the holocellulose and the lignin. It is extremely important to remove the extractives completely before subsequent analysis of the wood is undertaken.

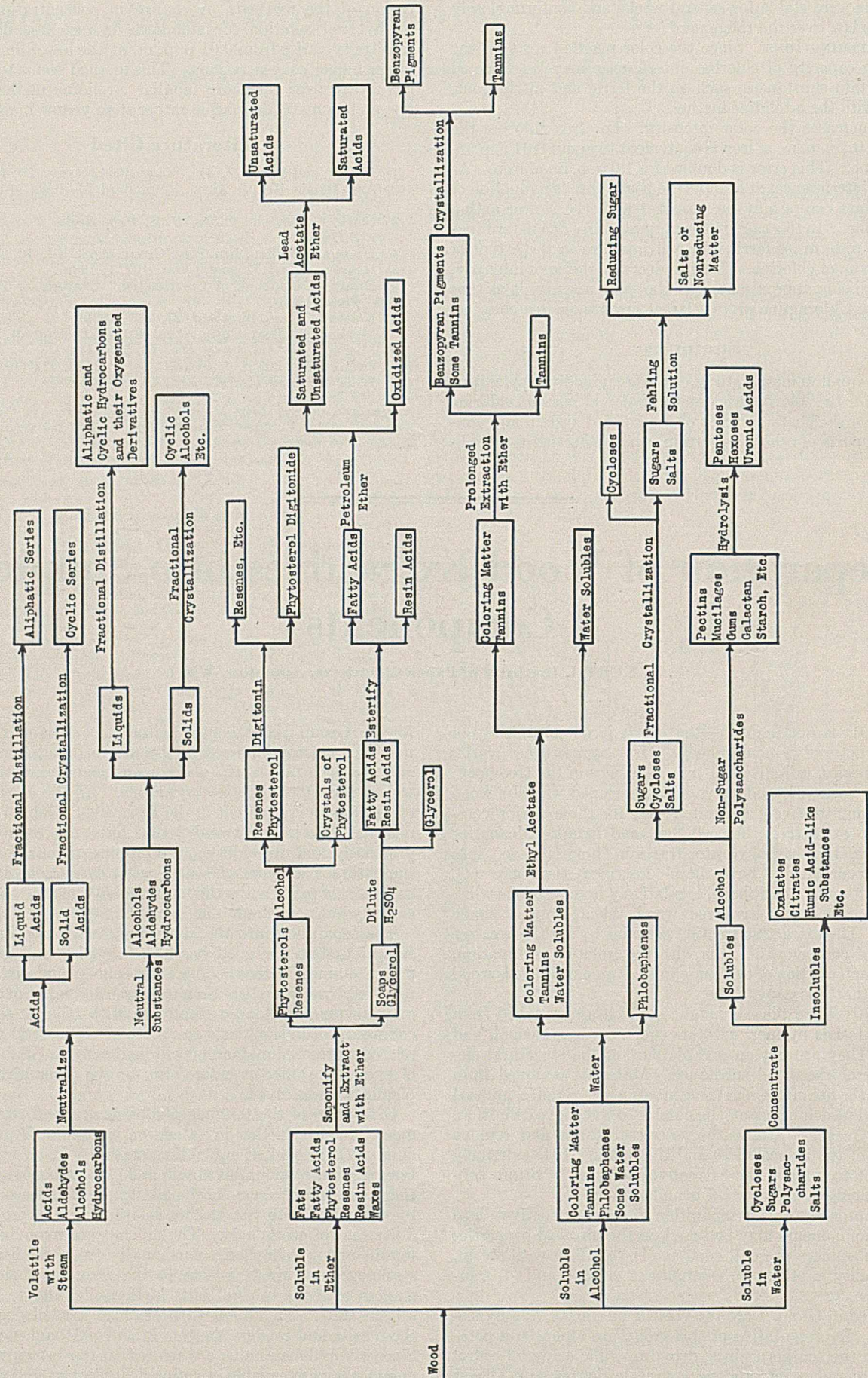
An approach to the separation of the extractives into simpler components may be based on the physical properties of the substances present, such as (1) volatility with steam, (2) solubility in ether, (3) solubility in alcohol, and (4) solubility in water.

Included in Group 1 are the volatile oils, acids, and hydrocarbons. Representative of this group are alpha- and beta-pinene in the southern pines, dehydroperillic acid and cedrol in western red cedar, and *n*-heptane in Jeffrey and Digger

pinus. Group 2 contains the materials in Group 1 that have not been removed previously by steam distillation and, in addition, the fats, fatty acids, resin acids, resenes, sterols, waxes, and nonvolatile hydrocarbons. All the above classes of substances are present in the *Pinaceae*. Group 3 contains materials in Groups 1 and 2 that have not been removed previously and, in addition, the tannins, phlobaphenes, and the natural pigments. Group 4, after extractions have been successively made with ether and alcohol, includes the soluble carbohydrates, cycloses, and salts.

The separation into the above groups is based on the assumption that the wood has been air-dried and ground to pass a 40-mesh screen. The ether-soluble material may be removed by 8 hours' continuous extraction in a Soxhlet type of extractor. Prolonged treatment with ether is to be discouraged, for in such instances some of the natural pigments related to the phlobatannins will be dissolved. Substitution of petroleum ether or chloroform for the ether leaves these pigments undissolved.

Extraction of the tannins, phlobaphenes, and related pigments, when a further investigation is desired, is preferably done with alcohol at room temperature. With wood containing a large amount of tannin and phlobaphene, it is sometimes necessary to remove the last traces of these substances by extraction with hot alcohol acidified with approximately 3 per cent of acetic acid. The difficulty of removing all the tannin and phlobaphene, particularly from old heartwood, stumpage, and roots, is due to the reaction of these substances with the mineral salts in the soil water to form insoluble salts. Treatment with acidified alcohol decomposes these salts and renders the tannin and phlobaphene soluble. Since the phlobatannins are related to the benzopyran pigments, they are capable of acting as indicators and they give



characteristic colorations with dilute alkalis. Testing the alcohol-extracted wood with a dilute solution of sodium carbonate will reveal whether or not the phlobatannins have been completely removed.

Extraction of the fourth group of materials is carried out with hot water following the treatment with ether and alcohol.

A further separation and estimation of the amounts of each component in the above groups may be made as follows:

Materials Volatile with Steam

Substances in this group are largely absent in broad-leaved trees or dicotyledons, but they occur in limited amounts in the xylem of softwoods or conifers. Exceptions may be found, however. Nonacidic materials are separated from the acidic materials by neutralization with dilute alkali followed by extraction with ether. Further separation into the individual components is performed by fractional distillation in the case of the liquids and by fractional crystallization in the case of the solids.

Materials Soluble in Ether

Saponification of the ether extract with alcoholic potassium hydroxide, followed by extraction of the mixture with ether, separates most of the neutral from the acidic components. The hydrocarbons, resenes, glycerol, phytosterols, and such alcohols as were part of the waxes will be present as unsaponifiable matter. In the case of the extractive from pine sapwood, this fraction will be largely phytosterol (3). Treatment of the unsaponifiable fraction with digitonin precipitates the sterols as digitonides (1). Usually a satisfactory separation of the components of the neutral fraction can be accomplished by fractional crystallization from hot alcohol.

The soap residue from the neutral fraction upon acidification and extraction with ether gives the free fatty and resin acids. Glycerol, as it is readily soluble in water and insoluble in ether, will be retained in the aqueous solution from these acids.

A quantitative separation of the resin acids from the fatty acids is accomplished by preferential esterification of the fatty acids with absolute alcohol in the presence of sulfuric acid (6). Separation is then readily effected by transforming the resin acids into their water-soluble sodium salts with sodium hydroxide solution, and extracting the esters of the fatty acids with ether.

After saponification of the esters and precipitation of the oxidized acids with petroleum ether, the saturated fatty acids may be separated from the unsaturated fatty acids by the lead salt-ether method (2). The percentage of oleic and linoleic acids in the mixture can be calculated from the iodine value.

Materials Soluble in Alcohol

Extraction of the ether-extracted wood residue with alcohol removes the tannin, phlobaphenes, and associated coloring matters. Most tannins occurring in wood belong to the phlobatannin class, in contrast to the depside class, such as gallotannin, penta-*m*-digalloylglucose, which occurs in gall nuts. It has long been held that the phlobatannins are related to the benzopyran pigments—e. g., fisetin, catechin, morin, and quercetin, with which they naturally occur. These pigments are crystalline and, since they give the same color reactions and the same phenolic degradation products, and are easily converted to amorphous tanninlike materials, they are said to be the precursors of the phlobatannins.

Occurring with the phlobatannins and the benzopyran

coloring matters are the phlobaphenes. They may be derived from the phlobatannins by any process which causes dehydration. Russell (5) has demonstrated that the phlobatannins are in reality hydroxyflavopinacols. Phlobaphenes are insoluble in water, whereas the benzopyran pigments and the phlobatannins are soluble. This fact is made use of in their separation. The alcohol is thoroughly removed from the extract by evaporation or by steam distillation and replaced with water. The insoluble phlobaphene separates as a colloidal dark-colored precipitate which, after drying, changes to a red amorphous powder.

Tannin and coloring matter in the aqueous solution from the phlobaphene precipitation are isolated by extraction with ethyl acetate. The amount of crystalline pigment occurring with the tannin is usually very small. Isolation and identification of the crystalline coloring matter are generally accomplished by prolonged extraction of the concentrated tannin extract with ether. Evaporation of the ether leaves the coloring matter in the form of impure crystals, which are then purified by recrystallization from alcohol or alcohol-benzene mixture.

In some instances, the aqueous solution from the ethyl acetate extraction of the phlobatannin and pigments will contain a small amount of additional materials, generally of the same nature as those substances present in Group 4. As the tannins are very susceptible to the action of heat and air, a tannin fraction, which is insoluble in ethyl acetate, may remain in the aqueous solution. This fraction may be readily separated from the other water-solubles by evaporating the solution to semidryness and then dissolving with acetone.

Materials Soluble in Water

The aqueous extract from the ether- and alcohol-extracted wood residue contains a mixture of miscellaneous substances, the nature of which depends to a large extent upon the species of wood under investigation. This group includes salts, sugars, cycloses, and such nonsugar polysaccharides as gums, mucilages, starch, pectinlike materials, and galactans. Seldom do all these materials occur in one extract.

Upon concentration of the extract by distillation *in vacuo*, the major portion of the more insoluble salts separates from solution and is filtered off. The nonsugar polysaccharides separate as colloidal precipitates when the concentrated extract is poured into five volumes of alcohol. The cycloses, when present, slowly separate as crystals in the alcoholic filtrate from the polysaccharide precipitation after standing 24 to 48 hours. The percentage of sugars is estimated by a reducing sugar determination. Identification and estimation of the individual sugars in a mixture of one or two sugars can be performed by preparing suitable hydrazones. Where complex sugar mixtures are obtained—e. g., glucose, galactose, mannose, arabinose, and xylose—these can be successfully determined through selective fermentations (4).

The cycloses occur in some softwoods and hardwoods. Both pinite and sequoyite are found in redwood, and pinite is also found in sugar pine. *l*-Inositol occurs in ash and oak. The scheme of separation is summarized in the diagram.

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Factors Influencing the Quantitative Determination of Sulfate as Barium Sulfate

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ALMOST the entire history of barium sulfate precipitates is marked by references to annoying, unexplained, and often uninvestigated interference by common substances, the presence of which might be expected from theoretical considerations to produce little or no interference. Of these one of the commonest and most troublesome has been the nitrate ion, usually present with the alkali elements (20, 27). The phenomenon has been variously blamed on adsorption, coprecipitation, occlusion (23), and the formation of various types of unisolated, insoluble complex-compounds (4).

Quantitative results based on the weight of precipitate range from slightly low to several per cent greater than the amount required by theory. These variations depend upon conditions observed during the formation and treatment of the precipitated material. It seemed desirable, as a basis for further study as well as for the purpose of limiting analytical conditions, to study in more detail the relationship between these errors and the conditions that influence them.

Equal amounts of sulfates were precipitated with an excess of barium chloride solution in the presence of various amounts of salts and acids. Potassium salts were used for the most part, and the results compared under certain conditions with other salts. A standard procedure for the treatment of the precipitate was adopted, and the effect of varying nearly all possible variable factors in this procedure was tested at certain regular intervals. The salts and acids used were of analyzed reagent grade, which were tested for freedom from interfering substances and found to conform in general to A. C. S. standards for reagent grade chemicals.

General Technique

Where precipitation was conducted above room temperature, the sulfate solution was maintained at that temperature on an electric hot plate. Solutions were stirred mechanically while barium chloride solution was added from a buret at a rate determined by the attachment of a calibrated delivery tip. After the measured volume of precipitant had been added, the stirrer and cover glass were cleaned, and the solution was allowed to stand, either on a steam plate or at room temperature, for a definite length of time. The solution was then decanted through a porcelain filtering crucible, and the filtrate tested for excess of barium ion. The precipitate, after having been washed by decantation, was transferred to the crucible, washed further, and finally dried to constant weight.

This investigation has considered the effect of some twenty different factors that are commonly encountered in the course of an ordinary sulfate determination.

General Conditions

The behavior of potassium sulfate in the presence of potassium nitrate under different conditions has been studied extensively, and the results have been compared with other sulfates and nitrates. Although the effect of

variation on nearly all conditions was studied at certain points, most conditions have remained fixed throughout the greater part of this investigation. To simplify comparison of the numerical results given, and to reduce the number of conditions that must be listed in connection with each set of figures, the following values apply, except where different values are specifically stated:

The precipitates were not ignited, but were dried to constant weight at 110° to 120° C.

The concentration of sulfate at the start of precipitation was 0.01 molar and the volume was 350 cc.

The concentration given for various salts and acids present is for the initial volume.

Barium chloride solution 0.05 molar at 25° to 30° C. was added to 5 per cent in excess.

Cold precipitation was at 25° to 30° C.; for hot precipitation the initial temperature of the sulfate solution was 95° to 100° C.

The final volume with 5 per cent excess barium chloride was 425 to 430 cc.; with 50 per cent excess, 460 to 465 cc.; and with 100 per cent excess, 495 to 500 cc.

Stirring was always by a motor-driven stirrer at uniform rate of speed.

Hot digestion was at the temperature maintained by a steam-heated plate, at 80° to 85° C.

Wash water was 200 to 300 cc. of distilled water at 25° to 30° C.

The sulfate used for precipitation was in each case theoretically equivalent to 0.8166 (± 0.0002) gram of barium sulfate. Each result quoted in the following tables should theoretically have been 0.8166 gram. The difference in each case represents the error.

Experimental Investigation of Factors

CONCENTRATION OF SULFATE ION IN SOLUTION. The figures given in Table I show the weight of barium sulfate obtained from equal weights of potassium sulfate at different concentrations, under the conditions indicated. Variations in the

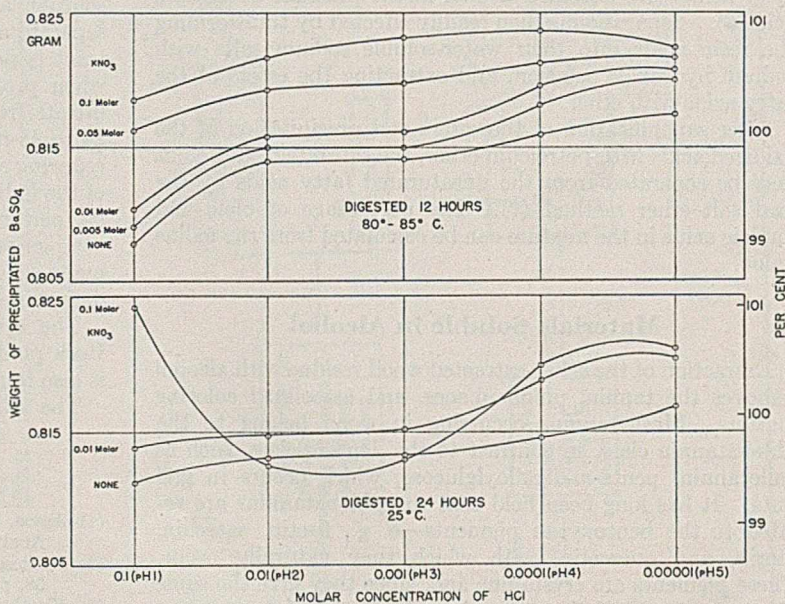


FIGURE 1. EFFECT OF HOT AND COLD DIGESTION

Unignited precipitate obtained by adding 0.05 molar BaCl_2 to 5 per cent in excess in 5 minutes to hot (95° to 100° C.) 0.01 molar K_2SO_4 solution of varying concentration with respect to HCl and KNO_3 .

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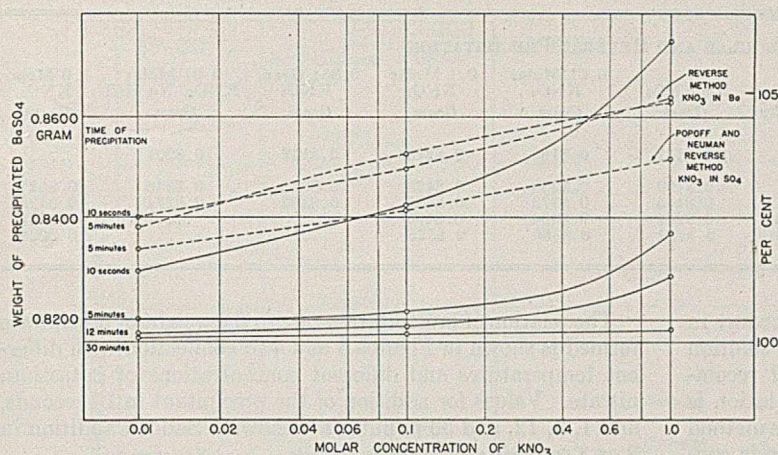


FIGURE 2. COMPARISON OF REVERSE AND REGULAR PRECIPITATION METHODS

Unignited precipitate obtained by adding 0.05 molar BaCl_2 to 5 per cent in excess to hot (95° to 100°C .) 0.01 molar K_2SO_4 at different rates, where sulfate solution is of varying concentration with respect to KNO_3 (solid lines), compared with results (broken lines) obtained by adding same weight of K_2SO_4 to hot BaCl_2 solution. No acid added except in the Popoff and Neuman determination.

concentration of potassium sulfate between 0.005 and 0.02 molar produced differences of less than ± 0.5 mg. in 0.815 gram of the precipitate if no potassium nitrate was present.

CONCENTRATION OF POTASSIUM NITRATE PRESENT. The effect of nitrates upon the weight of barium sulfate precipitates has been shown to be a function of the concentration of the nitrate (4), at least up to a certain point (1).

TABLE I. EFFECT OF VARYING CONCENTRATION OF SULFATE

[Same weight of K_2SO_4 , 0.01 molar KNO_3 , 0.01 molar HCl , BaSO_4 precipitated hot (95°C .) in 5 minutes by BaCl_2 to 5 per cent excess. Digested 12 hours hot]

0.005 Molar K_2SO_4 Gram	0.01 Molar K_2SO_4 Gram	0.02 Molar K_2SO_4 Gram
0.8141	0.8153	0.8161

The effect of potassium nitrate has been studied where the concentrations at the start of the precipitation were 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 molar. The effect of these concentrations upon the weight of the precipitate of barium sulfate is shown in Figures 1 to 4. (For the sake of brevity, only graphic data are given in some instances. For the numerical data the reader is referred to the original thesis.)

CONCENTRATION OF HYDROGEN ION IN SOLUTION. Sufficient hydrochloric acid was used to render the solution at the start of precipitation 0.1, 0.01, 0.001, 0.0001, or 0.00001 molar with respect to hydrochloric acid. These concentrations are equivalent to pH values of approximately 1, 2, 3, 4, and 5, respectively, for the initial volume of 350 cc. of water in which the potassium sulfate and potassium nitrate are dissolved and to which the barium chloride solution is added during the precipitation.

The curves (Figure 1) for hot and cold digestion differ in some cases, but are nearly parallel to the base line between 0.01 and 0.001 molar hydrochloric acid for concentrations of 0 to 0.01 molar potassium nitrate. In the case of hot digestion, all values lie within 3 parts per 1000 of the theoretical value required. The solution, then, should not be more than 0.01 molar with respect to nitrate and should be made from 0.01 to 0.001 molar with respect to hydrochloric acid (pH 2 to 3), preferably nearer 0.01 molar.

The sulfate is precipitated from hot solution in about 5 minutes and digested hot for 12 hours. If the solution is digested cold for 24 hours, the effect of larger concentrations

of potassium nitrate is less between 0.01 and 0.001 molar hydrochloric acid, but all results then carry a negative error of 2 to 3 parts per 1000.

KIND OF BARIUM SALT USED AS PRECIPITANT. Barium chloride was used throughout and always at room temperature. No other salt or acid was added to the barium chloride solution except in a few cases of reverse precipitation (Table IV). The results in these cases are abnormally high.

CONCENTRATION OF BARIUM SOLUTION. Barium chloride 0.05 molar was used in this investigation, and was compared under the conditions shown in Table II with 0.1 and 0.5 molar solutions. The latter solution gave slightly higher results in the presence of nitrates.

TEMPERATURE OF SOLUTION DURING PRECIPITATION. Temperatures were taken at the start of, rather than during, precipitation. The beaker was heated over a gas burner, then transferred to a small electric hot plate during precipitation. This plate furnished sufficient heat to keep the solution at the boiling temperature with slow ebullition.

TABLE II. CONCENTRATION OF BARIUM CHLORIDE SOLUTION (BaSO_4 precipitated hot in 5 minutes by BaCl_2 to 5 per cent excess. Digested 12 hours hot)

KNO_3 Molarity	HCl Molarity	Barium Sulfate Precipitated		
		0.05 molar BaCl_2 Gram	0.1 molar BaCl_2 Gram	0.5 molar BaCl_2 Gram
None	0.01	0.8142	0.8148	0.8146
0.01	0.01	0.8153	0.8161	0.8194
0.1	0.01	0.8211	0.8211	0.8239

Since the barium chloride was always used at room temperature, the heater did not entirely counteract the cooling effect of the added barium chloride in the more rapid additions (10 seconds, 1 minute, 2 minutes). Here the drop in temperature was less than 15°C . for boiling hot solutions. For additions in 5 minutes' time, the cooling effect was less than 5°C ., and for slower additions (12 and 30 minutes) it was practically canceled. In precipitations made at room temperature, this effect is absent. For precipitations at intermediate temperatures (45° , 60° , and 75°C .), heat from the hot plate was supplied during precipitation, and the temperature was kept within $\pm 5^\circ$ of the value given. Where 50 or 100 per cent excess barium chloride was added at the end of precipitation time stated, the solution was cooled further as a result.

TABLE III. EFFECT OF TEMPERATURE OF SULFATE SOLUTION DURING PRECIPITATION

(BaSO_4 precipitated by 0.05 molar BaCl_2 to 5 per cent excess, in 5 minutes)

KNO_3 Molarity	HCl	25° to 30° C.	40° C.	55° to 65° C.	75° C.	95° to 100° C.
		Gram	Gram	Gram	Gram	Gram
0.01	0.01	Digested 12 Hours Hot				
		0.8277	0.8197	0.8153
0.1	0.01	Digested 24 Hours Cold				
		0.8456	0.8187	0.8118
		0.8402	0.8329	0.8261	0.8223	0.8201
0.1	None	0.8710	0.8504	0.8360	0.8300	0.8203

The effect of temperature may be seen in Figures 3 and 4.

Cold precipitation (25°C .) increases errors of contamination somewhat in all cases (2, 17, 25), but much more where the addition of barium chloride is rapid (22), where the excess of barium chloride added is large, or where the concentration of nitrate is high. It is necessary to precipitate barium sulfate near the boiling point if these errors are to be reduced to a minimum.

TABLE IV. REGULAR AND REVERSE PRECIPITATION

Conditions	Precipitation Min.	HCl Molarity	No KNO ₃ Gram	0.01 Molar KNO ₃ Gram	0.1 Molar KNO ₃ Gram	0.354 Gram KNO ₃ Gram	0.01 Molar KNO ₃ , No HCl Gram	1.0 Molar KNO ₃ Gram
BaCl ₂ added to K ₂ SO ₄ , KNO ₃ in K ₂ SO ₄	5	0.01	0.8141	0.8153	0.8213	0.8153	0.8204
Popoff and Neuman reverse method:								
Dried at 115° C.	5	0.03	0.8190	0.8338	0.8423	0.8372	0.8346	0.8521
Ignited 1 hour at 600-700° C.	5	0.03	0.8165	0.8273	0.8335	0.8303	0.8271	0.8425
K ₂ SO ₄ added to BaCl ₂ , KNO ₃ in BaCl ₂ :								
10 seconds hot		None	0.8242	0.8404	0.8490	0.8639
5 minutes hot		None	0.8170	0.8386	0.8525	0.8636

MANNER OF ADDITION OR MIXING. The usual procedure in sulfate determination has been to add the barium solution to the sulfate solution. In the "reverse" method recommended by Popoff and Neuman (21) the sulfate solution is added to the barium solution. Figure 2 compares this method with the "regular" precipitation method. The chloride contamination is much higher in the case of reverse precipitation (1, 22).

The broken lines indicate the results of reverse precipitation in 10 seconds and in 5 minutes with potassium nitrate present in the barium chloride solution, in comparison with the Popoff and Neuman method where the potassium nitrate is in the sulfate solution and the barium chloride solution is made 0.03 molar with respect to hydrochloric acid. The solid lines show the results of the usual type of precipitation where barium chloride is added to the potassium sulfate solution containing potassium nitrate but no acid. The reverse method is more susceptible to contamination by nitrate at low concentration than is the regular method (23, 30); consequently this regular method has been adhered to elsewhere in this investigation. All these precipitations were made from the hot solution.

RATE OF ADDITION OF BARIUM SOLUTION. In the past this factor has been the subject of much attention and nearly as much disagreement among analysts (1, 13, 18, 19, 24). While undoubtedly the errors due to rapid addition will occasionally cancel out other errors and give the theoretical results desired, it is almost certain to be the wrong technique in the large majority of cases, especially where any nitrate is present.

In this investigation the barium chloride solution was added from a buret having interchangeable glass tips, calibrated to deliver in the desired length of time the theoretical amount of the solution required plus 5 per cent in excess.

The relation of precipitation rate to the weight of precipitate formed is shown in Figures 3 and 4 in connection with different temperatures and different concentrations of potassium nitrate. Values for addition of the precipitant in 10 seconds, and 1, 5, 12, and 30 minutes are shown. Sudden addition in 2 or 3 seconds gave erratic results.

RATE OF STIRRING DURING PRECIPITATION. A motor stirrer was used. This mechanical stirring was compared in a few experiments with hand stirring in which a straight glass rod was used. The results show no difference within the experimental error.

EXCESS OF BARIUM SOLUTION ADDED. The variation of this value explains to some extent the erratic results heretofore obtained when nitrates were present in sulfate samples (4, 7, 11, 25). For precipitates formed slowly in the absence of nitrates and hydrochloric acid, the excess of barium chloride added has no effect upon the weight of dry precipitate. Excesses of 50 or 100 per cent, if added after rapid precipitation at room temperature in the absence of potassium nitrate and hydrochloric acid, give slight increases of 2 and 4 mg. in 816 mg. (22). In the presence of increasing concentrations of potassium nitrate this effect increases greatly, being augmented always by conditions of rapid or cold precipitation until, for molar potassium nitrate, it produces a 50-mg. increase in weight of precipitate, over 6 per cent of the theoretical value.

The excess of precipitant above 5 per cent was added all at once, immediately after the timed addition of the first 105 per cent of barium chloride.

Figure 4 shows the effect of excess of barium chloride at different precipitation rates, for different temperatures, and in the presence of different concentrations of potassium nitrate. If the precipitate is formed in a solution acid with hydrochloric acid and is then subjected to hot digestion, a

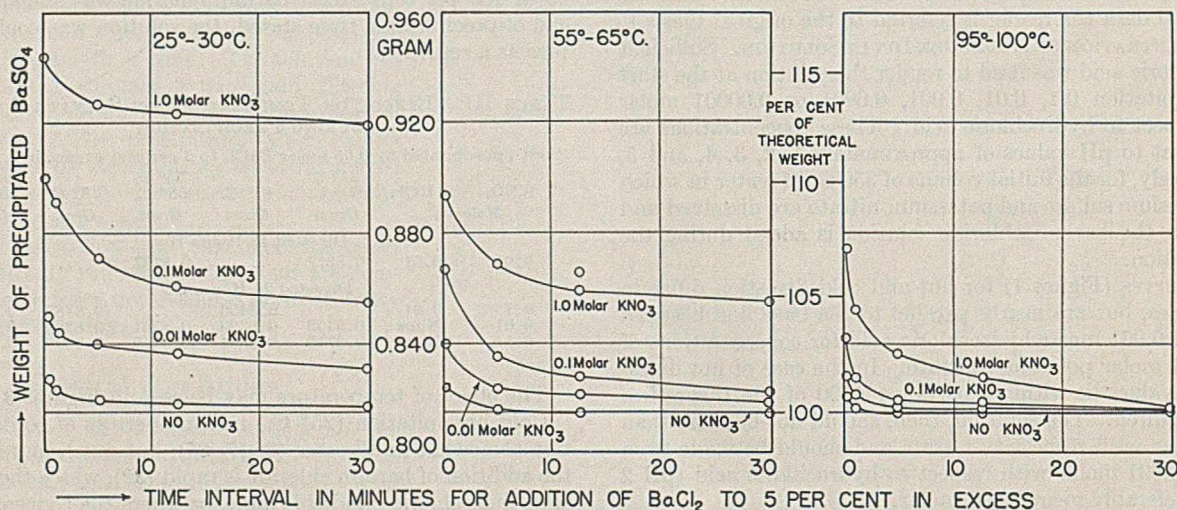


FIGURE 3. EFFECT OF TIME INTERVAL

Unignited precipitate obtained by adding 0.05 molar BaCl₂ to 5 per cent in excess at different rates to 350 cc. of unacidified 0.01 molar K₂SO₄ made 0.00, 0.01, 0.1, and 1.0 molar with respect to KNO₃. Temperature of sulfate solution at start of precipitation, 25° to 30° C., 55° to 65°, or 95° to 100° C. Precipitates digested 24 hours at 25° C.

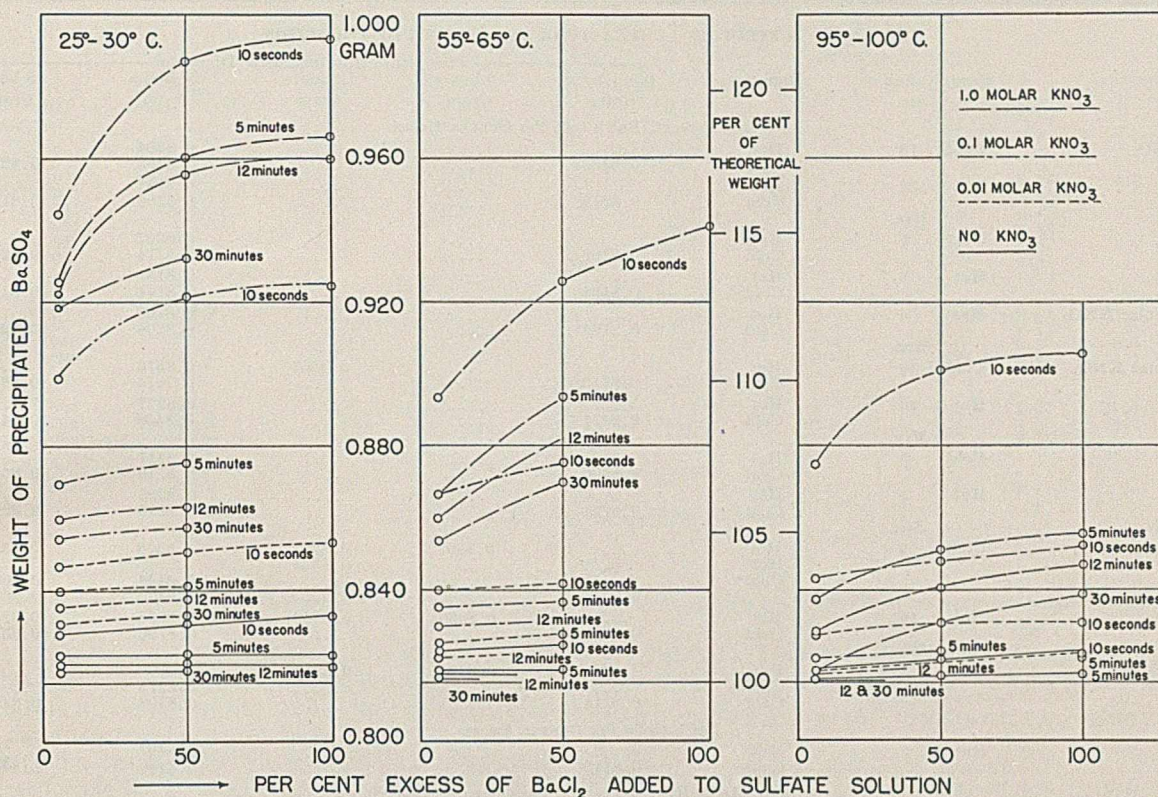


FIGURE 4. EFFECT OF EXCESS BARIUM CHLORIDE

Unignited precipitate obtained by adding 5, 50, and 100 per cent excess of 0.05 molar BaCl_2 to 350 cc. of unacidified 0.01 molar K_2SO_4 , made 0.00, 0.01, 0.1, and 1.0 molar with respect to KNO_3 , where first 105 per cent of BaCl_2 was added in 10 seconds and 5, 12, and 30 minutes. Temperature of sulfate solution at start of precipitation was 25° to 30°, 55° to 65°, or 95° to 100° C. Precipitates digested 24 hours at 25° C.

larger excess of barium chloride produces slightly lower results.

TEMPERATURE DURING DIGESTION. Digestions were conducted at room temperature or on a steam plate which maintained the solutions at a temperature of approximately 80° to 85° C.

Hot digestion removes more of the impurities from the precipitate and does so more rapidly than cold digestion. The difference is, of course, greater for greater contamination. The temperature of the supernatant liquid also affects the solubility of the barium sulfate in it. No correction was made for this slight error.

The results of hot and cold digestion are compared with length of digestion and other factors in Table V and in Figure 1.

DIGESTION TIME. Table V shows that under some conditions the length of this interval exerts a considerable influence upon the weight of precipitate obtained. This difference may amount to more than 5 per cent of the weight of the contaminated barium sulfate precipitated rapidly from cold unacidified solutions in the presence of a large amount of potassium nitrate. Weight is also influenced to a considerable extent by the concentration of hydrochloric acid present. The change in the precipitate during hot digestion is a loss in weight due to contaminating substances passing from the precipitate into the solution. Several per cent of potassium nitrate along with traces of chloride have been leached from such precipitates.

During the early part of the digestion period a gain in weight of precipitate is also taking place, due to the overlapping of the precipitation period, caused by temporary supersaturation of the solution with respect to barium sulfate.

Another type of delayed precipitation, of much longer duration, was observed in the case of precipitates obtained from solutions of molar potassium nitrate. Here gains in weight up to 35 mg. (out of more than 900 mg. of precipitate) occurred upon standing 48 hours, with additional gains of as much as 10 mg. beyond that point. This occurs in varying degrees whether the precipitates are formed in hot or cold solution, whether the barium chloride is added rapidly or slowly (10 seconds or 5 minutes), in 5 or 50 per cent excess, but only on cold digestion. This precipitation occurs even in the filtered supernatant liquid when it stands separated from the precipitate already formed. In this case the precipitate (as much as 43 mg.) was barium sulfate contaminated with considerable amounts of potassium and nitrate.

Clearly the phenomenon is related to the cold supernatant liquid, which must retain a considerable quantity of sulfate in solution and allow its slow release to some form from which it can subsequently precipitate.

The facts that much of the precipitate from the separated supernatant liquid forms upon the walls of the beaker, and that the liquid itself appears clear and free from turbidity seem to argue against the idea of the retained material's being suspended in ultramicroscopic crystalline form. The variety of conditions influencing crystal form and size, the complete filterability through fine porous refractory material or closely packed barium sulfate, and the high specific gravity of the precipitated material do not favor a suspension theory, nor does the fact that the precipitate forms a very closely adhering, crystalline frosting upon the beaker.

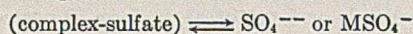
The observed facts suggest a complex ion or compound in the potassium nitrate solution (3, 6, 12, 15, 26, 29) withholding sulfate from precipitation and slowly releasing it into an ionic

TABLE V. EFFECT OF TEMPERATURE AND LENGTH OF DIGESTION

	Precipitation Sec.	Digestion	Precipitate Obtained after Digestion				
			0.5-1 hour Gram	6 hours Gram	12 hours Gram	24 hours Gram	48 hours Gram
No HCl Present, BaCl ₂ to 5 Per Cent in Excess							
No KNO ₃	Cold 10	Hot	0.8304
		Cold	0.8322	0.8283	0.8270
	Hot 10	Hot	0.8191
		Cold	0.8212	0.8206	0.8194
	Min. Cold 5	Hot	0.8207
		Cold	0.8198	0.8214	0.8209
	Hot 5	Hot	0.8181
		Cold	0.8164	0.8164	0.8169
0.01 molar KNO ₃	Hot 5	Hot	0.8203
	Sec. Cold 10	Cold	0.8194	0.8204	0.8211
0.1 molar KNO ₃	Cold 10	Hot	0.8563	0.8576
		Cold	0.9115	0.9016	0.8667
	Hot 10	Hot	0.8277
		Cold	0.8471	0.8428	0.8411
	Min. Cold 5	Hot	0.8417
		Cold	0.8730	0.8710	0.8619
	Hot 5	Hot	0.8226
		Cold	0.8214	0.8206	0.8228
1.0 molar KNO ₃	Cold 10	Hot	0.8307	0.8262	0.8328	0.8326
		Hot	0.8325
	Hot 10	Cold*	0.9118	0.9444	0.9607 ^a
		Cold	0.9248	0.9493	0.9611
	Min. Hot 5	Hot	0.8339	0.8270	0.8235	0.8257
		Cold	0.8700	0.8790	0.8818
	Hot 5	Hot	0.8378	0.8282
		Cold	0.8214	0.8375
	Hot 5	Cold	0.8306	0.8357
		Cold	0.8416	0.8421	0.8484
BaCl ₂ to 50 Per Cent in Excess							
0.01 Molar HCl, BaCl ₂ to 5 Per Cent in Excess							
No KNO ₃	Hot 5	Hot	0.8140	0.8141
		Cold	0.8126	0.8130
0.01 molar KNO ₃	Hot 5	Hot	0.8151
		Cold	0.8141	0.8144
0.05 molar KNO ₃	Hot 5	Hot	0.8186	0.8198
		Cold	0.8127
0.1 molar KNO ₃	Hot 5	Hot	0.8212	0.8228
	Sec. Hot 10	Cold	0.8120	0.8126	0.8138
	Hot 10	Hot	0.8266
		Cold	0.8307	0.8355

^a Digested cold 168 hours (7 days) = 0.9706 gram.

form capable of being precipitated from solution. In hot solution the complex is largely broken down; the speed of attainment of equilibrium of the reaction



may be greatly increased, so that precipitation of nearly all the sulfate is completed in a short time, or the point of equilibrium may be shifted in the direction to reduce the concentration of the complex sulfate. Another possibility is that the high concentration of nitrate ion by retarding the attainment of equilibrium may prolong the supersaturation period. Other investigators have recorded the retardation of barium sulfate precipitation by certain compounds (14, 15, 26). The effect of length of time of digestion under various conditions is shown in Table V.

SUPERNATANT LIQUID PRESENT DURING DIGESTION. When potassium nitrate was added to the supernatant liquid, after precipitation of the barium sulfate, there was no increase in the weight of the precipitate (4), but a loss was observed which was probably due to the increased solubility of barium sulfate in a strong solution of potassium nitrate. This loss was greater for hot solution.

TIME OF DRYING. Precipitates were usually dried from 12 to 18 hours. This gave results concordant to 0.2 mg. where the nitrate contamination was small. Some precipitates which were dried only 4 hours lost excessive amounts of weight upon subsequent drying, indicating that the first drying time was

TABLE VI. BARIUM SULFATE PRECIPITATED

(By 0.05 molar BaCl₂ to 5 per cent in excess in 10 seconds)

KNO ₃ Molarity	During precipitation	During digestion	Temperature during Digestion ° C.	BaSO ₄ Precipitated Gram
At 25° C., Digested 24 Hours				
None	None	None	25	0.8283
None	None	1.0	25	0.8276
None	None	1.0	85	0.8150
1.0	None	0.8 ^a	25	0.9563
At 95° to 100° C., Digested 48 Hours				
None	None	None	25	0.8184
None	None	1.0	25	0.8131

^a Dilution effect of added BaCl₂ solution.

insufficient. A second drying of 6 to 18 hours gave results that were usually 0.0 to 0.2 mg. lower for 800 to 900 mg. of precipitate.

IGNITION TEMPERATURE. To test the effect of drying vs. ignition upon precipitates formed under different conditions, a number of precipitates were first dried at 115° C., then held at temperatures of 300° ± 5° C. for two 1-hour periods, at 600° ± 15° for two 1-hour periods, and at 800° ± 25° for 1 hour. In the case of the less contaminated precipitates obtained under optimum conditions of precipitation the losses were small between 115° and 300° C., and much larger at higher temperatures. For the precipitates containing greater

TABLE VII. EFFECT OF IGNITION OF WEIGHT OF PRECIPITATES
(Precipitated in 5 minutes from 610 mg. of K_2SO_4 , 5 per cent excess barium chloride)

KNO ₃ Molarity	HCl	Precipitate Dried at 115° C. Mg.	Weight Lost during Ignition						Analysis of Original Precipitate		
			At 300° C.		At 600° C.		At 800° C.	Total		K	NO ₃
			1st hr.	2nd hr.	1st hr.	2nd hr.	1 hr.	Mg.	%	Mg.	Mg.
Precipitated Hot, Digested Hot for 12 Hours											
None	0.01	814.1	0.8	0.0	2.0	0.5	0.3	3.6	0.45	4.3	0.0
None	0.001	814.1	0.5	0.0	2.2	0.4	0.4	3.5	0.44
0.01	0.01	815.4	0.9	0.1	2.0	0.4	0.2	3.6	0.45	4.5	1.2
0.01	0.001	816.0	0.8	0.0	2.3	0.3	0.2	3.6	0.45
0.1	0.01	821.2	3.9	0.2	2.4	0.4	0.1	7.0	0.87	5.9	1.8
0.1	0.001	821.9	3.2	0.2	3.4	0.0	0.2	7.0	0.87
Precipitated Hot, Digested Cold for 24 Hours											
0.01	0.01	814.4	1.2	0.0	2.8	0.0	0.3	4.3	0.54
0.1	0.01	812.6	1.0	0.0	4.3	0.0	0.4	5.7	0.71
0.01	None	820.3	0.4	0.1	2.1	0.0	0.6	3.2	0.40	5.4	3.5
0.1	None	820.5	0.6	0.2	2.3	0.0	0.8	3.8	0.48	5.1	4.0
Precipitated Cold, Digested Cold for 24 Hours											
0.01	None	840.2	1.6	0.2	4.9	0.6	6.7	14.1	1.67	17.1	10.5
0.1	None	871.0	2.9	0.4	4.1	0.3	14.6	22.5	2.55	24.7	19.8
0.1 ^a	None	875.6	3.3	0.4	4.1	0.5	17.0	25.3	2.89
Precipitated Cold, No Digestion											
0.1	None	873.0	3.6	0.2	4.5	0.9	13.6	22.9	2.62
Precipitated Cold, Digested Cold for 48 Hours											
0.1	None	861.9	1.9	0.3	3.8	1.2	9.9	17.2	2.00

^a 50 per cent excess BaCl₂.

amounts of contamination (nitrates), the losses were much greater between 115° and 300° C., and in general greater than for the others at higher temperatures. The results of these ignition experiments are given in Table VII.

This investigation shows that in general more reliable and more reproducible results may be obtained by drying such contaminated barium sulfate precipitates to constant weight than by igniting them.

IGNITION TIME. Precipitates that had been ignited for 1 hour at 300° or 600° C. showed further loss in weight (Table VII) when they were heated at the same temperature for an additional hour (21). The virtual elimination of this variable is another point in favor of drying the barium sulfate rather than igniting it.

TABLE VIII. KINDS OF CATIONS ACCOMPANYING SULFATE

		No HCl. Digested 24 hours cold			
KNO ₃ Molarity	Precipitation	0.01	0.01	0.01	0.01
		Molar	Molar	Molar	Molar
		H ₂ SO ₄	K ₂ SO ₄	Na ₂ SO ₄	(NH ₄) ₂ SO ₄
		Gram	Gram	Gram	Gram
None	Hot	0.8174	0.8162	0.8171	0.8176
0.01	Hot	0.8143	0.8202	0.8201	0.8212
0.1	Hot	0.8139	0.8204	0.8201	0.8173
0.1	Cold	0.8562	0.8728	0.8731	0.8762
0.01 Molar HCl except in H ₂ SO ₄ , Digested Hot 12 Hours					
None	Hot	0.8162	0.8142	0.8160	0.8151
0.01	Hot	0.8145	0.8152	0.8151	0.8157

Composition of Unignited Precipitates

Some of the precipitates considered in Table VII were analyzed for potassium and nitrates.

A weighed portion of precipitate was dissolved in about 25 times its weight of 18 molar sulfuric acid, and reprecipitated by pouring dropwise and with stirring into about 25 times its volume of water. The filtrate and washings were evaporated to sulfur trioxide fumes, transferred to a platinum crucible, and evaporated to dryness in an air bath. The residue was dissolved in a little water, filtered, dried, and ignited to constant weight with a small lump of ammonium carbonate. The salt was weighed as potassium sulfate and calculated as potassium. This value was checked against an indirect determination of the potassium from this residue as platinum in potassium chloroplatinate. Other portions of these unignited precipitates were decomposed by boiling 1 hour with 15 times the theoretical amount of sodium carbonate (2 molar). Wolesensky (31) has shown that this con-

TABLE IX. EFFECT OF PRESENCE OF DIFFERENT NITRATES

(0.01 molar K_2SO_4 , hot precipitation in 5 minutes by 0.05 molar BaCl₂, 5 per cent in excess)

HCl	NO ₃	KNO ₃	NaNO ₃	NH ₄ NO ₃	LiNO ₃	Mg(NO ₃) ₂	HNO ₃
Molarity		Gram	Gram	Gram	Gram	Gram	Gram
Digested 24 Hours Cold							
None	0.01	0.8202	0.8180	0.8195	0.8192	0.8194
None	0.1	0.8204	0.8190	0.8219	0.8301	0.8304
Digested 12 Hours Hot							
0.01	0.01	0.8153	0.8144	0.8148	0.8163	0.8151	0.8154 ^a
0.01	0.1	0.8211	0.8191	0.8188	0.8290	0.8178	0.8196 ^a

^a No HCl added.

verts more than 99.5 per cent. of the barium sulfate to barium carbonate.

The filtrate and washings from this decomposition were neutralized with hydrochloric acid, additional potassium chloride was added, and the solution was made up to standard volume. Aliquot portions were mixed with sulfuric acid and sodium diphenylamine sulfonate, and the color was matched in a colorimeter with standards containing known amounts of potassium nitrate as recommended by Kolthoff and Nojonen (16). The nitrate determined in this way and the potassium removed by one reprecipitation are given in connection with the ignition losses in Table VII.

Qualitative tests were applied to both the first and the latter portions of material removed from contaminated barium sulfate precipitates by the above methods of decomposition. These gave direct confirmation to the belief that contaminating ions are not merely adsorbed on the crystal surface but are distributed throughout the body of the material.

COMPARISON OF POTASSIUM SULFATE WITH OTHER SULFATES. The weights of precipitates obtained from potassium sulfate have been compared under certain conditions with those obtained from sodium sulfate, ammonium sulfate, and free sulfuric acid. The results given in Table VIII show slight differences for the three salts. Since the free sulfuric acid makes the pH of the solution different from that where potassium, sodium, or ammonium salt was used, the results were not strictly comparable. Where hydrochloric acid was added in equal amount to all the solutions, even this difference became small. Since some of the original sulfate is always carried down by precipitated barium sulfate (1), the above differences are to be expected.

EFFECT OF DIFFERENT NITRATES. The effect of potassium on the weight of precipitate is compared in Table IX with that of sodium, ammonium, lithium, and magnesium nitrates,

and with nitric acid. The differences are slight for 0.01 molar nitrate. At 0.1 molar the effect of lithium and magnesium nitrates is more than twice that of the potassium, sodium, and ammonium salts.

PRESENCE OF CHLORIDES. The effect of alkali chloride has been tested under certain of the conditions that gave best results for precipitation in the presence of nitrate. Comparison of Table X with Figure 1 indicates that in the presence of alkali chloride the weight of precipitate is slightly lower (1). This effect is opposite in direction to that of nitrate, and where the two are present the errors partly compensate each other.

Under the conditions indicated by this investigation for the determination of sulfate in the presence of nitrate, the error due to the presence of alkali chloride is as great or greater than that due to the presence of nitrate.

TABLE X. EFFECT OF PRESENCE OF CHLORIDES

HCl Molarity	Barium sulfate precipitated hot in 5 minutes			
	BaCl ₂ to 5 Per Cent in Excess		BaCl ₂ to 50 Per Cent in Excess	
	KCl Molarity	BaSO ₄ Gram	KCl Molarity	BaSO ₄ Gram
	Digested 12 Hours Hot			
None	0.1	0.8153
0.001	0.1	0.8121
0.01	0.01	0.8132		
	0.1	0.8112	0.1	0.8094
	0.1 NaCl	0.8113		
	0.1 NH ₄ Cl	0.8132		
0.001 (+ KNO ₃)	0.1 KNO ₃ }	0.8176
0.01 (+ KNO ₃)	0.1 KNO ₃ }	0.8135	0.1 KNO ₃ }	0.8163
	Digested 24 Hours Cold			
0.01 (+ KNO ₃)	0.1 KNO ₃ }	0.8111

General Discussion

The results in Table VIII indicate that potassium sulfate gives lower results than free sulfuric acid or the sodium and ammonium salts, as Karaoglanow (15) has stated. All the nitrates studied except nitric acid (Table IX) cause high results (8, 15). Lithium (9) is especially bad in this respect and magnesium equally so under certain conditions. Usually the effect of potassium nitrate is slightly greater than that of sodium and ammonium nitrates (5, 15).

These differences and the errors themselves are small for solutions 0.01 molar with respect to nitrate where the precipitate is formed slowly from hot solution in the presence of 0.01 molar hydrochloric acid and digested for 12 hours.

The presence of hydrochloric acid in concentrations between 0.01 and 0.001 molar holds down the effect of concentrations of potassium nitrate up to 0.01 molar, but unless the solution is digested hot, the precipitation is incomplete in this range and this effect increases greatly for potassium nitrate concentrations above 0.01 molar. This may be explained by assuming the presence of a complex ion or compound in the nitrate solution which holds back a part of the sulfate.

The tables and figures indicate that there is a considerable tolerance of nitrates in quantitative barium sulfate precipitation within a certain range of conditions.

Recommended Procedure

For sulfate solutions 0.01 molar or less the solution is made acid between 0.01 and 0.001 molar with hydrochloric acid (1, 10). Barium chloride solution 0.05 molar is added slowly dropwise (about 5 minutes for equivalent amounts) to the hot solution with constant stirring until about 50 per cent excess is

present. The precipitate and solution are kept at about 80° to 90° C. on a hot plate for 12 hours, then filtered through a filtering crucible, washed by decantation and on the filter with 200 to 300 cc. of water, and dried to constant weight at 110° to 120° C. Under these conditions the weight of precipitate is low by 2 to 3 parts per 1000 in the absence of nitrates, 1 to 2 parts per 1000 low in the presence of 0.01 molar nitrate in the original solution, and 1 to 2 parts per 1000 high in the presence of 0.1 molar nitrate in the original solution, and 1 to 2 parts per 1000 high in the presence of 0.1 molar nitrate in the original solution if lithium is absent. The presence of alkali chlorides lowers the weight of precipitate, counteracting the effect of nitrate (15).

Summary

A study has been made of the influence of various factors upon the weight of barium sulfate precipitated from solution both in the presence and in the absence of potassium nitrate.

Evidence indicates the possible existence of a complex ion or complex-compound form of sulfate in potassium nitrate solutions which retards precipitation under certain conditions.

Barium sulfate precipitated from molar potassium nitrate solution carries down potassium nitrate within the precipitate at the time of precipitation. The precipitation is incomplete, however, and if the solution is allowed to stand at room temperature precipitation continues slowly for days with continued contamination of the precipitate. If the solution is kept hot (80° to 90° C.), the slow precipitation observed at lower temperature does not occur.

If potassium nitrate is not added until after precipitation, the precipitate of barium sulfate is not contaminated.

Barium sulfate precipitates formed in the presence of nitrate are more sensitive to influence by variations in conditions of precipitation and treatment than are the precipitates formed in the absence of nitrate.

Information as to the nature and extent of the contamination of barium sulfate precipitates formed in the presence of nitrates indicates that the contamination is distributed throughout the precipitated material.

Under most conditions the presence of potassium nitrate produces high results. This overweight may be as much as 230 parts per 1000 above the value required by theory.

Conditions have been defined within which barium sulfate may be determined quantitatively to a precision of 2 parts per 1000 in the presence of nitrate in amounts equivalent to that of the sulfate present.

The effect of ignition upon precipitates contaminated with potassium nitrate has been studied and losses in weight have been found to increase with increased contamination. The extent of contamination of precipitates has been studied while the contaminants are in their original, unignited form.

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Determination of Copper in Paris Green and Ores

A Ceriometric Method

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THE development of many analytical methods wherein ceric sulfate is used as the standard oxidant has been reported in recent years (5, 6, 7). The progress shown in the past ten years has been due to the production of a better grade of ceric salts, an increased interest in the reagents of higher oxidizing potentials, and the development of suitable indicators for these reagents. Diphenylamine, the first indicator used for ceric sulfate, has largely been replaced by more stable and more sensitive compounds having higher oxidizing potentials, such as *o*-phenanthroline ferrous complex and sodium diphenylamine sulfonate (2, 6, 10). In comparison to the more commonly used oxidants, potassium dichromate and permanganate, ceric sulfate has many distinct advantages (6, 9, 11).

Recently Stegeman and Englis (9) reported a method for determining reducing sugars in which a standard solution of ceric sulfate is used to oxidize the cuprous oxide formed by the action of those sugars on Fehling's solution. It should therefore be possible to make use of this reaction between cuprous oxide and ceric sulfate for the determination of copper in Paris green and ores. The present work is a study of the application of ceric sulfate as a standard oxidant to such a procedure, which also involves the preliminary separation of cuprous oxide free from interfering substances. In the case of Paris green there is sufficient arsenite present to reduce all the copper to cuprous oxide which is insoluble in alkaline solution, but in the case of copper ores not only must any interfering substances, such as iron and lead, be removed, but arsenite must also be added to reduce the copper. In either case the cuprous oxide can be filtered, washed free from excess arsenite, and quantitatively oxidized with standard ceric sulfate solution, using either *o*-phenanthroline ferrous complex or sodium diphenylamine sulfonate as indicator.

Preparation of Solutions

Sodium Hydroxide. A 2 per cent solution.

Sodium Arsenite. Fifteen grams of arsenic trioxide were dissolved in 20 ml. of 6 *M* sodium hydroxide solution, the solution was filtered if not clear, and diluted to 100 ml.

o-Phenanthroline Ferrous Complex. A 0.025 *M* solution obtainable in the regular trade channels (12).

Sodium Diphenylamine Sulfonate. A 0.01 *M* solution prepared in the usual manner from the barium salt (10).

Ceric Ammonium Sulfate. A 0.1 *N* solution made as described by Willard and Furman (12) and standardized against a standard iron ore. A solution of ceric ammonium nitrate may be used as indicated by Smith, Sullivan, and Frank (8).

Ferrous Ammonium Sulfate. A 0.1 *N* solution prepared in the usual manner and standardized against the ceric ammonium sulfate solution at the time of use.

Procedure for Paris Green

An accurately weighed sample of 0.3 to 0.4 gram was transferred to a 400-ml. beaker to which were added 100 ml. of 2 per cent sodium hydroxide solution. The mixture was heated to boiling and stirred until all the green compound was converted into the red cuprous oxide. Normally Paris green contains more than enough arsenite to reduce all the copper to cuprous oxide. If the precipitate should contain any black particles, it should be dissolved in dilute sulfuric acid, 2 to 5 ml. of sodium arsenite solution should be added followed by 6 *N* sodium hydroxide solution until a green precipitate forms, and the mixture should then be heated and digested until only a red or yellowish-red precipitate remains.

After digestion on the hot plate until the supernatant liquid was clear, the solution was filtered cold on a Gooch crucible and the residue on the filter was washed with cold distilled water until the volume of the filtrate was about 250 ml. Since cuprous oxide is slowly oxidized by atmospheric oxygen the filter was not sucked completely dry during the filtration. The crucible containing the residue was placed in the original beaker, an excess of 0.1 *N* solution of ceric ammonium sulfate was added, and the mixture was stirred thoroughly. Excess was indicated by the yellow color imparted to the solution. Special care was taken to disintegrate the asbestos mat thoroughly, heating carefully to boiling and stirring until all the cuprous oxide had dissolved.

To the cold solution 100 ml. of recently boiled and cooled distilled water were added, followed by an excess of accurately weighed ferrous ammonium sulfate or 15 to 20 ml. of a 0.1 *N* solution of the salt. In the presence of excess ferrous ions the yellow color of the solution changed to the pale blue of cupric ions. With either 2 drops of *o*-phenanthroline ferrous complex or 8 drops of sodium diphenylamine sulfonate solution as indicator the excess ferrous ammonium sulfate was titrated with more of the 0.1 *N* solution of ceric ammonium sulfate and the total volume was noted. The volume of ceric ammonium sulfate solution equivalent to the ferrous ammonium sulfate added was calculated, subtracted from the total volume used, and from

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TABLE I. DETERMINATION OF COPPER IN PARIS GREEN

Sample Number	Cupric Oxide Found	Ceric sulfate method	Deviation	Indicator
	A. O. A. C. iodide method			
	%	%	%	
19	24.99	25.03	+0.04	Diphenylamine
20	25.09	25.05	-0.04	Diphenylamine
21	26.42	26.46	+0.04	<i>o</i> -Phenanthroline
22	27.38	27.35	-0.03	Diphenylamine
23	30.45	30.50	+0.05	Diphenylamine
24	30.91	30.92	+0.01	Diphenylamine
25	29.81	29.78	-0.03	<i>o</i> -Phenanthroline
26	29.98	29.94	-0.04	Diphenylamine
27	29.93	29.89	-0.04	<i>o</i> -Phenanthroline
28	49.41	49.40	-0.01	<i>o</i> -Phenanthroline
29	29.79	29.80	+0.01	<i>o</i> -Phenanthroline
30	30.13	30.12	-0.01	<i>o</i> -Phenanthroline

TABLE II. DETERMINATION OF COPPER IN ORES

(Indicator, *o*-phenanthroline ferrous complex)

Sample Number	Copper Found		Deviation
	Iodide method	Ceric sulfate method	
	%	%	%
1	3.03	3.04	+0.01
2	3.94	3.89	-0.05
3	5.37	5.32	-0.05
4	6.27	6.22	-0.05
5	7.27	7.29	+0.02
6	15.02	15.02	0.00
7	14.36	14.39	+0.03
8	13.23	13.22	-0.01
9	22.31	22.35	+0.04

the remaining volume the percentage of copper as cupric oxide was calculated.

Procedure for Copper Ores

An accurately weighed sample of 0.25 to 1 gram, depending upon the copper content, was transferred to a casserole and warmed on the hot plate with a mixture of 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid for at least half an hour. With sulfide ores any small globule of melted sulfur which formed a dark lump on solidification was removed and washed and then ignited in a crucible. The dark residue was dissolved in nitric acid and the solution was rinsed into the main solution.

After the addition of 5 ml. of concentrated sulfuric acid the mixture was carefully heated until dense white fumes of sulfur trioxide were evolved. The copper sulfate in the residue was dissolved by warming with 25 ml. of water. To the cooled solution an excess of 15 *N* ammonium hydroxide was added with thorough stirring to precipitate the iron as ferric hydroxide and to convert the copper into the deep blue soluble complex.

The mixture was filtered into a 400-ml. beaker and the residue on the paper was washed with 3 *N* ammonium hydroxide until the washings came through colorless. By means of a stream of water from the wash bottle the residue was rinsed back into the casserole and just enough concentrated sulfuric acid was added to dissolve the iron precipitate. Ferric hydroxide was then reprecipitated by slowly adding 15 *N* ammonium hydroxide until the solution was basic after thorough stirring. With bits of filter paper added to hasten filtration, the solution was filtered through the original paper and the residue was washed with 3 *N* ammonium hydroxide until the volume of the combined filtrates was about 250 ml. This method of double precipitation of the iron, which is also used in the colorimetric determination of copper with ammonia (3), is more accurate, more conveniently carried out, and much more rapid than the process of precipitating the copper by aluminum strips as originally done in the iodide method for copper. According to Heath (3), results with samples containing from 25 to 35 per cent of iron and aluminum oxides showed never more than 0.04 per cent of copper in the residue on the filter after the second precipitation and sometimes no copper at all.

After the addition of glass beads to the filtrate to lessen the danger of bumping, it was carefully evaporated to about 100 ml. to remove excess ammonia. The solution was then boiled with 10 ml. of 6 *N* sodium hydroxide solution until black cupric oxide precipitated and the supernatant liquid was colorless, using more sodium hydroxide if necessary. The black precipitate was dissolved in dilute sulfuric acid, 2 ml. of sodium arsenite solution were added, the solution was diluted to about 100 ml., and 6 *N* sodium hydroxide solution was added as long

as any yellowish green precipitate was formed. This mixture was heated to boiling and stirred to convert the precipitate into the red cuprous oxide. From this point the same procedure was followed as for Paris green above. This precipitate is likely to be more flocculent and more yellowish red than that from Paris green. To ensure successful filtration it should be digested a longer time than in the case of Paris green, and for thorough washing a much larger amount of water should be used.

Results

The results of the determination of copper in twelve samples of Paris green and nine ores are shown, respectively, in Tables I and II, which also include for comparison the figures obtained by the iodide method (1, 4). Each result is the average of duplicate determinations.

Discussion

Commercial Paris greens were used with the exception of No. 28, which was a sample of cupric arsenite requiring the addition of sodium arsenite to cause complete reduction of the copper to cuprous oxide.

The ceric sulfate method is capable of giving results for copper in Paris green and ores which are within ± 0.05 per cent of those obtained by the iodide method. Results may be duplicated on the same sample with a precision of ± 0.10 per cent.

Summary

A method has been developed for the use of ceric sulfate as the standard oxidant in the determination of copper in Paris green and in ores and the results have been favorably compared with those obtained by the iodide method.

The advantages of the ceriometric method over the iodide method are: It is more rapid and much less tedious, as fewer steps are involved; in the titration the end point is much more easily detected because of the distinct change in color; the solutions of the indicators, *o*-phenanthroline ferrous complex and sodium diphenylamine sulfonate, are stable for many months in contrast to the unstable starch solution; and although ceric sulfate is generally regarded as being somewhat expensive, the cost of the amount used in a determination is less than that of the potassium iodide required in a determination by the iodide method.

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Determination of Strontium in the Presence of Calcium

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FOR some years a study has been under way in these laboratories involving the preparation of various alkaline earth salts with the help of organic solvents (2, 4, 7, 9, 10, 11, 14). For this work, accurate analysis of strontium salts in the presence of calcium compounds was necessary.

Many methods have been suggested for the separation of strontium from calcium, which is made difficult by the small differences in the solubilities of the salts of the two metals. To increase the solubility the use of certain solvents other than water has been recommended. Browning (3) found that calcium nitrate is completely soluble in amyl alcohol while strontium nitrate is practically insoluble. Fresenius (6) separated the nitrates of barium and strontium from calcium by using a mixture of ether and ethyl alcohol. Rawson (8) separated calcium nitrate from strontium and barium nitrates by means of concentrated nitric acid, in which calcium nitrate is soluble. Treadwell and Hall (12) offer a procedure for the analysis of alkaline earth metals in which calcium nitrate is dissolved by absolute alcohol while the nitrates of barium and strontium remain undissolved.

TABLE I. SOLUBILITIES OF NITRATES OF CALCIUM AND STRONTIUM

Solvent	(Per cent of salt in solution at 25° C.)	
	Sr(NO ₃) ₂	Ca(NO ₃) ₂
Ethyl alcohol	0.02	52.0
Propyl alcohol	0.02	36.5
Isobutyl alcohol	0.01	25.0
Amyl alcohol	0.003	13.3
Acetone	0.02	58.5

Ans and Siegler (1) present a comparison of the solubilities of the nitrates of strontium and calcium in different solvents. From their data, which were obtained from studies by Eidman (5) and are only semiquantitative in character, ethyl, propyl, isobutyl, and amyl alcohols and acetone may be selected as suitable solvents to use in the separation of calcium nitrate from strontium nitrate. The quantitative effects of these solvents are shown in Table I, taken from an article by Williams and Briscoe (13).

TABLE II. SEPARATION OF STRONTIUM NITRATE FROM CALCIUM NITRATE BY ACETONE

Strontium Nitrate Taken Grams	Calcium Nitrate Added Grams	Strontium Nitrate Recovered Grams	Recovery %
1.5000	0.10	1.4981	99.88
2.0000	2.00	1.9977	99.89
1.0010	0.50	1.0008	99.98
1.5001	0.50	1.4996	99.97
2.0006	0.50	1.9999	99.97

Because of the usual difficulty in making this separation, an outline of the procedure which the authors have used may be of interest. This is based on the observation of Williams and Briscoe (13), that at 25° C. strontium nitrate is only 0.02 per cent soluble in acetone while calcium nitrate dissolves in acetone to the extent of 58.5 per cent.

Since acetone appeared to be favored for the separation of calcium nitrate from strontium nitrate, quantitative data were obtained. Weighed amounts of strontium nitrate and calcium

nitrate were dissolved in water, 2 ml. of concentrated nitric acid were added, the solution was evaporated to dryness on a steam hot plate, the mass was allowed to cool, and 25 ml. of acetone were added. The acetone was allowed to remain in contact with the solid for one hour with occasional shaking. The undissolved portion was transferred to a weighed Gooch crucible, washed with acetone, and weighed as Sr(NO₃)₂. The results are shown in Table II.

The following method, which proved convenient and accurate, was evolved from the above:

A synthetic mixture of strontium chloride with calcium chloride and calcium sulfate was extracted with methanol, filtered, and made up to exactly 250 ml. with distilled water. The extract contained strontium chloride and calcium chloride, since calcium sulfate is insoluble. Calcium sulfate was added to the synthetic mixture because in the analysis for which this method was desired calcium sulfate was present. Fifty milliliters of the extract were pipeted into a 250-ml. beaker and warmed to 50° C. on a steam hot plate, and 10 ml. of freshly prepared ammonium carbonate solution were added slowly. This converted the strontium chloride and calcium chloride into the corresponding insoluble carbonates which were left on a hot plate for 10 minutes, then allowed to cool.

The mixed carbonates were filtered into a Gooch crucible, then dissolved in dilute nitric acid. This gave an aqueous solution of the mixed nitrates which was evaporated to dryness on a steam hot plate. After cooling, 25 ml. of anhydrous acetone were added and left in contact with the mixed nitrates for one hour with occasional agitation. The acetone dissolved all the calcium nitrate and left the strontium nitrate, quantitatively. The strontium nitrate was transferred to a weighed Gooch crucible, washed with more acetone, dried in an oven, and weighed.

TABLE III. SEPARATION OF STRONTIUM CHLORIDE FROM CALCIUM CHLORIDE

(Using the procedure outlined above. The following are blanks.)

Strontium Chloride Centimoles	Calcium Chloride Centimoles	Calcium Sulfate Centimoles	Strontium Recovery %
1.000	0.500	1.000	99.7
1.000	0.500	1.000	99.9
1.000	0.500	1.000	99.7
1.000	1.000	1.000	99.9
1.000	1.000	1.000	99.8

Blanks run on synthetic mixtures according to the above procedure gave results varying from 99.7 to 99.9 per cent recovery, as detailed in Table III.

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Electrometric Indicators with the Dead-Stop End-Point System

Applications to Neutralization and Precipitation Reactions

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IT HAS been suggested by Foulk and Bawden (2) that the dead-stop electrometric indicator system is applicable to neutralization reactions as well as to oxidation-reduction reactions, and a slightly modified system of polarized platinum-platinum electrodes has been described by Wright and Gibson (4).

In the present work the suggestion of Foulk and Bawden with regard to neutralization reactions has been extended to include precipitation reactions. A procedure is described for the use of substances to obtain an electrometric end point in titrations by the dead-stop end-point system in those cases in which an end point is otherwise not given. The name "electrometric indicator" is proposed for such substances, as their role in electrometric titrations is analogous to that of color indicators in volumetric analysis. Willard and Fenwick (3), the first to give an example of such an indicator, found that the addition of hydrogen peroxide to acid or alkaline solutions gave a sharp, but not permanent, end point in neutralization titrations by their bimetallic electrode system. For a discussion of the apparatus and the essential features of the procedure the work of Foulk and Bawden (2) should be consulted.

Neutralization Reactions

IODATE AND IODIDE AS ELECTROMETRIC INDICATORS.¹ If both iodate and iodide are added to a solution of a base, no reaction takes place but the anode of a polarized electrode system will be depolarized by the reducing action of the iodide. If, now, the base is titrated with acid, a reaction between the iodate and iodide occurs as soon as the pH value becomes slightly less than 7. The trace of iodine liberated depolarizes the cathode. Both electrodes being depolarized, current flows, giving the end point which is registered by the permanent deflection of the galvanometer pointer.

TABLE I. WEIGHT TITRATIONS

(Approximately 0.50 *N* sodium hydroxide with 0.25 *N* hydrochloric acid)

Weight of Alkali Grams	Weight of Acid Grams	Ratio of Alkali to Acid
23.5191	46.8729	20:39.94
20.6122	41.1440	20:39.92
19.9538	39.8288	20:39.92
20.5849	41.0705	20:39.90
19.6670	39.2446	20:39.90

To demonstrate the use of potassium iodide and iodate as electrometric indicators, titrations were made of 25-ml. portions of 0.5 *N* sodium hydroxide with 0.25 *N* hydrochloric acid. An impressed potential of a fraction of a volt was used to balance the e. m. f. of polarization; 10 drops each of 0.1 molar potassium iodate and iodide were added to the alkaline solution.

The resistance was then adjusted so that the pointer of the galvanometer took a position at or near zero. When the volume of the solution added from the buret was within a milliliter or so of the equivalence point, momentary deflections of the galvanometer needle, increasing in intensity, gave warning of the approaching end point, and when the end of the titration was reached the pointer took up a permanent position away from zero. A series of titrations was made by using weighing burets, and completing the titration with 0.0125 *N* hydrochloric acid added from a volume buret, this volume being converted to weight of 0.25 *N* hydrochloric acid. The results are shown in Table I.

¹ The first experimental work with a mixture of iodide and iodate as an electrometric indicator was done at Professor Foulk's suggestion by Henry F. Palmer, a graduate student in the Department of Chemical Engineering in The Ohio State University.

Potentials ranging from 1 to 10 millivolts were impressed during a titration, other conditions being kept constant. Largest deflections at the end point were obtained by employing as large an impressed voltage as possible, and still maintaining a state of balance with the back e. m. f. of polarization.

Simple colorimetric measurements of the amount of iodine set free with various ratios of iodide and iodate were made, using 0.1 molar solutions of potassium iodide and iodate and the same concentrations of acid. It was found, as was expected, that an excess of iodate over the reaction quantity set free a larger amount of iodine. The molecular reaction quantities measured into a color-comparison tube formed the standard by which the colorimetric measurements were made. The intensities of color produced by varying the concentrations of iodide-iodate were then measured. Equimolar concentrations of iodide and iodate liberated the largest amount of iodine with the same pH value.

TABLE II. WEIGHT BURET TITRATIONS

(Approximately 0.5 *N* hydrochloric acid with 0.5 *N* sodium hydroxide)

Weight of HCl Solution Grams	Weight of NaOH Solution Grams	Ratio of HCl to NaOH	Deviation from Average, 10:10.397
12.8684	13.3755	10:10.394	-0.003
21.9421	22.7686	10:10.377	-0.020
5.7419	5.9812	10:10.415	+0.018
10.9194	11.3594	10:10.403	+0.006

Keeping the molecular ratio of iodide-iodate the same, titrations were then made in which the concentration of the iodide-iodate mixture in the titrated solutions was varied in order to find the optimum amount of indicator substance in this ratio to be used in a titration. An amount corresponding to 10 drops each of the 0.1 molar solutions was found to be the most suitable and was therefore used in all titrations.

The pH value necessary to produce the end point was observed to be near the neutral point. That the acidity required to give the dead-stop end point is very slight was proved by results obtained from potentiometric measurements of the pH value of solutions of completed titrations. The average pH value of the solutions was found to be 6.67.

IODINE AS ELECTROMETRIC INDICATOR. The iodate-iodide mixture described above will not work in acid solution because the two substances react; therefore another indicator was sought. Iodine was found to serve the purpose. When added to an acid solution, it keeps the cathode depolarized but has no effect on the anode. On titration, the first excess of alkali reacts with the iodine to form a trace of iodide which then depolarizes the anode. This permits a flow of current which registers on the galvanometer, thus giving the end point. A 3 per cent alcoholic solution of iodine in alcohol was used for the indicator substance in the titrations of acids with bases. Experiments showed that 2 drops produced a maximum decrease in the polarization potential of the cathode. This amount of the iodine indicator was then used in the subsequent titration.

A series of titrations was made with approximately 0.5 *N* hydrochloric acid and sodium hydroxide using volume burets, and finally, to prove the precision of the method, with weight burets. Table II gives these latter results. The

end point coincides with the color changes of dibromothymolsulfonphthalein.

The titration of a strong acid with a weak base, such as hydrochloric acid with ammonium hydroxide, gave a reproducible end point. Two drops of iodine indicator were used. The end point was sensitive and coincided closely with the color change of phenol red.

HYDROGEN PEROXIDE AS ELECTROMETRIC INDICATOR. Experiments showed that hydrogen peroxide is an admirable indicator for titrations with both acids and bases, its action depending on the sharp difference in its reduction potential in acid as compared with that in alkaline solutions. In alkaline solutions the degree of polarization of the anode is low and that of the cathode high. As the equivalence point is approached in the titration of bases with acids, this difference in degree of polarization of the two electrodes increases, and at the equivalence point the increase is sharp; the anode becomes completely polarized and the depolarization of the cathode is increased. These two effects are additive, which makes the end point as registered by the galvanometer all the sharper. On titrating an acid with a base, the above conditions are reversed. Hydrogen peroxide, therefore, is a reversible electrometric indicator for the dead-stop end-point system, in which it differs from the iodate-iodide mixture and the iodine.

TABLE III. WEIGHT BURET TITRATIONS

(Approximately 0.5 *N* hydrochloric acid with 0.5 *N* sodium hydroxide)

Weight of HCl Solution Grams	Weight of NaOH Solution Grams	Ratio of HCl to NaOH	Deviation from Average, 10:10.393 ^a
10.5835	10.9800	10:10.375	-0.018
12.4222	12.9415	10:10.418	+0.025
10.9563	11.3750	10:10.382	-0.011
16.8931	17.5637	10:10.397	+0.004

^a Average ratio of HCl to NaOH using I₂ as the indicator, 10:10.397 (see Table II).

Hydrogen peroxide is unique in its action as an indicator substance because it may be used in either acid or alkaline solutions. The same experimental conditions governing titrations with the iodide-iodate indicator were found to apply to the titrations with peroxide. The indicator used was the ordinary 3 per cent commercial solution which had been neutralized with sodium hydroxide. By experimentation it was found that 4 drops of this solution was the optimum amount to use in the titrations of acid with base. Table III gives results by this method.

Precipitation Reactions

NITRITE AS ELECTROMETRIC INDICATOR. The scheme of electrometric analysis as described for neutralization reactions may with appropriate indicators be applied to titrations of the halides and cyanides with silver nitrate. The apparatus is identical with that for neutralization titrations.

The general conditions that obtain when one attempts to titrate the halides with silver by the dead-stop end-point system are the same as those in neutralization reactions—that is, no end point is given. In a search for an indicator it was found that sodium nitrite served to keep the anode depolarized during the titrations; therefore, it was used as the indicator in all cases save those of iodides and cyanides which are themselves anodic depolarizers. Silver ions serve to depolarize the cathode at the equivalence point, and a sharp reproducible end point is obtained.

That the action of silver ions at the cathode is responsible for the end point was proved by segregating the electrodes by means of a salt bridge and then studying the action of silver nitrate, sulfate, and acetate on the cathode and anode separately. In no case did the addition of a silver salt affect

the anode, while each of the above-named salts produced a reduction of potential at the cathode.

As an explanation of the phenomena at the cathode, it is assumed that the cathode during the titration has atomic hydrogen adsorbed on its surface, not as a static layer but in equilibrium with hydrogen ions in the solution. At the equivalence point there is a sudden increase in the concentration of silver ions, which tend to discharge on the cathode at a lower potential. A new system of lower equilibrium potential is thereby established—namely, that between silver and silver ions. The cathode acquires the electromotive characteristics of a silver electrode, although there is no visible deposit of that metal.

TABLE IV. WEIGHT TITRATION

(Approximately 0.1 *N* potassium iodide with 0.1 *N* silver nitrate)

Weight of AgNO ₃ Solution Grams	Weight of KI Solution Grams	Ratio of Weights of Solutions, AgNO ₃ :KI
22.1525	21.5623	1.0278
15.9615	15.5150	1.0283
11.9770	11.6480	1.0284
11.3260	10.9970	1.0290
19.2619	18.7355	1.0281
		Av. 1.0285

To prove that the end point coincides with the equivalence point, two portions of the filtrates from several completed titrations were tested by adding 0.1 *N* silver nitrate solution to the one portion and the same volume of 0.1 *N* sodium chloride solution to the other. The turbidities were then compared. The tubes containing the excess chloride showed only a slightly greater turbidity than those with the excess of silver, proving that only a very small excess of precipitant is necessary to give the end point.

The optimum amount of nitrite indicator substance to be added was established by measuring the cell potentials after the addition of a 0.1 *N* sodium nitrite solution to be titrated. The amount which was most effective in depolarization of the anode was found to be 2 drops of 0.1 *N* solution.

A test was made to find the minimum concentration of silver ions that would produce a sharp end point. Twenty-five milliliters of 0.1 *N* sodium nitrate solution were diluted to 100 ml. in the titration vessel, this being the quantity of electrolyte present at the end of a typical titration. The addition of one drop of 0.001 *N* silver nitrate to this sodium nitrate solution gave a sharp end point.

Typical titrations were run with the same volume of reagents but varying the alkalinity by adding different volumes of 0.1 *N* sodium hydroxide solution, keeping the pH value below 8.5, above which value silver oxide is supposedly formed. Making the solution slightly alkaline gives a more sensitive end point, decreasing the degree of reversibility of the electrode reaction. Effects of varying pH values on the acid side were observed by adding increasing volumes of 0.1 *N* nitric acid and finally more concentrated reagent. As the acidity of the solution was increased, the end point became more sluggish but was still reproducible.

The reproducibility of the end point is very high, owing to the large galvanometer deflections produced at the equivalence point. There is no difference in the degree of reversibility of the electrode reaction before and after the end point. That the end point is reproducible with a high degree of precision is indicated in Table IV.

Mixed Halide and Cyanide Determinations

Following a suggestion from the method of Behrend (1), a successful attempt was made to titrate mixtures of chloride and iodide, and of bromide and iodide. Addition of sufficient ammonium hydroxide kept the chloride or bromide in solution

in the form of the ammonia complex until the first drop in potential indicated the complete precipitation of iodide. The solution was then neutralized with nitric acid and the titration continued until the second drop in potential occurred, corresponding to the complete precipitation of chloride or bromide. Excellent results were obtained.

In following up the possible uses of silver nitrate with the dead-stop end point, potassium cyanide was titrated with interesting results. This salt was found by experiment to be an anodic depolarizer like potassium iodide and sodium nitrite, which makes it unnecessary to add an indicator. In titrating potassium cyanide, two galvanometer deflections are produced which correspond quantitatively to the complete formation of $KAg(CN)_2$ and $Ag_2(CN)_2$, respectively. When 0.1 *N* silver nitrate is used as the titrating agent, the galvanometer deflection produced at the potassium argenticyanide equivalence point is only a flash, the light spot returning immediately to zero, but the deflection is very pronounced, going the full galvanometer scale, so that results are very readily reproduced. The second deflection corresponds to the complete precipitation of silver cyanide. A tentative explanation of the two end points produced is based on the assumption that the lag between complete formation of the silver cyanide complex and the beginning of precipitation of the silver cyanide is sufficient to furnish a concentration of silver ions which will momentarily depolarize the cathode.

Experiments in which 25 ml. of approximately 0.1 *N* potassium cyanide were titrated with 12.9 ml. of 0.1 *N* silver nitrate at the potassium argenticyanide equivalence point

gave 25.75, 25.85, 25.80, 25.65, 25.80, and 25.80 ml. of total silver nitrate.

Summary

This paper describes a simple and accurate method for the electrometric titration of acids, bases, halides, cyanides, and silver ions. Results are as highly reproducible as those obtained by the present accepted methods of electrometric analysis. The method has the advantage of using two simple platinum wire electrodes, and it eliminates the use of a reference electrode. The electrodes are seldom, if ever, poisoned, which removes the difficulty in the use of certain other electrode systems. Adequate warning of the approach of the end point is given by momentary deflections of the galvanometer pointer. Since the end point is reversible, back-titration is possible.

Titrations of copper, mercury, and other metallic ions should be possible by the same principle employed in the titrations of silver ions. This opens a new field for the volumetric determination of the metallic ions with a low deposition potential.

The titration of zinc with ferrocyanide should be investigated, because the ferrocyanide would serve as an anodic depolarizer.

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Preparation of Carbon Electrodes for Spectrographic Analysis

Two Useful Lathe Tools

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THE exposure time for complete volatilization of a sample of plant ash in spectrographic analysis is dependent, among other factors, on the depth of the cavity drilled in one end of an electrode to receive the sample, and on the thickness of the crater wall. The diameter of the carbon rods used in this study is 8 mm. (0.3125 inch). A cavity size which has proved suitable in this work has the following dimensions: inside diameter, 6 mm. (0.25 inch); depth, 3.5 mm. This crater will hold 10 to 25 mg. of dried plant material or 0.1 ml. of liquid. A wall thickness of 0.3 mm. is a good compromise. Using electrodes of the above dimensions (with a 15-ampere and 150-volt current) pointed upper electrodes (8-mm. rods pointed in a pencil sharpener) and an arc length of 3.0 mm., the ash in a 10-mg. sample of dried plant tissue is volatilized completely in 60 seconds.

If the wall is too thin, liquid will leak through, and salt will be deposited on the outside of the wall when the solution is evaporated to dryness; if the wall is too thick, the arc will wander and too much time is required to burn the wall down to the cavity floor, which is essential if the last trace of fused ash is to be burned off. Too thick a wall also unduly increases background on the plate. Since in the course of analytical routine, a large number of electrodes are prepared, it is desirable that facing the end of the electrode, drilling the hole,

and cutting down the outside wall be accomplished in one operation.

A tool was made that answers the above specifications. It was designed to produce craters of uniform wall thickness but variable depths by an adjustment of the set screw as is shown in Figure 1.

By machining the outside of the cavity wall, uniformity of thickness is ensured, so that irregularities in graphite electrodes as purchased become unimportant; a long outside cut of 9.5 mm. when the cavity depth is only 3.5 mm. has the advantage of the smaller diameter 6-mm. (0.25-inch) electrode. It will be noted from Figure 1 that the angle on the cutting edge of the bit has been reduced, so that the depression in the floor of the cavity is comparatively slight. This ensures a rapid cleanup of traces of the ash residue when the wall has burned down to the floor.

In spectrographic determination of mercury in plant tissue the authors found that a more intense mercury line is produced at 2536.7 Å. by using an unusually deep electrode cavity (about 15 mm.). With the use of 8-mm. electrodes, pointing the wall at the top serves to prevent arc wandering during the short exposure needed to volatilize the mercury present. A tool designed to perform the operations of drilling and pointing, simultaneously, is shown in Figure 2. It

consists of a standard 6-mm. twist drill and a steel collar with a set screw on which projects a cutting edge at a suitable angle (about 20°). The depth of the cavity here again can be varied by merely sliding the collar along the drill and tightening the screw.

Also, a good drill press combined with an electrode-holding device (chuck, collet, etc.), attached firmly to the bed or base plate, can be substituted where a lathe is not available. For successful production of this thin-walled cavity, both tool and carbon electrode must be held immovable as in a chuck or collet.

Performance has demonstrated that the use of these tools makes possible rapid preparation of electrodes with the desired uniformity of dimensions. Electrodes can easily be produced at the rate of two a minute. The tools should be operated at a minimum speed of 1300 r. p. m.; at slower

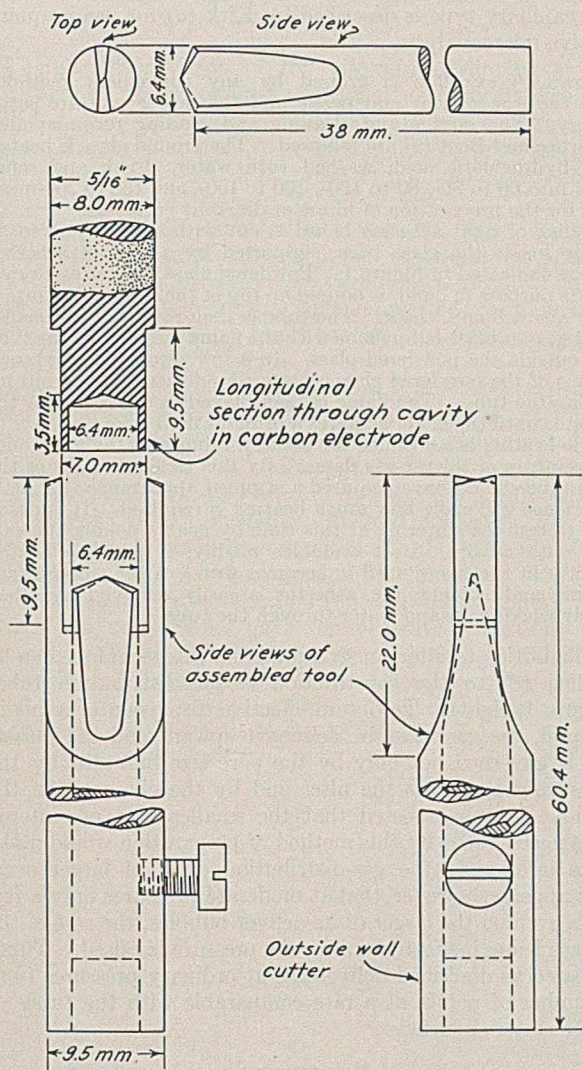


FIGURE 1. CARBON DRILLING AND CUTTING TOOL DRILL BIT

The tools should be made of tool steel and tempered to keep an edge on the cutting parts. Any good tool steel will be satisfactory, but must be protected against corrosion under high humidity conditions by storage in a desiccator or by wrapping in an oiled cloth.

Suitable alterations in the given dimensions will permit the use of these designs for producing cavities on electrodes of different diameter than the one the authors are using, and will give different wall thicknesses to suit the requirements of any special material.

The electrodes are machined in a small bench lathe in the laboratory. The carbons are allowed to revolve held in a collet on the headstock end, while the tool is fastened in a chuck in the tailstock. This lathe is kept clean and is reserved for the production of electrodes. With a suitable lathe and equipment the procedure can be reversed, with a resultant increase in the number of electrodes produced.

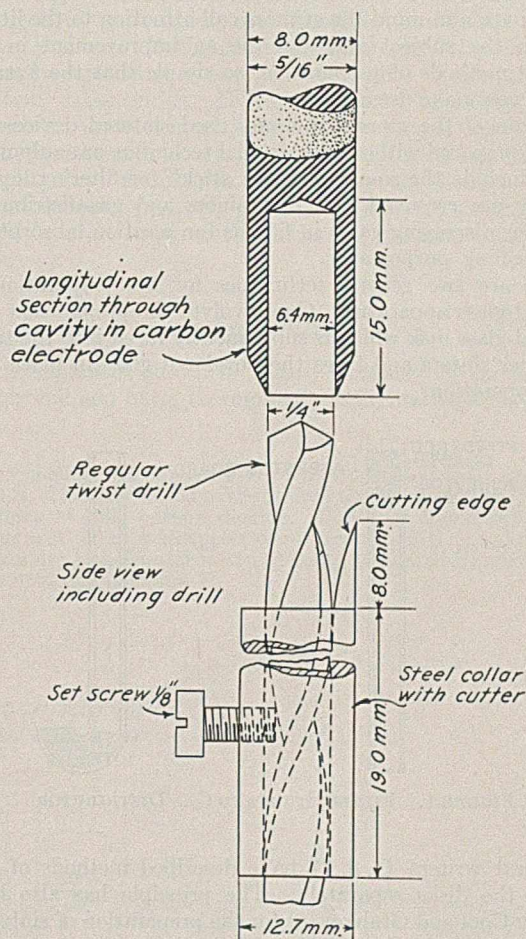


FIGURE 2. CARBON DRILLING AND POINTING TOOL

speeds breakage of the electrode wall is apt to occur. It was pointed out to the authors that this type of tool is less subject to borrowing than the ordinary drills, therefore the contamination danger is avoided.

Acknowledgment

Acknowledgment is hereby made of the help of Leonard Smith of the Bendix Corporation who made the experimental models for this study.

Sintered-Glass Filters and Bubblers of Pyrex

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SINTERED- or fritted-glass filters and gas distributors have come into general use during recent years (10). Their manufacture is covered by the patents of Schott and Gen., Jena, Germany, who offer an extensive line of fritted-glass filters in the Jena glass (9). Because of the difficulty of sealing the sintered equipment of Jena glass with the borosilicate glass so widely used in this country, workers have made their own sintered Pyrex in various ways. With this situation in mind the authors call attention to the literature on the subject and describe an improvement in the existing methods of preparation, so simple that the average worker can make use of it.

Certain of the more commonly used sintered devices are readily prepared without any special technique or equipment. These include the so-called "filter stick" for filtering liquids as they are removed from containers and gas-distribution tubes for dispersing gases in liquids for aeration, absorption, and washing purposes.

There are two general techniques for the preparation of sintered-glass apparatus. One involves the preparation of a sintered-glass disk which is subsequently fused into the tube; the other sinters and fuses the powdered glass in place in a single operation.

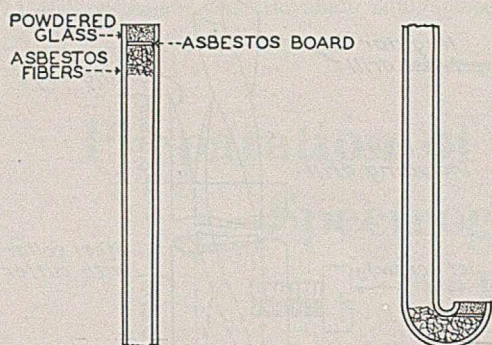


FIGURE 1. FILTER STICK AND GAS DISTRIBUTOR

Several writers (1, 2, 7) have described methods of preparing the disks separately. The principle has also been used by Cool and Graham (3) for the preparation of sintered-glass aeration thimbles. The chief advantage of preparing the disks separately lies in the fact that larger and more uniform disks may be prepared. Its disadvantages are that more elaborate apparatus, greater skill, and a longer time are required.

The second technique, in which the powdered glass is sintered and sealed in place in a single operation, has several modifications. Shatenshtein (11) holds the powdered glass in the tube with carbon rods and sinters in a blast-lamp flame. Kirk (5) places the powdered glass in a small bulb at the end or side of the tube for sintering and then exposes the sintered surface by grinding.

Furnstal and Johnson (4) make use of both techniques and recommend methods involving the use of a temperature-controlled muffle furnace. This is very satisfactory for those who have a large number of sintered-glass devices to prepare, but the equipment and technique are unnecessarily involved for the needs of the average chemist.

The authors have developed a very simple method for preparing sintered-glass plugs in the ends of tubes which satisfy many of the sintered-glass laboratory requirements.

It has been used successfully on tubing up to 10 mm. in outside diameter and on capillary tubes by flaring the ends. The capillary type is described by Kirk (6) for use in quantitative microanalysis.

Scrap Pyrex glass is ground by any convenient method; both the iron mortar and pestle and the power mill are satisfactory. The methods of cleaning and grading recommended by Bruce and Bent (2) are followed. The ground glass is heated with hydrochloric acid, washed with water, dried, and separated into 60 to 80-, 80 to 100-, 100 to 150-, and 150 to 200-mesh sizes for the preparation of filters of different porosities.

A disk of light asbestos board is cut with cork borers to fit snugly inside the glass tube, supported by a wad of asbestos fiber as indicated in Figure 1. Powdered glass, of a size selected for the purpose in hand, is poured on top of the asbestos to form a layer about 5 mm. thick. The tube is then rotated in a needle-point gas-air blast-lamp flame with the flame directed on the tube just outside the powdered glass. In a few seconds the exposed surface of the powdered glass is sintered sufficiently to permit inverting the tube. The flame is then played in the region of the asbestos until the latter acquires a brilliant flesh color.

The heating is continued for about a minute at the maximum temperature of the air-gas flame. By this time the walls of the glass tube should have acquired a stippled appearance. A little experience will show how much heating is required. It is desirable to test the sintering at this time by gently poking the surface with a wire. If it crumbles readily, it may be heated directly in the flame until it becomes firm. After suitable annealing and cooling, the asbestos is easily removed by alternately sucking air and water through the tube.

In addition to filters in straight tubes this technique can be applied (8) to the construction of gas-distribution tubes (Figure 1, right). To obtain effective dispersion of a gas in a liquid, the gas must be delivered upward and the bubble size is governed not only by the pore size but also by the pressure drop across the filter and by the character of the liquid. It was expected that the smaller area of sintered glass necessitated by this method of preparation would make disks inferior to the gas-distribution disks of larger area.

It appears, however, that at moderate pressures only a few spots even on the larger disks deliver bubbles, the rest of the surface being ineffective unless the pressure is raised. Tubes prepared as described deliver gas at ordinary pressures from a number of points at a rate comparable with the tubes of larger sintered surfaces.

Summary

Although sintered-glass filters have many applications, their use has been limited by the lack of a commercial supply in the borosilicate glass and of adequate directions and facilities for making them. This paper presents a technique for sintered-glass preparation, requiring a minimum of skill and equipment.

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Thermostatic Bath for Low-Temperature Viscosity Determinations

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THE determination of the viscosity of liquids at low temperatures presents a number of mechanical difficulties which cannot be overcome without the use of elaborate setups. The main sources of error are due to poor temperature control and also, if a pressure instrument is used, to difficulties in maintaining constant pressure. Since the viscosity of fluids increases very rapidly with decreasing temperature, the importance of proper control of temperature is evident in order to avoid large variations in results. Moreover, such close temperature control must be maintained for much longer periods of time, particularly when using viscometers of the capillary type.

The viscosity of lubricating oils at low temperatures has been determined by a number of authors, in particular Okochi and Majima (7), Schlenker (8), Tonomura (12), Tausz and Mellner (11), Ferry and Parks (2), Tanaka, Kobayasi, Tsukuda, and Ono (10), FitzSimons (3), Ivanov and Gutzeit (5), Jordachescu (6), and Schwaiger (9). In general either no data were furnished on the accuracy of the temperature control or such control was limited to $\pm 0.5^\circ\text{C}$., which is too wide a variation for precise measurements. The FitzSimons apparatus gave temperature variations not exceeding 0.01°C . by circulating ethyl alcohol at -60°C . in a copper coil inserted in a Dewar flask containing ethyl alcohol. The desired temperature was then obtained by heating the bath with an immersion electric heater, the cur-

rent being controlled by means of a mercury thermoregulator connected to a vacuum tube relay. No description of the bath used for cooling the circulating alcohol was given.

The work of the above investigators shows that the determination of low-temperature viscosities is a fairly complicated problem. Such determinations are therefore not generally considered a part of the routine of petroleum inspection laboratories. However, special problems often require the use of viscosity data at low temperatures and to meet this demand a setup capable of furnishing accurate data at short notice was designed by the authors. This setup has been found very satisfactory and, for this reason, it should be of interest to other laboratories engaged in similar work.

Apparatus

The apparatus shown in Figure 1 consists of three parts: cooling coil and bath, thermostatic bath, and viscometer and bath.

The cooling coil, *C*, consists of a copper coil immersed in a bath, *B*, of alcohol cooled to the desired temperature by occasional additions of solid carbon dioxide. Coil *C* is connected to the cooling coil, *D*, of a Hoyer ultrathermostat, *H* (4), the liquid (a suitable alcohol-water mixture) being circulated by means of a small centrifugal pump, *P*.

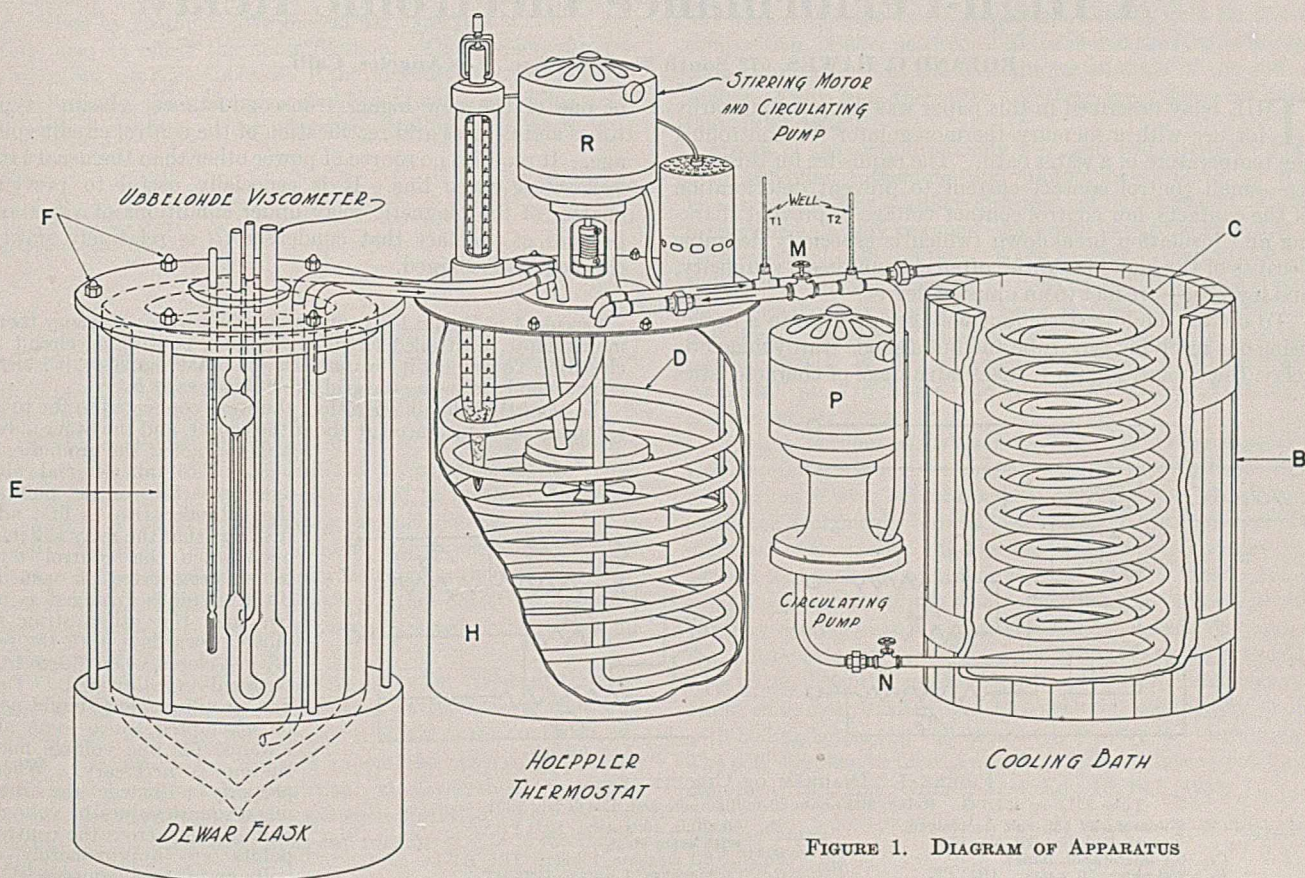


FIGURE 1. DIAGRAM OF APPARATUS

Bath *E* is an unsilvered Dewar, of 10-liter capacity, covered with a grooved hard-rubber head surmounted by a brass plate held firmly by means of the rods and bolts, *F*. A tight joint is obtained by inserting a rubber gasket in the groove of the hard-rubber head. The brass cover is provided with a tapered hole through which a Ubbelohde viscometer (13) held by a rubber cork is inserted. The viscometer is calibrated in accordance with A. S. T. M. procedure (1). Baths *B* and *H*, as well as all connecting lines, should be heavily insulated with cork in order to prevent moisture condensation.

The Hoespler falling-ball viscometer (4) can be substituted for bath *E* for temperatures above 0°, but cannot be used for temperatures much below 0°, because of frost formation on the surface of the outer jacket. For this reason, a Dewar bath is more preferable.

In carrying out a determination, bath *B* is filled with either alcohol or acetone (isopropyl alcohol being very convenient); and a suitable water-alcohol mixture is introduced through cock *M* into the cooling coil system as well as into baths *H* and *E*. The freezing point of the alcohol-water mixture must be at least 20° C. below the desired viscosity temperature. The viscometer is then inserted in bath *E*, the thermostat is plugged in, and circulation pumps *P* and *R* are started. The alcohol in bath *B* is rapidly cooled by additions of solid carbon dioxide to the desired temperature. In general, it is necessary to maintain the coil temperature about 8° to 10° C. lower than the temperature desired in bath *E* in order to obtain the best thermostatic control with the Hoespler apparatus. This can be accomplished by regulating the addition of solid carbon dioxide so as to maintain the temperature of bath *B* about 10° lower than that of the coils. Still better procedures consist of regulating the circulation rate by means of a rheostat attached to the motor, or adjusting the pressure by means of stopcocks *M* and *N*. The temperatures of the incoming and outgoing fluids are read by means of thermometers *T*₁ and *T*₂—for example, if a temperature of -10° C. is desired in bath *E*, the coil temperature must be about -18° to -20° C. and bath *B* about -30° C.

Under the above conditions, the thermostat is capable of temperature control within ±0.03° C. in bath *E* as read with a Leeds & Northrup Type 8662 potentiometer.

The thermostat is generally supplied with a mercury regulator for temperatures down to -25° C. For lower temperatures the authors have replaced this mercury control with a Burling metallic thermostat which has been attached to the Hoespler bath. With this thermostat temperatures as low as -52° C. have been maintained within ±0.03° C. for hours without difficulty. The Burling thermostat used for this work was designed for temperatures of about -60° C.; it did not give such good control around -30° C., the variations being about ±0.1°. In ordering this thermostat the temperature range must be specified for best results.

Acknowledgment

The authors wish to express their appreciation to E. M. Fry and W. J. Troeller of these laboratories for their valuable suggestions.

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A High-Performance Electronic Relay

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THE relay described in this paper was designed primarily for use with a mercury thermoregulator for controlling the temperature of a water bath. The requisites for this service—small control contact current to prevent deterioration of the contacts, low control contact voltage to prevent sparking and insulation breakdown (which is especially desirable because of the high humidities often encountered), simplicity, and low cost—are met to an unusual degree.

To obtain the lowest contact voltages possible in a design using one receiving type tube and but a single sturdy magnetic relay, the circuit, Figure 1, takes advantage of characteristics

of one of the new higher transconductance, "beam" type tubes and utilizes grid rectification of the control circuit voltage. It requires no source of power other than the usual 110-volt single-phase line. It is especially useful to prevent chatter of the magnetic relay under conditions of vibration because of the fact that condenser *C*₁ is relatively slowly charged or discharged.

Circuit *A* of Figure 1 is connected for use with a mercury thermoregulator (controlled circuit open when controlling circuit is closed). To connect it for use with a bimetal regulator, it is necessary merely to rewire the grid circuit leads as at *B*.

To place the relay in operation, the strap connected to the tube cathode should be placed at about the center, and the other movable contact at the ground end of *R*₂. To obtain minimal voltage across the contact points, the cathode strap is first adjusted so that the relay will just open when the control terminals are shorted (or opened, if the circuit is arranged as in *B*), then the other strap is moved towards it until the relay just closes, when the control terminals are opened. Too fine an adjustment should not be attempted, since some allowance for line voltage fluctuation is necessary. When properly adjusted, the root mean square values of voltage and current across the control points are approximately 8 volts and 0.1 milliamperes.

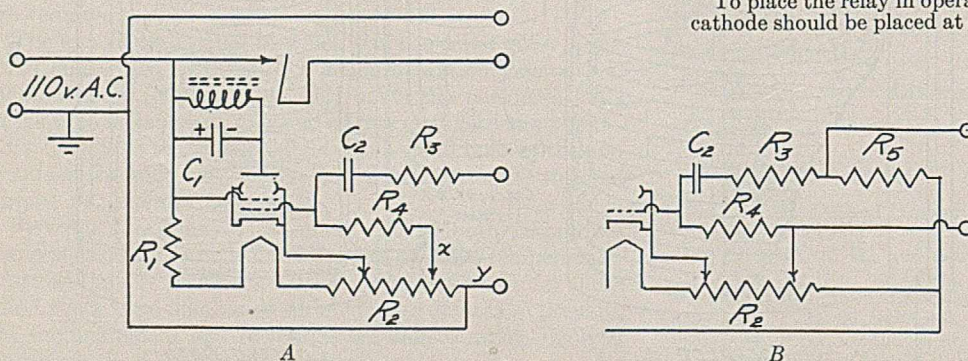


FIGURE 1. DIAGRAM OF CIRCUIT

Tube 25L6 or 25L6-G. Relay, 3000-ohm 20-milliamperes coil, Leach No. 1201

*C*₁. 8-microfarad 150-volt electrolytic, Cornell Dubilier BR No. 875

*C*₂. 0.1 microfarad, paper

*R*₁. 250 ohms, 50 watts; IRC PE

*R*₂. 50 ohms, 10 watts; IRC PBA,

with extra strap

*R*₃, *R*₄. 0.1 megohm, 1 watt; IRC BT-1

*R*₄. 1.0 megohm, 1 watt; IRC BT-1

If the relay performs erratically, which it may if long unshielded leads go to the control contacts, the values of R_3 , R_4 , and R_5 may be changed to one tenth of those shown, and C_2 increased in the same ratio. The current through the control contacts then becomes 0.8 milliamperes.

It is important that the grounded side of the line be connected as shown. If one side of the regulator is grounded, it must obviously be connected to the same point. A mercury regulator is preferably connected so that the lead which remains in contact with the mercury when the mercury column falls is on the grounded side. One side of a bimetal regulator, or other controller requiring the relay to make the control contacts close, may be grounded only if a break-when-energized relay is used in circuit *A*.

A 50-watt light globe may be substituted for R_1 , but it is not recommended because the first cost is only a few cents less, and the resistor is more dependable.

If a quicker acting relay is wanted, condenser C_1 may be changed to the smallest value which will keep the relay from buzzing (about 1 microfarad), condenser C_2 shorted out in circuit *A*, and the straps readjusted on resistor R_2 . With these changes the circuit becomes nearly identical with one described by Hersh, Fry, and Fenske (1), except for the use of the beam power tube and of resistor R_3 to limit the current of the control grid during the part

of the cycle when it is positive with respect to the cathode. This modification is suitable for use on direct current power lines, but for alternating current use it imposes about twice the voltage across the regulator contacts for any particular plate current requirement. This circuit may be used with a bimetal regulator by interchanging the grid leads at points *x* and *y*.

The magnetic relay is rated to handle 500 watts. Should larger amounts of power be required, there is available a current of about 40 milliamperes at voltages up to 50 volts (about 20 milliamperes at 100 volts) for operation of a heavier relay, if the contact voltage may be increased to 16 volts. Condenser C_1 should be as large as is practical (say, 32 microfarads) to obtain maximum power to operate the relay.

The total cost for the parts is less than \$8.00, more than half of which is for the magnetic relay. Parts are available from any radio supply house.

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Correspondence—Determining Gold in Cyanide Plating Solutions

SIR: Kushner's article on a method for determining gold in cyanide plating solutions [*IND. ENG. CHEM.*, Anal. Ed., 10, 641 (1938)] might lead some to think that the Weisberg method there referred to was originated by me. That is not the case. The sulfuric acid decomposition method has been employed in this laboratory for a number of years. Its use here was started by William B. Stoddard, Jr.

We seldom encounter difficulty due to failure of the gold to coagulate. However, our procedure is a little different from that described by Kushner. We seldom use more than 25 ml. of sulfuric acid to effect the decomposition. The decomposition is carried out in a Kjeldahl flask. If the mixture is not overheated at the beginning, the gold can be readily coagulated by adding water after decomposition is completed and boiling the mixture for a few minutes.

LOUIS WEISBERG

71 WEST 45TH ST.
NEW YORK, N. Y.
November 28, 1938

♦ ♦ ♦ ♦ ♦

SIR: At the time of writing, I was aware that the method might not be original with Dr. Weisberg, but since he communicated it to me, I credited him with suggesting it. If the method was initiated by Stoddard, he deserves full recognition.

Regarding the second paragraph of Dr. Weisberg's letter, the difficulty was not that the gold failed to coagulate, but that some of the finer particles of the metal failed to precipitate and remained in colloidal suspension in the sulfuric acid solution. It may have been a negligible amount, but it was almost always there. I tried varying the rate of heating, but had no success in completely eliminating the effect. Another objection to adding water after decomposition has been completed is the danger involved in adding it to hot acid.

While the Kjeldahl flask is now in use in Dr. Weisberg's laboratory, I was under the impression that an Erlenmeyer flask was employed. The long neck of the Kjeldahl is no doubt an advantage in condensing the acid vapors and conserving the sulfuric needed to effect decomposition. However, the sloping walls of the cone flask bring about the same result to a large degree, besides permitting easy washing and transfer of gold to the Gooch crucible.

I feel that I did not stress sufficiently the fact that fumes given off during the reaction are violently poisonous. The list of constituents of these fumes reads like a Who's Who of toxic and irritating gases. Any or all of the following may be evolved: HCN, (CN)₂, CO, CO₂, NH₃, SO₂. The first five are given off at the beginning of the process as the sulfuric acid decomposes the cyanides, formates, and carbonates that are usually present in the plating solution, and the last gas is generated as the sulfuric acid starts to boil, just before the gold is precipitated. It is therefore very important that a good draft hood be used for the decomposition. Under no circumstances should the face be brought close to the mouth of the flask during addition of the sulfuric acid or at any time thereafter. If these precautions are taken there is no danger.

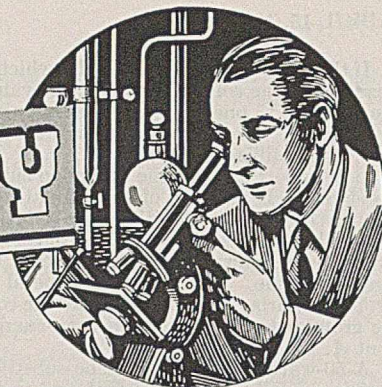
Metals of the platinum family if present will interfere. Platinum, rhodium, ruthenium, and iridium never occur in commercial gold plating solutions and need not be considered. Rarely some palladium may be found—generally in what is known as an "optical pink" gold solution. When present it precipitates partially with the gold. The gold no longer coagulates into a sponge, but comes down as a brownish black powder contaminated with palladium. In such a case, it is best to use the evaporation method (Scott, W. W., "Technical Methods of Metallurgical Analysis," pp. 718-19, D. Van Nostrand Co., New York, 1923) and the regular fire assay.

Of the more common metals, iron, if present in large quantities, also interferes. While the commercial gold plating baths of today seldom if ever contain sodium or potassium ferrocyanide, single-cell (commonly termed "salt water") gold solutions still make use of these salts. If present, they are decomposed by the sulfuric acid with the formation of ferric sulfate. Ferric sulfate, being insoluble in sulfuric acid, comes down as a grayish white powdery coating over the gold sponge. After decanting most of the sulfuric acid and carefully washing the precipitate in the flask with water, decanting repeatedly, several alternate washings with dilute sodium hydroxide and hydrochloric acid, finally ending with boiling hot water, will completely remove the ferric sulfate. The gold can then be filtered onto a Gooch crucible as previously described [*IND. ENG. CHEM.*, Anal. Ed., 10, 641 (1938).]

304 ECHO PLACE
NEW YORK, N. Y.
December 23, 1938

J. B. KUSHNER

MICROCHEMISTRY



Determination of Antimony in White Metals

A Volumetric Semimicromethod

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THE present method is an application of a dilute bromate solution, 0.005 *N*, for the determination of antimony in tin and lead and in alloys of the metals with antimony. The procedure has grown out of previous work (1), in which a more concentrated bromate solution was used on 1.5-gram samples.

The method may be used in the analysis of alloys such as hard lead, containing about 1 per cent of antimony, and tin-base bearing alloys, containing about 7 to 11 per cent of antimony. The procedure is usually applied to quantities of antimony in the range from 0.01 to 0.10 per cent in tin and lead and in solder made with the metals, and is identical in principle with that employed in the conventional method. To enable the application of 0.005 *N* bromate solution, the quantities of the reagents used have been greatly decreased. The use of pure arsenic trioxide for standardizing the bromate solution is an aid to the attainment of accurate results. The degree of precision of which the method is capable is shown by Table I, presenting data obtained in determining antimony in Bureau of Standards tin-base bearing metal, containing 7.32 per cent of antimony, and another tin-antimony alloy found to contain 10.60 per cent of antimony.

The antimony content of tin and lead tested in this labora-

tory varies over a narrow range; in tin it is seldom greater than 0.02 per cent and in lead often less than 0.01 per cent. A semimicrotip attached to the 10-ml. buret is used for titrating in the analysis of lead samples, and is an aid to attaining greater accuracy. A piece of glass tubing, 5 to 6 mm. in diameter, is drawn out to nearly capillary size, is attached to the buret by rubber tubing, and should deliver about 4 drops for 0.05 ml. of bromate solution.

Antimony determinations on tin samples, and tin-antimony and lead-antimony alloys can be performed in less than 1 hour; on lead and solder samples in 1.5 to 2 hours.

Reference Standards

Bureau of Standards samples 42b and 54A were used as reference standards in the development of this method. The antimony content of the tin sample, No. 42b (Table II), is 0.018 per cent. This is in close agreement with the value, 0.02 per cent, assigned to the sample when the former work was in progress.

The tin-base bearing alloy, No. 54A, contains tin 88.61, antimony 7.32, copper 3.75, lead 0.21, iron 0.041, arsenic 0.039, and bismuth 0.019 per cent. Experimental analyses with this sample (Table I) show the antimony content to be 7.31 per cent.

Bureau of Standards arsenic trioxide, sample 83, with a purity of 99.98 per cent, is used for standardizing the bromate solution. Metallic antimony, often used for standardizing solutions of the salt, is difficult to obtain in the pure form. Samples of antimony tested show the presence of arsenic and silica. Potassium bromate is obtainable in a highly purified form. When solutions of the salt have been standardized by means of arsenic trioxide, the values obtained have always been in very close agreement with the theoretical, making the application of a correction factor unnecessary.

TABLE I. DETERMINATIONS ON TIN-ANTIMONY AND LEAD-ANTIMONY ALLOYS

Sample	Weight of Sample Gram	0.005 <i>N</i> KBrO ₃ ML.	Antimony	Antimony	Total	Antimony	Error Mg.	Recovery %
			Originally Present Mg.	Added Mg.	Antimony Present Mg.	Found Mg.		
Bureau of Standards Sample 54A, tin- base bearing metal	0.01	2.40	0.732	0.731	-0.001	99.9
	0.01	5.60	0.732	1.00	1.732	1.705	-0.027	98.4
	0.01	5.05	0.732	0.80	1.532	1.537	-0.005	100.3
	0.02	4.80	1.464	1.461	-0.003	99.8
	0.02	4.75	1.464	1.446	-0.018	98.7
	0.02	7.65	1.464	0.875	2.339	2.329	-0.01	99.6
	0.02	7.75	1.464	0.90	2.364	2.359	-0.005	99.8
Another tin-antimony alloy	0.01	3.50	1.065
	0.01	3.45	1.05
	0.01	3.50	1.065
	0.01	3.50	1.065
	0.02	6.95	2.116
	0.02	6.95	2.116
	0.02	8.35	2.116	0.425	2.541	2.542	+0.001	100.04
	0.02	8.95	2.116	0.625	2.741	2.724	-0.017	99.4
	0.02	9.25	2.116	0.70	2.816	2.815	-0.001	99.96
Lead-antimony alloy	0.20	8.00	2.435
	0.10	4.15	1.263
	0.10	4.10	1.248
	0.10	4.10	1.248
	0.10	4.10	1.248
	0.10	7.35	1.248	1.00	2.248	2.237	-0.011	99.5
	0.10	6.55	1.248	0.75	1.998	1.994	-0.004	99.8
	0.10	8.95	1.248	1.50	2.748	2.724	-0.024	99.1

TABLE II. ANALYSES OF TIN AND SOLDER

Sample	(Using 0.6-gram samples)				Antimony Found Mg.	Error Mg.	Recovery %
	0.005 N KBrO ₃ Ml.	Antimony Originally Present Mg.	Antimony Added Mg.	Total Antimony Present Mg.			
Antimony	4.90	...	1.50	...	1.492	-0.008	99.5
	4.95	...	1.50	...	1.507	+0.007	100.5
	3.90	...	1.20	...	1.187	-0.013	98.9
Bureau of Standards tin sample 42b	0.35	0.107
	2.50	0.107	0.65	0.757	0.761	+0.004	100.5
	3.30	0.107	0.90	1.007	1.005	-0.002	99.8
Tin sample, Cempure, from In- ternational Tin Research & Development Council, London Continental Can Co. No. 1 No. 2 No. 3	0.35	0.107
	3.00	0.107	0.80	0.907	0.913	+0.006	100.7
	4.45	0.107	1.25	1.357	1.355	-0.002	99.8
	0.25	0.076
	2.30	0.076	0.63	0.706	0.700	-0.006	99.1
	0.40	0.122
	2.85	0.122	0.75	0.872	0.868	-0.004	99.5
No. 3	0.50	0.152
	3.10	0.152	0.80	0.952	0.944	-0.008	99.2
Solder samples from Mount Royal Metal Co., Canada No. 2 No. 3	0.15	0.046
	2.10	0.046	0.60	0.646	0.639	-0.007	99.0
	1.05	0.32
	3.85	0.32	0.85	1.17	1.172	+0.002	100.2
No. 3	1.35	0.411
	2.10	0.411	0.225	0.636	0.639	+0.003	100.5

Solutions and Reagents Required

Bromine Solution. Dissolve 12 ml. of pure bromine in 100 ml. of concentrated hydrochloric acid by shaking vigorously in a glass-stoppered bottle.

Methyl Orange Indicator. Dissolve 0.10 gram of methyl orange powder in 100 ml. of hot water and filter.

Anhydrous Sodium Sulfite.

Potassium Bromate Solution, 0.005 N; 1 ml. = 0.3044 mg. of antimony. Weigh 0.1392 gram of the salt, dissolve in water, and make up to volume in a liter flask. Standardize against pure arsenic trioxide. Weigh a quantity of the trioxide, 4.95 mg., then dissolve in 1 drop of a saturated solution of sodium hydroxide. Add a few milliliters of water and 1 ml. of concentrated sulfuric acid, and titrate as in the regular analysis. The quantity of bromate required in this titration is 20 ml. after deducting the reagent blank correction, 0.15 ml.

Procedure for Tin, Lead, and Solder

Weigh a 0.6-gram sample of filings, 80-mesh for lead, into a 50-ml. beaker. Add a few milliliters of concentrated hydrochloric acid and about 5 ml. of the bromine-hydrochloric acid solution. Heat over a small flame, adding small quantities of bromine solution as required to complete solution of the metal. At this stage in the process, the solution should appear pale yellow in color, indicating a slight excess of free bromine. The presence of any considerable amount of free bromine upon solution of the metal may prevent suitable reduction of the antimony by sodium sulfite.

Add to the hot solution 20 mg. of anhydrous sodium sulfite, followed by 5 ml. of concentrated hydrochloric acid, and evaporate to a volume of 7 to 8 ml. to expel any arsenic present. Add 1 ml. of concentrated hydrochloric acid and 5 ml. of water and place over the small flame again until gentle boiling begins. Pass a gentle current of air through the solution for 30 seconds. Remove from the burner, wash off the cover glass and sides of the beaker, and titrate with 0.005 N potassium bromate solution, using a 10-ml. buret graduated in 0.05-ml. divisions. After the addition of a drop of methyl orange indicator add the bromate solution drop by drop to the disappearance of the pink color of methyl orange. During the titration keep the temperature of the solution near the boiling point. The high temperature aids in obtaining a more distinct end point. From the final buret reading deduct 0.15 ml., the amount obtained in the titration of a blank

run under the conditions obtaining in this determination. It is advisable to determine the reagent blank correction occasionally. The amount of this correction may vary according to the purity of the reagents used.

Procedure for Tin-Antimony and Lead-Antimony Alloys

Analyses of these alloys are performed with 0.10-gram samples of 80-mesh filings for lead-antimony alloys, and 0.02-gram samples for tin-antimony. To these quantities add 5 to 10 ml. of concentrated hydrochloric acid, using 50-ml. beakers, and heat gently over a small flame for 5 to 10 minutes. At this stage some of the antimony, separated in black powdery form, can be observed on the bottom of the beaker. Add a few drops of bromine-hydrochloric acid solution which has

been diluted with about 2 volumes of concentrated hydrochloric acid. Heat over the flame, adding a few drops of bromine solution as required, to complete solution of the antimony, avoiding more than a slight excess of bromine. Upon addition of 35 to 40 mg. of sodium sulfite, the process is continued as in the procedure for tin, lead, and solder.

In the first three experiments of Table II, quantities of antimony, taken from a solution prepared by dissolving powdered antimony in concentrated hydrochloric acid with the addition of potassium chlorate, were carried through the regular course of analysis. In all the experimental analyses of Tables II and III, the error is less than the antimony value of 0.05 ml. of the bromate solution.

TABLE III. ANALYSES OF LEAD

Sample	(Using 0.6-gram samples)				Antimony Found Mg.	Error Mg.	Recovery %
	0.005 N KBrO ₃ Ml.	Antimony Originally Present Mg.	Antimony Added Mg.	Total Antimony Present Mg.			
Continental Can Co. lead samples	0.20	0.061
	0.20	0.061
	3.50	0.061	1.00	1.061	1.065	+0.004	100.4
Sample 2	0.15	0.046
	2.10	0.046	0.60	0.646	0.639	-0.007	99.2
Sample 3	0.10	0.03
	1.45	0.03	0.42	0.45	0.441	-0.009	98.0
Sample 4	0.05	0.015
	2.35	0.015	0.70	0.715	0.715

The antimony content of the second tin-antimony alloy shown in Table I was found to be 10.60 per cent, the average of several determinations. The third and fourth experiments using 0.01-gram samples, and the fifth and sixth, in which 0.02 gram was used, were carried out consecutively. The average value for the antimony content obtained in these four analyses is 10.61 per cent. The average value obtained in the six experimental analyses, determining the antimony content of this alloy, is 10.60 per cent.

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Analytical Balances in Quantitative Microanalysis

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Many analytical balances possess precisions ranging from ± 10 to ± 50 micrograms and can be used as substitutes for microchemical balances in the performance of quantitative microanalyses. The method of weighing developed by Bunge and Kuhlmann (8), which is employed with microchemical balances, is recommended for general use with analytical balances; the calculated deflection is explained as that ideal deflection which would be directly observed, if it were possible to free the method of single deflection (3) from manipulatory distortions.

The question of the minimum size of sample required for attaining a specified precision of the analytical result is treated mathematically. The results are summarized in Table I in a form which permits their practical application without making it necessary to refer to the details of the theoretical discussion. It is hoped that the possibility of employing analytical balances will assist in spreading the use and teaching of quantitative microchemical procedures.

PREGL performed the first series of his investigations on the feasibility of microprocedures for the quantitative elementary analysis of organic substances, using an assay balance (4) whereby the weights were determined to the nearest hundredth milligram (12, 13). Later the use of sensitive analytical balances was repeatedly suggested (2, 7, 11, 14, 15, 16), and semimicromethods were recommended with the intention of evading the exacting requirements for the precise determination of mass with the microchemical balance. The possibility of enlisting analytical balances in the service of microanalysis may be of interest to industrial and commercial laboratories, and may facilitate the spreading of instruction in quantitative micromethods which often must be limited to a few promising students for lack of a sufficient number of microchemical balances. In consideration of these possible benefits, but with no intention of denying the superiority of microchemical balances, the following discussion attempts to prove that precise analytical balances may be employed not only in semimicroanalysis, but also in the performance of certain determinations on milligram samples. In addition, the range of applicability of such balances in the field of quantitative micromethods is clearly defined.

Method of Weighing

The method of short swings combined with the calculation of the deflection is recommended for all precise work with analytical balances operated without damping devices. The time required for a weighing compares favorably with that needed when using a damped balance, and the precision with the swinging balance should be somewhat better than that obtained when reading the equilibrium position of the pointer with the balance at rest.

The procedure of weighing is described in the microchemical literature (5, 10) and may be applied to analytical balances as follows:

When the approximately correct weight has been found by preliminary trial, the rider is brought as exactly as possible into position, so that it appears from the front as one perpendicular line coinciding with the selected division of the rider scale. There is no reason, with analytical balances to use any other divisions of the rider scale but those corresponding to a whole number of milligrams. In releasing and arresting the balance the functioning of the arresting mechanism of the microchemical balances, and analytical balances of European make, is copied—i. e., the beam is released last and arrested first, contrary to the usual American practice with balances having a separate pan-arresting mechanism. The first two complete swings are discarded and the following three consecutive points of inflection are read, counting the divisions of the pointer scale as tens and taking the center of the scale as zero—e. g., left -11 , right $+30$, left -9 . The deflection is calculated by averaging the two readings on one side of the swing, $\frac{1}{2}(-11 - 9) = -10$, and algebraically adding the result to the reading on the other side of the swing, $-10 + 30 = +20$.

The deflection may be defined as the other point of inflection of an ideal swing having zero for one point of inflection. In the example cited above, the points of inflection of such a swing would be 0 and $+20$. It is obvious that the needle would point to $+10$ when the swing dies down and the balance is at rest or, generally speaking, that the deflection is equal to twice the rest point. The use of the deflection (*Ausschlag*), also referred to as "deflection difference" (5) or "deflection sum" (10) in the American literature, originated with Paul Bunge and Kuhlmann (8) who adjusted the sensitivity of their balances so that the use of the deflection led to simple figures for the sensitivity, 0.1 or 0.01 mg. per division of the pointer scale. The usual objection to their procedure of evaluating the swing of the balance is that the deflection has no physical meaning. This, of course, is not justified. An attempt at direct observation of the deflection is made in the "single deflection method" described by Brinton (3) where the balance is adjusted and released in such a way as to permit the pointer to perform a nearly perfect swing starting at the zero division of the pointer scale. Only the first point of inflection is read and is considered as the deflection. It is obvious that the procedure of Bunge and Kuhlmann for the calculation of the deflection from observations on the freely swinging balance must give more reliable results.

The sensitivity is determined by shifting the position of the rider for a distance corresponding to a change in weight of 1 mg. and determining the deflection, which now might be -57 . The sensitivity is calculated as the fraction, "change of mass over change of deflection":

$$\frac{1 \text{ mg.}}{+20 - (-57)} = 0.013 \text{ mg.}$$

per unit of the pointer scale.

The evaluation of the observed deflections in terms of milligrams is performed in the usual way by multiplying the deflection by the sensitivity. Thus the deflections quoted as examples correspond to the masses:

$$\begin{array}{r} 20 \times 0.013 = 0.26 \text{ mg.} \\ 57 \times 0.013 = 0.74 \text{ mg.} \\ \hline 1.00 \text{ mg.} \end{array}$$

The sum, 1.00 mg., corresponds to the mass represented by the displacement of the rider. Generally one may say that the deflection is converted into mass by use of the formula

$$\text{Mass} = \text{deflection} \times \text{sensitivity} = \text{deflection} \times \frac{1 \text{ mg.}}{\text{deflection change}}$$

This equation shows clearly the futility of calculating the rest point. Since the latter is one half of the deflection, the formula shows that the user of the rest point is amusing himself by dividing by two the numerator and denominator of a fraction.

As to the general procedure of weighing, treatment of balance, and selection of balance room, the customary precautions (5, 10) should be more closely approximated the higher the precision needed. If the precision of the weighings is to be ± 0.01 mg. or better, it becomes advisable to keep the temperature of the balance room reasonably constant and to eliminate changes of the buoyant effect by the use of tares of suitable density.

Determination of Precision of Balance

The determination of the average deviation of a single weighing has been described (1); it appears advisable to base the calculation on the results of a series of at least ten weighings, and to verify the precision by redetermination at reasonable time intervals. The manufacturers' specifications on the "sensitivity" of their balances usually do not permit conclusions concerning the precisions obtainable but in general the efficiency of analytical balances is very gratifying, a fact which has been known for a long time. Felgentraeger (6) predicted in 1907 that the precision of a correctly constructed balance could be one thousandth of the weight of the rider. Manley (9) tested a balance with a beam of Invar steel and determined average deviations of a few micrograms for weighings with loads from 0 to 200 grams. Analytical balances and "semimicrobalances" of a "sensitivity" of 0.01 mg. are offered by American and European manufacturers. Inexpensive students' balances of American manufacture, tested after 3 and 5 years of use, showed average deviations ranging from 0.005 to 0.05 mg. (1). Finally, the inherent ability of the correctly constructed analytical balance for the attainment of high precision is also suggested by the fact that the modern microchemical balance is essentially a reproduction of Kuhlmann's assay balance (4) which, in turn, is a small-scale model of his analytical balance with constant sensitivity from zero to maximum load (200 grams).

Calculation of Required Amount of Sample

The percentage, P , of constituent X , as calculated from the measurements of a quantitative determination, is directly proportional to the measure, M , of X (mass of the weighing form, volume of standard solution, etc.) and inversely proportional to the mass, S , of the sample. Therefore, the relative precision, π' , of the result, P , is determined as follows by the relative precisions, μ' and σ' , of M and S (1):

$$\pi' = \pm \sqrt{\mu'^2 + \sigma'^2} \quad (1)$$

While in general the error, μ , of the measure, M (weight of the precipitate, volume of standard solution or gas), is determined by the shortcomings of the "chemical" procedure to such a degree that the weighing error becomes insignificant, in the present case, where the balance is utilized to the limit of its efficiency, the conditions are exactly reversed. Thus, if the employing of analytical balances is coupled with the use of proper, truly microchemical procedures, it may be justly assumed that the precision of the result will be influenced solely by the determinations of mass.

In chemical work the mass of a substance is always determined from the difference of two weighings, even if the material be placed directly on the pan of the balance, and it appears that every determination of mass is affected by the errors of two weighings. The average deviation of the difference of two weighings of the precision, ω , is now equal to 1.4ω (1), and this quantity is to be considered as the absolute average

deviation of any analytical determination of mass performed with a balance giving the average deviation, ω , in a single weighing.

The relative average deviation of the determination of any weight, W , may be calculated as follows (1):

$$\omega' = 1000 \frac{1.4 \omega}{W} \% \text{ (parts per 1000 parts)} \quad (2)$$

The equation shows that the relative precision, ω' , may be adjusted by a proper variation of W , but, as a rule, the relative error, ω' , is determined by the precision requirements of the analytical work and the minimum weight, W , of the substance is thus fixed as a function of ω' and ω .

$$W = 1000 \frac{1.4 \omega}{\omega'} \quad (3)$$

Usually, analysts prefer to specify the required relative precision as the largest permissible deviation—e. g., "the results are expected to check within 10 parts per 1000 parts of the determined constituent." In accordance with this custom the relative average deviation, ω' , may be replaced by the relative maximum deviation, ω'_m , by substituting $1/4 \omega'_m$ for ω' in Equations 2 and 3.

$$\omega'_m = 5600 \frac{\omega}{W} \quad (4)$$

and

$$W = 5600 \frac{\omega}{\omega'_m} \quad (5)$$

If a specified maximum deviation, ω'_m , is not to be exceeded, Equations 4 and 5 indicate that the amount of material weighed at any stage of a quantitative determination must not be less than W . This statement is sufficient for all analyses in which only one determination of mass is required. Additional restrictions become necessary if more than one weighing is included in the computation of the result, P . The following possibilities may be considered: (1) The balance is used for the weighing of the sample only, (2) the sample and the isolated constituent, X , are weighed, and (3) the balance is used for the weighing of the isolated constituent only.

BALANCE USED FOR WEIGHING OF SAMPLE ONLY. In all those analyses where the determination of X is carried out by titrimetric, gas volumetric, colorimetric, nephelometric, etc., methods, the balance is required for the weighing of the sample only. Provided that the precision of the measure of X is high, the maximum error of the result, P , becomes practically equal to the maximum deviation of the weight, S , of the sample. From Equations 1 and 4 follows:

$$\pi'_m = \sigma'_m = 5600 \frac{\omega}{S}$$

and the minimum mass of the sample is consequently

$$S = 5600 \frac{\omega}{\pi'_m} \quad (6)$$

a simple function of the permissible maximum deviation of the result.

BALANCE USED FOR DETERMINATION OF MASSES OF SAMPLE AND WEIGHING FORM. A large number of the gravimetric determinations actually performed belong in this group.

The discussion must be broken up into four sections, since the effect of the weighing error, $\pm 5.6 \omega$, on the relative precision varies with the magnitude of the mass determined, and the mass, M , of the weighing form may be larger or smaller than the mass, S , of the sample, depending upon the content of these two substances on determined constituent X . If the procedures are properly executed, sample and weighing form

contain the same absolute amount of determined constituent, X . Consequently, the masses, S and M , of sample and weighing form must be inversely proportional to their percentages on X , P , and $100f$, respectively. Since the approximate percentage, P , is usually known and the "chemical factor for the calculation of gravimetric determinations," f , can be found in generally available tables, the following subsections have been arranged in accordance with the relative magnitudes of P and $100f$.

1. *100f is equal to or smaller than $\frac{1}{2}P$.* The mass, M , of the weighing form is twice or more than twice as large as the mass, S , of the sample. The square of the relative precision μ' of M can be neglected in Equation 1

$$\pi'_m = \sigma'_m$$

and the precision of the result depends upon the precision σ'_m of S only. The minimum mass of sample is given by Equation 6.

2. *100f is greater than $\frac{1}{2}P$ and smaller than or equal to P .* The masses, M and S , are approximately equal, and M is never smaller than S . Therefore, the relative deviation μ' is approximately equal to σ' , but never exceeds it. It is safe to substitute the value σ' for μ' in Equation 1.

$$\pi'_m = \pm \sqrt{2\sigma_m'^2} = \pm 1.4 \sigma'_m$$

Consideration of Equation 4 shows that

$$\pi'_m = 7800 \frac{\omega}{S}$$

and the required minimum mass of sample becomes

$$S = 7800 \frac{\omega}{\pi'_m} \quad (7)$$

3. *100f is greater than P but smaller than $2P$.* The masses, M and S , differ little, but M is always smaller than S ; μ' is slightly greater than σ' , and it is preferable to substitute μ'_m for σ'_m in Equation 1.

$$\pi'_m = 1.4 \mu'_m = 7800 \frac{\omega}{M}$$

Substitution for M in the simple relation (1)

$$P = \frac{100fM}{S}$$

gives the minimum mass of the sample as

$$S = 7800 \frac{\omega}{\pi'_m} \times \frac{100f}{P} \quad (8)$$

4. *100f is equal to or greater than $2P$.* S is considerably greater than M ; σ'^2 becomes insignificant when compared with μ'^2 in Equation 1

$$\pi'_m = \mu'_m = 5600 \frac{\omega}{M}$$

and the minimum mass of sample becomes

$$S = 5600 \frac{\omega}{\pi'_m} \times \frac{100f}{M} \quad (9)$$

It is obvious that whenever M is smaller than S , sections 3 and 4, mass M must be kept above a minimum value which is determined by ω and π'_m . The factor $\frac{100f}{P}$ adjusts the size of the sample so as to keep M at this minimum value.

BALANCE USED FOR DETERMINATION OF THE MASS OF ISOLATED CONSTITUENT ONLY. In this group belong gravimetric determinations on gases and liquids which are measured without the use of the balance. Most examples are found in the analysis of aqueous solutions.

Only the precision, μ' , of the determination of the mass, M , needs to be considered. The equation for the calculation of the required minimum volume, S , of the sample becomes identical with Equation 9, providing that proper dimensions for S , P , and ω are chosen.

Conclusion

Equations 6, 7, 8, and 9 show that analytical balances of a precision not worse than ± 0.05 mg. can be used rather generally in quantitative microanalysis, if the requirements concerning the precision of the results are not too exacting. A relative maximum deviation of 20 parts per 1000 parts of the determined constituent could be considered adequate. It certainly suffices in those instances where the determinations are carried out for the purpose of the acquisition of microchemical technique.

The amounts of samples required to satisfy the requirement of a maximum deviation, π'_m , of 20% may be calculated by the use of Table I. In all those determinations where the

TABLE I. SIZE OF SAMPLE AS FUNCTION OF AVERAGE DEVIATION OF A SINGLE WEIGHING

The acceptable maximum deviation is chosen as 20% of the result, P . Since the size of the sample, S , and the precision of the determination are inversely proportional, the values of S required for any other specified maximum deviation may be easily calculated from the values of S computed from this table.

f is the chemical factor for the calculation of gravimetric analyses and is found in generally used tables.

ω is to be given in milligrams; its determination is described in an earlier paper (1).

P is to be given in the dimension "per cent," if the sample is to be weighed, and in "gram per liter," if the sample is to be measured.

S is obtained in milligrams for weighing, and in cubic millimeters for measuring.

Sample Only	Balance Used for Determination of Mass of:—					Weighing Form Only
	Sample and Weighing Form—					
	100f smaller than or equal to $\frac{1}{2}P$	100f between $\frac{1}{2}P$ and P	100f between P and $2P$	100f equal to or greater than $2P$		
S to be made equal to or greater than	300ω	300ω	400ω	$400\omega \frac{100f}{P}$	$300\omega \frac{100f}{P}$	$300\omega \frac{100}{P}$

balance is used for the weighing of the sample only, or where $P \geq 200f$, the minimum weight of the sample depends upon the precision of the balance only. In this group belong, aside from volumetric determinations, many of the gravimetric procedures which are widely used as students' experiments: the determination of chloride ion as silver chloride in sodium chloride, the determination of sulfate ion as barium sulfate in potassium sulfate, the determination of sulfur as barium sulfate in pyrite, the determination of phosphorus pentoxide as magnesium-ammonium phosphate hexahydrate in apatite, and the determination of calcium oxide as calcium oxalate monohydrate in calcium carbonate or high-grade limestone. All these determinations may be carried out on a milligram scale, if the average deviation of a single weighing does not exceed ± 0.02 mg.; with this precision of the balance 6 to 8 mg. of the sample are required. The corresponding figures are 15 and 20 mg., if the average deviation of a single weighing is equal to ± 0.05 mg.

Whenever P is smaller than $100f$, the amount of sample must be increased by $100f/P$ so as to keep the mass, M , of the weighing form equal to 300 or 400 ω . In all the examples of Table II, the mass, M , of the weighing form is either 6 or 15 mg., depending upon the precision assumed for the balance. Table II shows that those determinations in which the determined substance is weighed as such, as in ash determinations and electrolytic precipitations, require large samples. That the analysis of substances containing little of the determined constituent requires large samples, is common knowledge. The last example of Table II shows, however, that a small chemical factor of the weighing form is able to counteract the effect of a low content of the material in question.

As to the precision obtained in the results of actual analyses, one must not expect that the maximum deviation π'_m

TABLE II. SIZE OF SAMPLE AS FUNCTION OF COMPOSITION OF ANALYZED MATERIAL AND WEIGHING FORM
 100*f* is greater than *P*. Acceptable maximum deviation is chosen as 20% of *P*

Type of Determination	<i>P</i> %	<i>f</i>	<i>S</i>	
			$\omega =$ ± 0.02 mg. <i>Mg.</i>	$\omega =$ ± 0.05 mg. <i>Mg.</i>
K as K_2SO_4 in $KHC_4H_4O_6$	20.8	0.449	12	30
Cu electrolytically in $CuSO_4 \cdot 5H_2O$	25.5	1	24	60
SiO_2 as SiO_2 in a silicate	30	1	18	45
Ni as dimethylglyoxime in steel	4	0.203	30	75
	<i>G./l.</i>		<i>Cu. mm.</i>	<i>Cu. mm.</i>
Cl as AgCl in sea water	20	0.247	7.5	19
P as phosphomolybdate in serum	0.2	0.016	48	120

will occur frequently. Assuming proper manipulative technique, the deviation of the results will be less than π'_m in more than 99.5 per cent of the determinations, less than $1/2 \pi'_m$ in more than 80 per cent, and less than $1/4 \pi'_m$ in more than 50 per cent of the determinations. The average deviation of a single weighing seems to be a constant of a properly constructed balance and, apparently, does not change unless the instrument is abused or becomes worn out as the natural consequence of years of service. Since the cleaning of a balance is more liable to upset the characteristics of the instrument than any other operation of the normal use, it may be mentioned that Rolf Paulson determined the average deviation of an American balance which had been used by students for 5 years and, during the vacation months, had acquired a coating of dust. Computation of the results of ten weighings furnished an average deviation $\omega = \pm 28$ micrograms. Without special care, the balance was then transferred to another floor and underwent a thorough cleaning by the expert hands of Victor Niederl. Finally R. H. Nagel undertook a re-determination of the precision of a weighing and calculated $\omega = \pm 34$ micrograms from the results of thirty weighings. The weighings with the balance in question are seriously af-

fectured by changing the positions of the masses on the pans which is obviously caused by lack of flexibility in the pan suspensions. Nevertheless, the precision appears reproducible within satisfactory limits, if care is taken to simulate closely, in determining the precision, the conditions of actual weighings.

Experimental proof of the correctness of the predictions of Table I does not appear necessary. Residue determinations by the author and experiences in the laboratory of J. B. Niederl so far fully support the mathematical deductions.

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A Modified Pregl Spiral Tube For Sulfur and Halogen Determinations

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THE Pregl spiral combustion tube (4) makes it necessary to remove the platinum catalysts before the combustion products can be washed out, and to dry the tube before the catalysts can again be inserted. It was thought that if the tube were cut and a ground-glass joint made of the two parts, one section could be removed to wash out the products of combustion, and the other retained in the furnace with the platinum catalysts. Such a tube was made and has been used with success in this laboratory.

Hallett (2) has devised a quartz tube which does not have to be removed from the furnace. The time saved using the

tube described in this article is about the same as that saved by the use of Hallett's apparatus.

Procedure

A Pregl spiral combustion tube 640 mm. long is cut 20 mm. from the indenture. A ground-glass joint is made at that point, not by fusing one on, but by grinding on the ends of the two sections. Section B is placed in the split-type electric furnace (Fisher), so that the joint protrudes beyond the end. The sample is then introduced and oxygen admitted. Section A, containing the absorbing medium, is attached to section B without lubricant, and the tube is pulled back so that the joint is inside the furnace. This step ensures collecting the products of combustion in section A. After the combustion, the joint is pushed outside the furnace and left to cool for 2 or 3 minutes. Section A is removed and allowed to cool to room temperature, and the products of combustion are washed out.

The analyses for sulfur were made according to Saschek, (5) but water, instead of hydrogen peroxide, was used as the absorbing medium. Saschek's technique with the crucible (1), filter stick (3, 6), and small amounts of wash liquid was adapted, for the first time, to the gravimetric determination

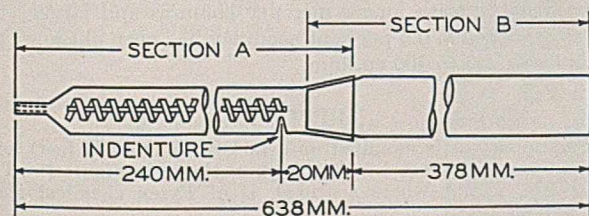


TABLE I. TYPICAL RESULTS

	Sulfur Calcd. %	Sulfur Found %		Chlorine Calcd. %	Chlorine Found %
Methionine, C ₅ H ₁₁ O ₂ NS	20.50	20.46	2-Hydroxy-4,5,6-trimethoxy- α -chloracetophenone, C ₁₁ H ₁₃ O ₆ Cl	13.55	13.34
2-(<i>N</i> -methylamino)- <i>d</i> -camphane-10-sulfonic acid, C ₁₁ H ₁₇ O ₂ NS	12.98	12.95			
<i>p,p'</i> -Dibromodiphenylsulfide, C ₁₂ H ₈ Br ₂ S ₂	17.03	16.97		Bromine Calcd.	Bromine Found
<i>N'</i> -(<i>n</i> -amyl)- <i>m</i> -nitrobenzenesulfonanilide, C ₁₇ H ₂₁ O ₄ N ₂ S	9.19	9.22	1-(4-Bromophenyl)-2,2-diphenylethanol, C ₂₀ H ₁₇ OBr	22.66	22.70
<i>p</i> -Carbathoxyaminobenzenesulfonamide, C ₉ H ₁₂ O ₄ N ₂ S	13.11	12.95	<i>p</i> -Bromoacetanilide, C ₈ H ₉ ONBr	37.38	37.51
	Chlorine Calcd.	Chlorine Found	<i>m</i> -Hydroxy- <i>m'</i> -(10-bromo- <i>n</i> -decyloxy)-diphenyl, C ₂₂ H ₂₅ O ₂ Br	19.75	19.91
Methyl- α -chloro- <i>p</i> -toluate, C ₉ H ₉ O ₂ Cl	19.25	19.15		Iodine Calcd.	Iodine Found
<i>p</i> -Chlorobenzaldehyde, C ₇ H ₅ OCl	25.26	25.12	Methyl-3-iodoanisate, C ₈ H ₉ O ₂ I	43.48	43.41
5-Chloro-7-nitroisatoic anhydride, C ₈ H ₅ O ₅ N ₂ Cl	14.64	14.64	<i>o</i> -Iodobenzoic acid, C ₇ H ₅ O ₂ I	51.21	51.04
<i>o</i> -Methylallothreoninebetainehydrochloride, C ₅ H ₁₅ O ₃ NCl	16.98	16.95			

of the halogens. The substitutions made in Saschek's procedure were as follows: The spiral was moistened with a saturated solution of hydrazine sulfate, dilute nitric acid (1 to 300) was used as the wash liquid, 1 cc. of 5 per cent silver nitrate was used to precipitate the halogen ion, and the crucible containing the filter stick and silver halide was dried at 120° C.

Typical results from about fifty analyses made with the tube are reported in Table I.

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Apparatus for Microanalysis of Gas

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This article describes modern refinements of apparatus and technique for the rapid analysis of minute amounts of gas. On samples of 5 to 25 cu. mm. at normal temperature and pressure, analyses may be made with errors for each component within 2 per cent of the total sample. The errors are within 5 per cent on quantities of gas as small as the proverbial limit of 1 cu. mm. The methods described are available for the gases water, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane. One hour is required for a complete general analysis. Under special conditions the least detectable quantity of a component may be pushed to a limit of 0.025 cu. mm., equivalent to the carbon monoxide in 1 sq. cm. of a monomolecular film.

IN CONNECTION with contemporary work on the correlation between thermionic activity and the free alkaline earth metal content of an oxide-coated filament (3) the authors have had the problem of assaying extremely small amounts of active metal. This was accomplished by oxidation with carbon dioxide and analysis of the gaseous reaction products, computing active metal from the equivalent carbon monoxide formed.

The general methods of analysis are related to conventional vacuum technique, handling the gases at low pressures over

mercury and solid reagents. The gases are transferred by Toepler pumps, isolated by mercury cutoffs, and measured in a capillary pipet operating in a fashion analogous to a McLeod gage. The detailed apparatus and methods are an extension and refinement of those previously described by one of the authors (2).

Using this apparatus on a sample of from 1 to 25 cu. mm. at normal temperature and pressure, a general determination may be made for the components water, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane, the residual gas being taken as nitrogen. The errors vary from 5 per cent on the smaller samples to 2 per cent on the larger. We may define the error as the difference, between the amount of any one component and the value obtained for this amount by the authors' method of analysis, divided by the total amount of the sample. In a general analysis, the least detectable quantity of an individual component is about 0.06 cu. mm. In simpler analyses, such as on the carbon monoxide-carbon dioxide mixtures encountered in the filament studies, on account of the fewer manipulations required, it was possible to detect a quantity as small as 0.025 cu. mm., or about the amount of carbon monoxide in 1 sq. cm. of a monomolecular film.

This sensitivity has been obtained with intentional sacrifice of the accuracy obtainable with former variations of this type of equipment. On apparatus more similar to that previously described (2), with longer mercury columns and larger volumes of reagents, 0.5 per cent accuracy has been obtained on samples of 200 to 400 cu. mm.

Apparatus

The apparatus is mounted on a rack 1.5 meters (5 feet) long and 2.2 meters (7 feet 4 inches) high as shown in Figure 1. The glassware, except where specified, is of Pyrex chemical glass throughout.

The detail of the capillary pipet is shown in Figure 2, *A*. This is a 1-mm. capillary 10 cm. long, on which is ground a series of graduations. In taking a measurement the mercury is raised to one of these graduations (by applying compressed air to the mercury reservoir) and the pressure read on the comparison column made from the same piece of capillary tubing. The pressure-volume product measures the quantity of gas. The mercury level, normally standing as shown in Figure 2, is drawn down to permit the gas to flow into the absorption train. The gas is circulated by operation of the Toepler pump (Figure 2, *B*), pumping the gas back into the pipet. The gas is collected by allowing the mercury column of the pipet to assume its normal level and continuing pumping as before.

This Toepler pump is actuated by compressed air and is arranged for automatic operation. Air from the laboratory high-pressure line is led through a reducing valve, measured by a gage, and admitted to the mercury well of the pump by an electric solenoid valve. This is installed to operate as a two-way stopcock, connecting the mercury well first to the controlled pressure line and then to the atmosphere. Three electrical contacts sealed into the pump actuate a vacuum tube circuit (Figure 4) and a polarized telegraph relay which in turn operates the solenoid valve.

The particular design of the Toepler pump reduces the volume of mercury flowing past the cutoff which traps the gas forced over at each stroke of the pump. A simpler design (2) permitted some small bubbles of gas to escape by being trapped and swept out in the moving mercury column.

The same controlled air pressure offers a convenient means of adjusting the mercury in the pipet when measurements are taken. In fact, the most convenient, though not foolproof, method of handling all the pipets, Toepler pumps, etc., has been to pipe each mercury reservoir through a needle valve into a manifold to which could be connected at will the atmosphere, rough vacuum, the controlled pressure line, or the same pressure line in series with the solenoid valve.

To evacuate the system and admit gases, etc., the analysis apparatus proper, gas reservoir, and auxiliary equipment as well, are connected to a "header" which leads, through a large mercury cutoff (Figure 2, *C*), to the pumps. These, not shown, are a water-cooled mercury diffusion pump and a mechanical oil fore pump.

The absorption train consists of a series of reagent tubes, each of which is placed between a pair of mercury cutoffs (Figure 2, *D*). Each tube is bypassed by a third, so that by raising or lowering the proper cutoffs, the gas may be forced through the desired reagent or diverted around it. In order to keep the volume of the system as small as possible, the cutoffs were made approximately 2.5 cm. (1 inch) high of 0.6-cm. (0.25-inch) diameter tubing. To compensate for fluctuations in barometric pressure, small leveling bulbs are set in an adjustable platform 76 cm. below the absorption train. The bulbs have downward tubular extensions, and slide up and down on the vertical tube containing the mercury column as the cutoffs are raised or lowered, or the platform is adjusted by means of thumbscrews.

The reagents used in the absorption train are copper oxide, magnesium perchlorate, and soda lime. The absorption tubes used for the magnesium perchlorate and soda lime follow the design shown in Figure 3, *D*. In each

tube about 0.3 gram of the reagent is retained between plugs of glass wool. For most of their work the authors have used a copper oxide tube of the same design. This was packed with Pyrex glass wool upon which was evaporated and decomposed a solution of about 1 gram of cupric nitrate. This produced a tube of relatively high flow resistance.

In the last evolution of the apparatus the authors have used a miniature mercury diffusion pump (Figure 3, *F*) to circulate the gases. This required a copper oxide tube of lower flow resistance which was constructed as shown in Figure 3, *E*. Cupric oxide, in wire form (0.8 gram), was powdered and placed in a transverse sandwich between layers of Pyrex wool and copper screen, retained by indentations in the wall of the glass tube. This was reduced and reoxidized before use. A similar construction was tried for the magnesium perchlorate and soda-lime tubes, but the absorption was inefficient.

A platinum filament lamp (Figure 3, *A*) served as a slow-combustion pipet. This was mounted between cutoffs in the absorption train. The authors have used filaments of either c. p. platinum or the stronger alloy 80 per cent platinum, 20 per cent rhodium. Contrary to expectation, either filament is readily attacked by oxygen at 700° C., or above, to an extent sufficient to limit its use to the combustion of oxygen in an excess of hydrogen or carbon monoxide.

The water-cooled tube is constructed of Pyrex glass and the filament leads are very heavy platinum wire. The authors attempted to seal the platinum through the Pyrex glass using a silver burnishing paste. The seals were not quite tight and have been backed up with sealing wax. This procedure has so far caused no difficulty but is not to be recommended.

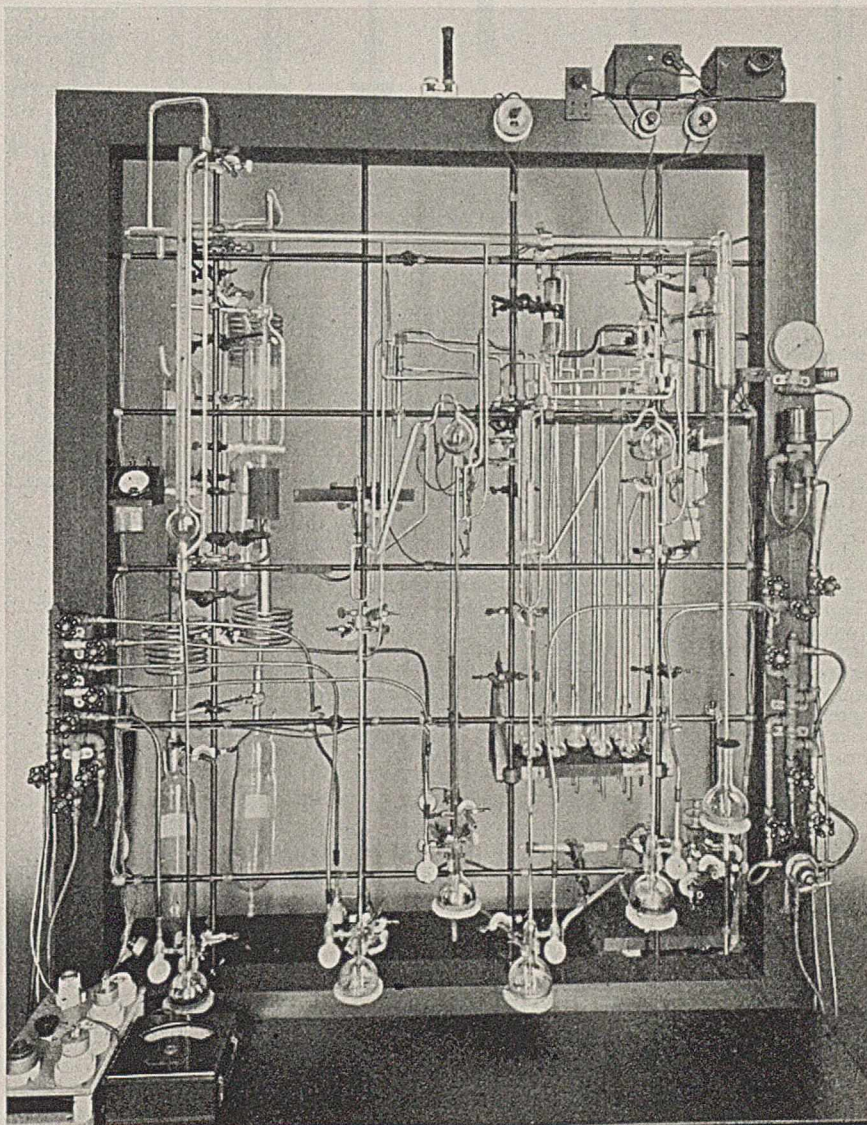


FIGURE 1. APPARATUS FOR ANALYSIS OF GAS

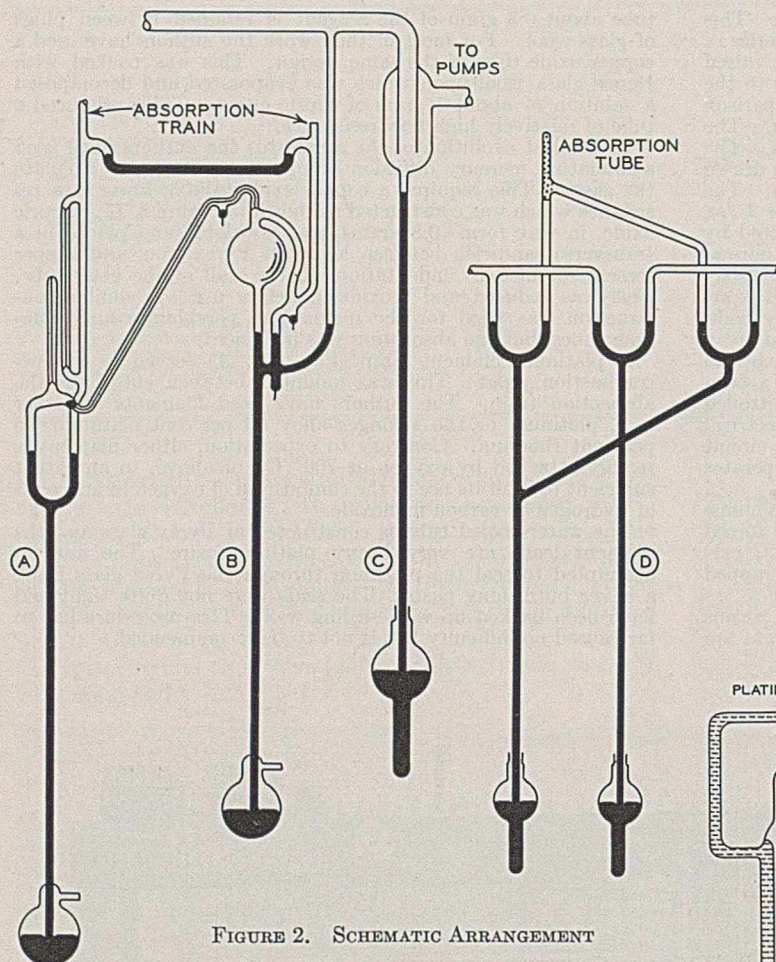


FIGURE 2. SCHEMATIC ARRANGEMENT

A method more in accord with standard practice would be to weld in a short section of tungsten which should be completely embedded in a bead of Corning g702p glass.

An explosion pipet is shown in detail in Figure 3, B. This is a small tube of soft lead glass, with barely exposed platinum leads, connected to its support by a graded seal. This pipet and a second Toepler pump are mounted the same as Figure 2, A and B. The inlet and exit tubes, however, are led to a reagent position in the absorption train.

One further element in the absorption train is a small liquid air trap similar in construction to the absorption tube shown in Figure 3, D (but without the constrictions to retain glass wool), mounted in an inverted position.

The gas reservoirs, made of soft glass, are shown in Figure 3, C. The method of admitting gas depends on the surface tension of mercury and the fact that porous plugs of baked Italian lavite may be sealed tightly to soft lead glass. One such plug is attached to the container and another to a flexible glass helix connected to the header, both being kept below the surface of a mercury reservoir. The plugs are too dense to permit the flow of mercury, but, on bringing the plugs into contact, gas flows through from the container into the header.

Procedure

Prior to an analysis the reagent tubes must be thoroughly outgassed. The magnesium perchlorate and soda lime are baked at 250° C. for a half hour. The copper oxide is baked at 350° C. and then maintained at 300° C. during the analyses. The platinum filament is glowed at 1000° C. *in vacuo* previous to use. If the apparatus has been down to air, the filament is also conditioned for the removal of oxygen. A sample of hydrogen is circulated over the filament and through the magnesium perchlorate tube till there is no further reduction in quantity. When the filament was first installed a sample of carbon dioxide was circulated over the filament to burn out

traces of carbon. This filament is operated at a current corresponding to an observed temperature *in vacuo* of 720° C.

A sample of gas to be analyzed may be introduced into the header, or, if 100 per cent of the gas is to be collected, it should be evolved in apparatus associated with the absorption train. By operation of the Toepler pump (Figure 2, B) the sample is collected and measured in the capillary pipet (Figure 2, A).

The gas is then analyzed by circulation in turn through combinations of reagents in the absorption train. After each absorption the remaining gas is collected and measured. The amounts of water, carbon dioxide, hydrogen, carbon monoxide, nitrogen, and oxygen or methane may be computed from the progressive differences. The various steps follow in serial order.

1. Water vapor is first absorbed by circulation through the magnesium perchlorate.

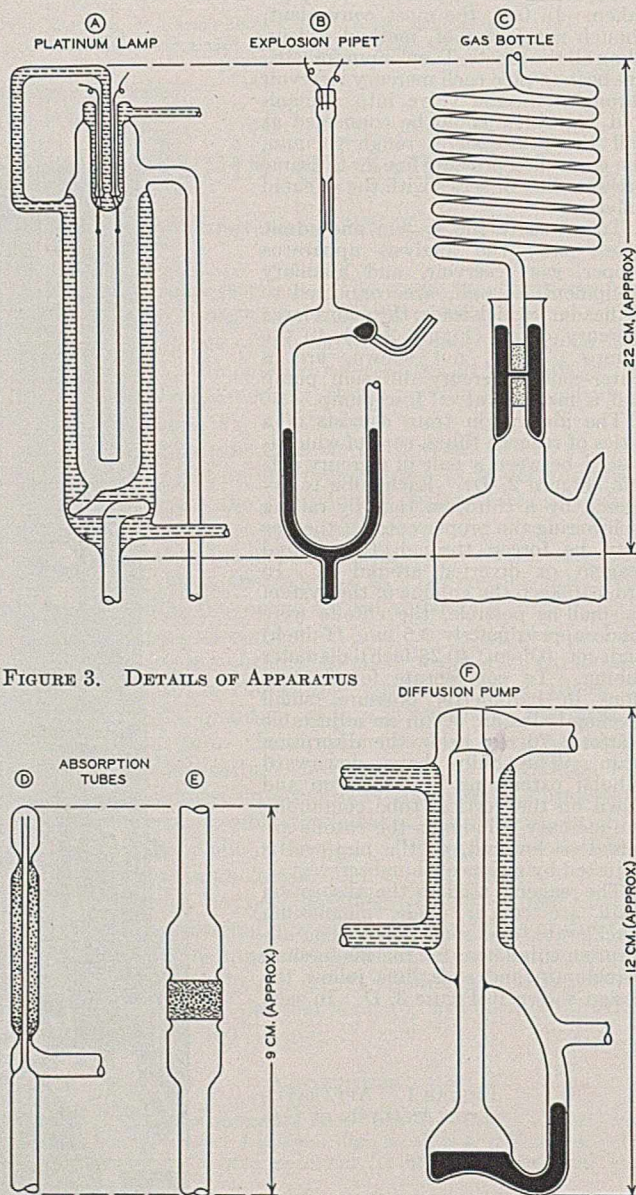


FIGURE 3. DETAILS OF APPARATUS

2. Carbon dioxide is next absorbed by circulation through the soda lime.
 3. If analysis be made for oxygen (with methane absent), the gas is next circulated through the platinum lamp and magnesium perchlorate in series. This removes oxygen and some hydrogen. There must be an excess of hydrogen plus carbon monoxide.

4. Any carbon dioxide produced in step 3 is absorbed in the soda lime.

5. Next hydrogen is absorbed by passing through the copper oxide and magnesium perchlorate in series. Carbon monoxide is also oxidized, but this involves no change in the amount of gas measured.

6. Finally carbon monoxide is absorbed by circulation through the copper oxide and soda lime.

The residue should be nitrogen. If methane be present the analysis cannot be made for oxygen, as the platinum lamp step would be indeterminate. Since methane is unaffected by the copper oxide, it will remain in the residue from step 6.

7. To this residue is added 2.5 to 3 times as much oxygen. The gas is pumped into the explosion pipet, compressed to around 17 cm., and exploded by a spark from an induction coil. The gases are recovered and measured, first pumping through magnesium perchlorate and then direct. A circulation through copper oxide and magnesium perchlorate till absorption is complete removes any water or hydrogen. Excess oxygen is also removed, since the copper oxide tube contains reduced copper as well.

8. Finally carbon monoxide, plus carbon dioxide, equivalent to the original methane, is removed by circulation through copper oxide and soda lime.

In most of the authors' work the gas has been circulated and recovered by the use of the Toepler pump. In general, twenty strokes of the pump each were adequate for circulation and for collection. During collection the by-pass cutoff for each absorption tube was lowered to reduce the flow resistance. Each absorption was repeated till duplicate measurements were obtained. With a pump cycle of 25 seconds a duplicate circulation and collection required a minimum of 35 minutes. In view of other manipulations required and the fact that carbon monoxide absorption was usually slow, the time for a general analysis was 5 to 6 hours.

TABLE I. ANALYSES OF SYNTHETIC MIXTURES

		Composition by Analysis			
		%	%	%	%
		Mixture 1			
		Initial Volume*			
Composition by Synthesis		8.36	22.4	1.66	1.83
%		cu. mm.	cu. mm.	cu. mm.	cu. mm.
CO	36.9	35.7	35.4	32.1	31.9
CO ₂	15.7	15.8	16.8	18.3	20.5
O ₂	13.0	11.9	13.8	14.9	13.5
H ₂	34.4	35.2	33.3	30.8	30.6
N ₂	..	1.4	0.7	3.9	3.5
		Mixture 2			
		Initial Volume			
Composition by Synthesis		21.8	6.34	1.57	0.946
%		cu. mm.	cu. mm.	cu. mm.	cu. mm.
CO	22.3	22.4	21.2	22.8	21.8
CO ₂	9.3	9.8	10.0	10.7	10.8
H ₂	35.5	35.8	36.5	32.7	32.9
CH ₄	32.8	31.5	31.2	30.2	29.4
N ₂	..	0.5	1.1	3.6	5.1
		Mixture 3			
		Initial Volume			
Composition by Synthesis		6.46	11.14	1.74	0.598
%		cu. mm.	cu. mm.	cu. mm.	cu. mm.
CO	31.8	31.0	30.5	29.8	38.3
CO ₂	22.5	21.6	21.5	21.9	15.3
O ₂	8.1	8.1	8.0	9.8	7.0
H ₂	37.6	37.9	38.8	35.0	32.7
N ₂	..	1.4	1.2	3.5	6.7

* At normal temperature and pressure.

In the latest form of the apparatus the authors have incorporated a miniature diffusion pump (Figure 3, F) close to the receiver of the Toepler pump. This is similar to a design shown by Norton and Marshall (1). This pump is mounted between cutoffs and with a by-pass so the equipment can be

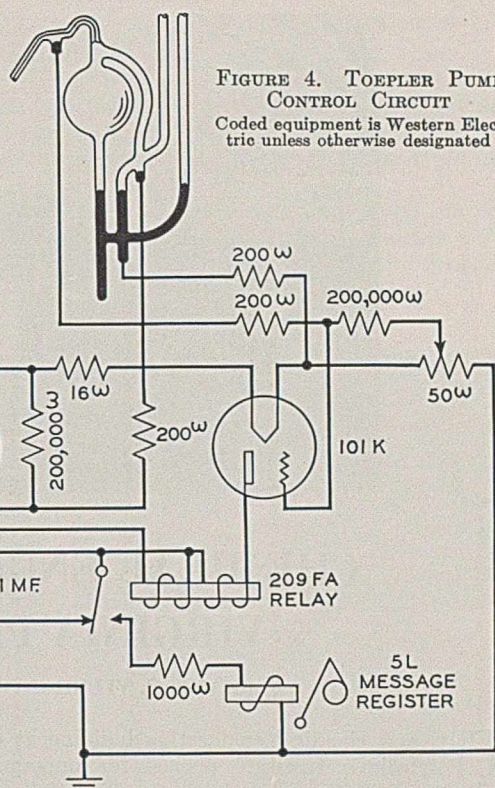


FIGURE 4. TOEPLER PUMP CONTROL CIRCUIT
 Coded equipment is Western Electric unless otherwise designated

operated as before. Another cutoff connects with the front of the absorption train, so that the diffusion pump can be used either to circulate the gas or to pass it into the Toepler pump. With this arrangement, and the new copper oxide tube (Figure 3, E), 2 minutes are sufficient for circulation, and four strokes of the Toepler pump for collection. This permits a duplicate circulation and collection in 8 minutes. Since the absorptions are usually complete and a third circulation is rarely required, the total time of a general analysis has been reduced to one hour. There is no reaction between hot mercury vapor and any of the gases considered.

Analytical Results

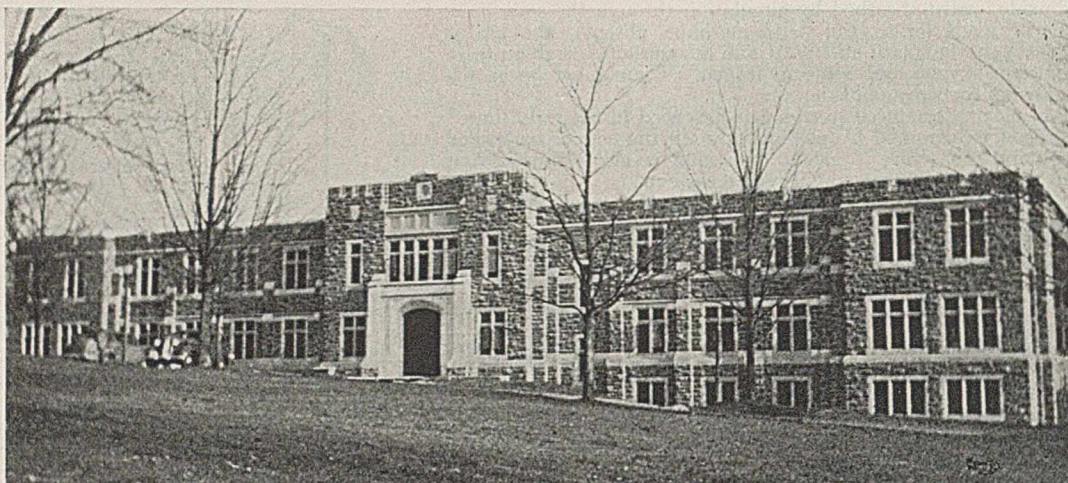
As examples of the results obtainable with this apparatus, analyses upon three synthetic mixtures are included. The samples range from 0.6 to 25 cu. mm. at 0° C. and one atmosphere. The original proportions were determined by measuring each gas in the calibrated pipet. The analyses of these mixtures indicate errors ranging from 2 per cent on the larger samples to 5 per cent on the smaller, the smallest sample showing errors of 7 per cent.

These results are shown in Table I. Mixtures 1 and 2 were analyzed using the Toepler pump technique, while mixture 3 was manipulated using the miniature diffusion pump.

The errors seem due to the adsorption and desorption of gases on the apparatus, particularly the powdered reagents, and therefore increase progressively with decreasing size of the sample. This is evidenced by the appearance of nitrogen which is absent from the synthetic mixtures. Correction could be made for this systematic error in nitrogen, but this has seemed hardly justified, since other errors are of the same order of magnitude.

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CHEMICAL ENGINEERING BUILDING AT THE VIRGINIA POLYTECHNIC INSTITUTE

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THE new chemical engineering building at the Virginia Polytechnic Institute opened for undergraduate and graduate instruction at the beginning of the fall quarter of the 1938-39 session. The new structure, with exterior wall of local blue limestone, adjoins the present geology, physics, and chemistry building, known as Davidson Hall, conforming in architecture and construction.

The size, shape, and interior arrangement are shown in the floor plans. The building is rectangular, with one section three stories high, and the other with a headhouse or room extending open to the same level as the three-story section. The building provides 11,416 square feet of laboratory, office, classroom, storage, and library area. The over-all dimensions are 171 × 35 × 31 feet, and cost \$76,000 or 41 cents per cubic foot. This includes plumbing, heating, ventilating, and electrical work, and process piping. The present installed equipment value approximates \$31,000.

The interior of the building is of 3-inch cinder block and concrete, with some rooms finished with cement-sand plaster, followed with three coats of paint. The cinder block provides an inexpensive acoustic material for the walls. The floors are of reinforced concrete, surface-treated to prevent dusting.

Unit Operations Laboratory

This laboratory, in which permanent equipment is erected, has a ground floor area of 2330 square feet and a balcony area of 400 square feet. The ground floor is provided with concrete floors 6 inches thick and three lines of floor drains running the length of the laboratory; the drains are covered with removable cast-iron grid covers 1 × 2 feet; the floors slope to the drains with a pitch of 1 inch in 8 feet. The open area, extending up to the 31-foot level, is approximately 32 feet wide and 56 feet long, with a rolling bridge on a track at the 25-foot level. This bridge is constructed to support a 5-ton load, a beam-trolley permitting attachment of hoists; the flooring on the bridge makes it also a work area. On the walls inserts are placed on 4-foot centers for attachment of equipment and intermediate supports. There are no windows on the lower portion of the side and end walls, the lower edge of the first level of windows being at the 12-foot level. The upper bank of windows is on the balcony level.

Service provided in this area consists of high- and low-pressure steam, hot and cold water, high- and low-pressure air, gas, and power lines. The process lines run at the 17-foot level underneath the balcony and service the equipment from that level; all piping service is overhead in this area.

A section of this laboratory is enclosed for grinding equipment. A dust collector and a fume fan provide clean air for grinding room; this provides for 35 air changes per hour. The crushing and grinding equipment housed in the grinding room consists of a ball mill, a hammer mill, a disk mill, a jaw crusher, a standard shaking machine, and a Williams roller mill with complete dust-separation equipment.

Around the remainder of the laboratory are located the following:

Filter area with 18-inch Sperry plate and frame press, a 24-inch stoneware vacuum filter, a 500-, 100-, and 42-gallon sedimentation system, a Feinc continuous filter, and a 6-foot Dorr double-tray thickener; still and 15-plate fractionating column; batch vacuum still; Pyrex heat exchanger with fluid flow assembly combined; triple-effect evaporator with one 24-inch diameter vertical-tube effect, one 88-tube horizontal-tube effect, and one 10-long forced-circulation-tube effect, the system capable of running under any modifications of feeds and order of effects; absorption tower assembly of stoneware, 24 feet high, 18 inches in diameter; drying area with a 12-tray atmospheric dryer, a Buflovac vacuum double-drum dryer, a 4-tray vacuum shelf dryer, and an experimental air-conditioned dryer; centrifugal area with a 26-inch basket centrifugal and a high-speed supercentrifuge; vacuum impregnator; water softener; 3 small open kettles of copper and cast iron; mixing kettles; two electric furnaces; two Hytor compressors; crystallization pans; and three-roll compounding mill.

The balcony is provided with steep sloped floors and drains, curbing, and subway grating sections which may be removed, so that equipment may be erected up through the balcony floor.

Two small blast heaters on the balcony and one large unit on the lower floor provide for movement of air and heating. Two powered ventilators in the roof assist in the removal of air from the laboratory. These units provide for 35 changes of air per hour.

Development and Projects Laboratory

The development and projects laboratory occupies 1300 square feet of the other end of the ground floor from the main

unit operations laboratory, at the same level and with the same drainage and floor construction. The height of this area is 10 feet with inserts in the ceilings and side walls at 4-foot centers. No permanent equipment setups are provided for this area. Senior research problems and development laboratory studies use this laboratory for the temporary assemblies; movable heavy oak laboratory tables, $8 \times 3 \times 3$ feet, are available. Three fume ducts assist in carrying away confined fumes through flues to the roof. Heating and ventilation of this laboratory are accomplished by means of an automatic blast heater connected with outside air at the end of the laboratory, carrying heat and air through the laboratory, through the center piping areas, thence into the main laboratory. This unit can be operated to provide 35 changes of air per hour.

Miscellaneous

GRADUATE RESEARCH ROOMS. Four research laboratories are provided on the second floor, above the development laboratory; these are approximately 10×23 feet in dimensions, provided with sinks, tables, desks, and floor drains. These provide for eleven men. Additional space for increased enrollment of graduate students is available in the connected section of adjoining Davidson Hall.

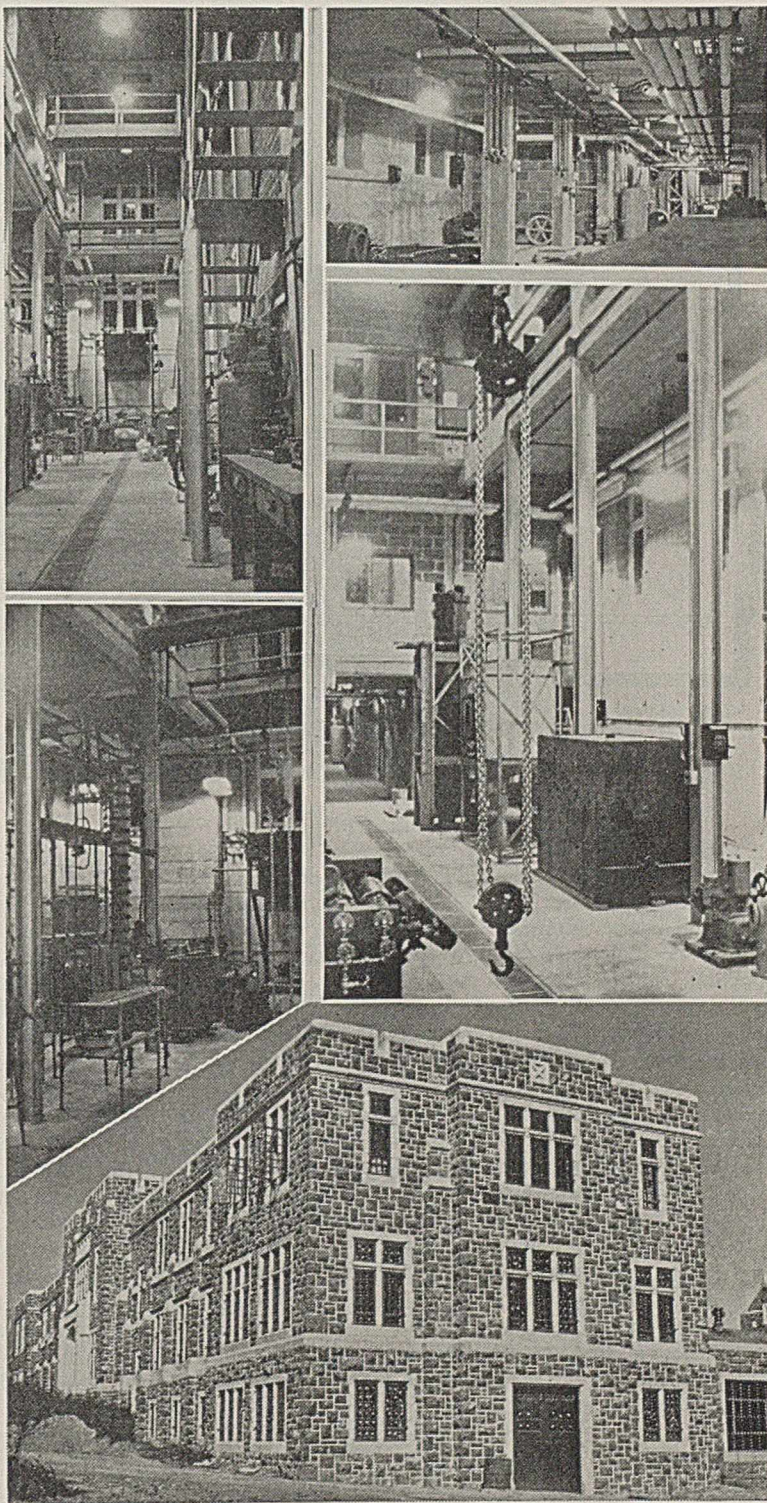
WORKSHOP AND PIPING AREA. The workshop and piping area are located on the ground floor, occupying a portion of the center section. A lathe, tool grinders, drill press, and appropriate tool cases are located there. In the piping area a rack holds various sizes of pipes. Here are also located a pipe work-bench with two pipe vises and a machine-bench with machine vises. A separate room for all fittings is located in this area.

STORAGE AND INSTRUMENT ROOMS. The chemical storage is located on the ground floor in the central section and provides 10×14 feet of floor space. A flue keeps the air fresh. The instrument room is located next to the chemical stores and opens upon

the main laboratory. A second instrument room is provided on the second floor.

OFFICES. The main office is located on the second floor, near the main entrance, and overlooks the main unit operations laboratory; the three smaller offices are located on the third floor, readily accessible to the classrooms and the balcony.

CLASSROOMS. The main classroom is located on the second floor and has a capacity of sixty students. The small classroom is located in the center of the third floor and

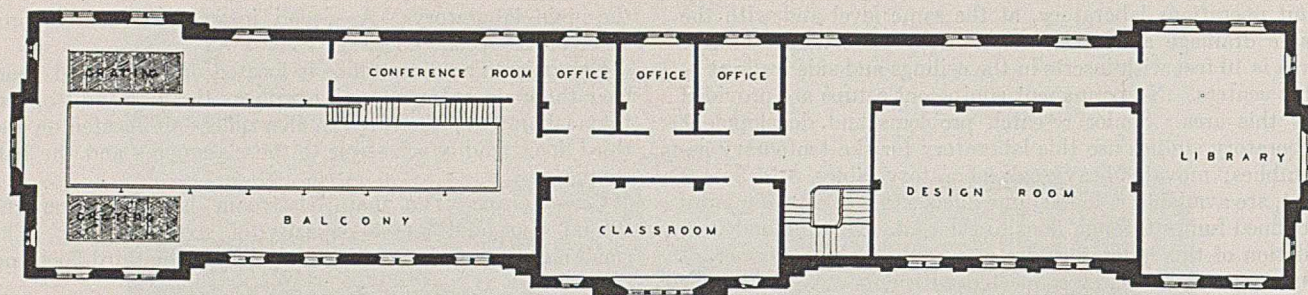


Upper left and left center. VIEWS OF UNIT OPERATIONS LABORATORY

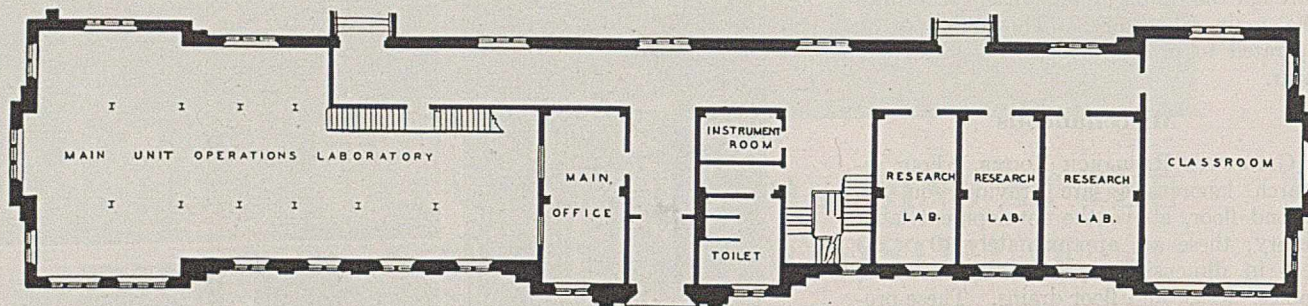
Upper right. SENIOR PROJECTS AREA

Right center. UNIT OPERATIONS LABORATORY, WITH CRANE IN FOREGROUND

Bottom. EXTERIOR, FACED WITH NATIVE LIMESTONE AND TRIMMED IN WHITE ARTIFICIAL STONE



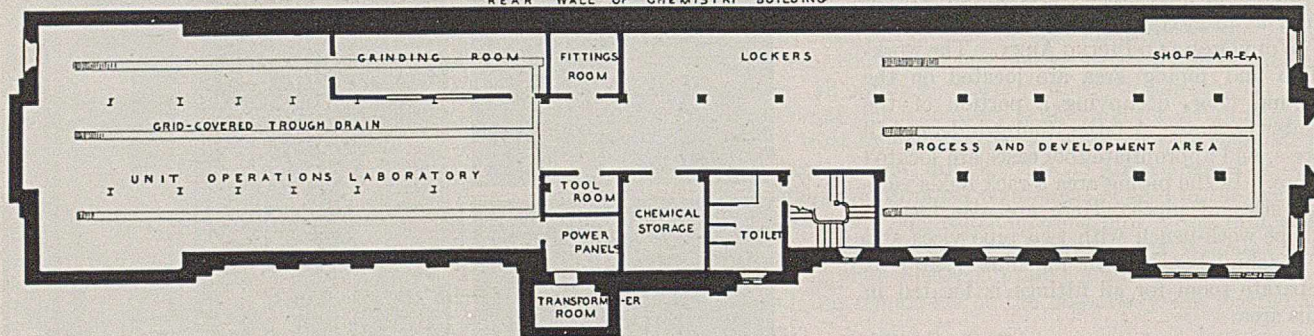
SECOND FLOOR PLAN



SCALE: 1/8" = 1'

FIRST FLOOR PLAN

REAR WALL OF CHEMISTRY BUILDING



GROUND FLOOR PLAN

accommodates thirty students. The design room is fitted with twenty desks for design, the class being conducted on a section basis; this room also serves as a classroom. The conference room is located over the corridor and accommodates from four to eight men.

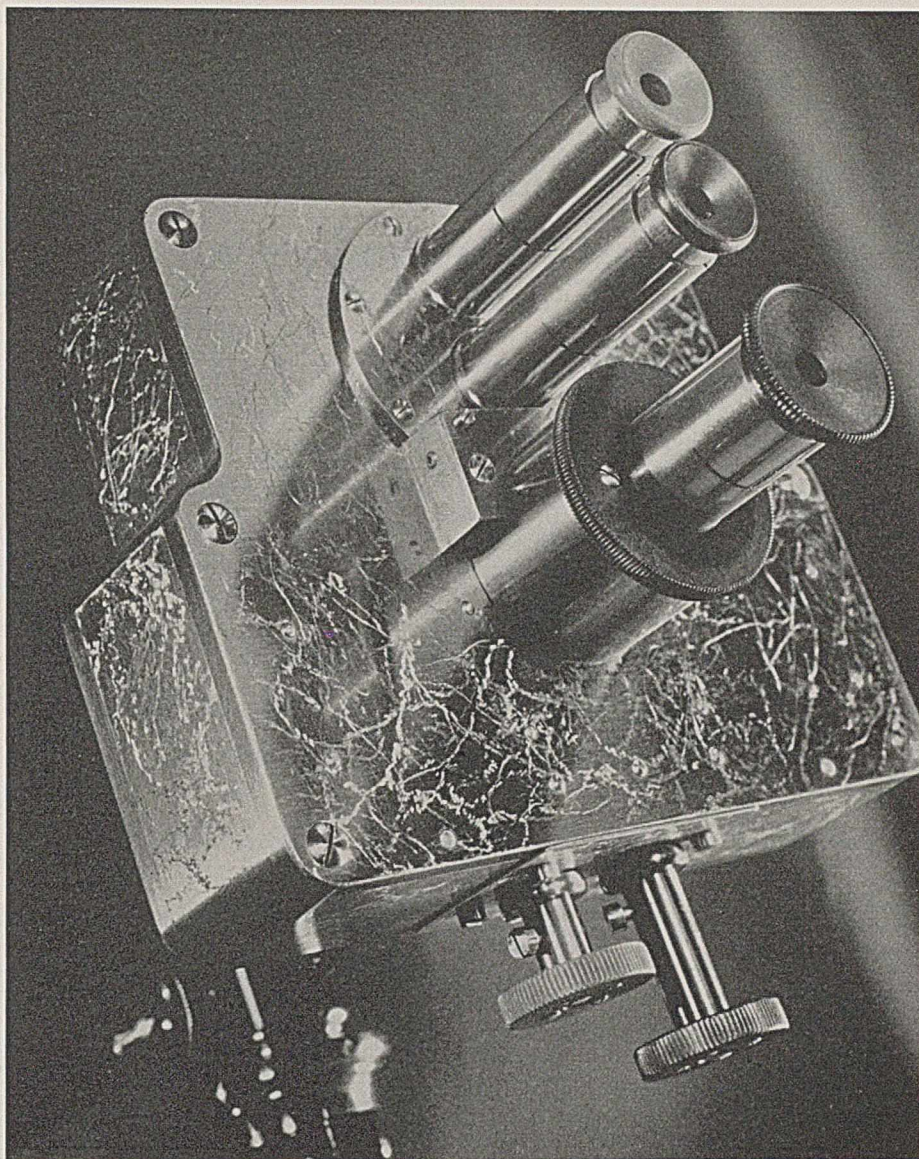
Heating of small rooms and classrooms is carried out by low-pressure steam radiators. Corkboard bulletin boards are provided on each floor; blackboards in all classrooms; and hat and coat racks on each floor.

LIBRARY AND STUDY HALL. The library is located on the third floor and is the same size as the large classroom which is located directly underneath it. It is provided with six cases with 30 feet of books each. Four study tables, 8 feet long and 3 feet wide, provide the facilities for reading and study and also serve for conferences. A 24 drop-leaf compartment periodical case with current issues is also provided.

ELECTRICAL SERVICE. Electrical service for the building is taken from the campus underground system into the transformer room, at 2300 volts, 3-phase, 60-cycle. Three 75-kva. transformers are connected in delta in the primary side and star connected on the secondary to give a 4-wire, solid neutral service with 208-volt single-phase, 208-volt 3-phase, or 120-volt single-phase from any phase to ground. The Busway system of power lines is used to distribute the service to

all parts of the laboratories. Boxes are provided at 16-foot intervals to permit additional servicing; at present 3-way 120-volt plugs are placed at 4-foot intervals and safety switches for from 3 to 10 horsepower at 8-foot intervals on laboratory walls and columns. Each set of four 208-volt safety switches and each set of eight 120-volt 3-way plugs are provided with dead-front "no fuse" circuit breakers. All equipment and the plugs are grounded through a ground wire in the system. The general lighting system is provided on a separate system; solaire light fixtures are provided in the offices, classrooms, and library, and dome fixtures in the laboratories.

PROCESS PIPING. The process piping, consisting of 60-pound, 15-pound, and 1-pound-gage steam, hot and cold water, air, and gas are installed in the overhead all-exposed manner. Service cocks and valves are provided at 8-foot intervals in all working areas. In the large laboratory the piping for each piece of equipment is taken off the central balcony lines down to the equipment, eliminating any cross lines over the working areas. The main supply lines are as follows: 1.5-inch for 60-pound, 3-inch for 15-pound, and 4-inch for 1-pound-gage steam pipe; 2-inch soldered-fitted copper water pipe, hot and cold; 1.25-inch gas and air black iron pipe. All fittings on the water lines are stream-lined soldered.



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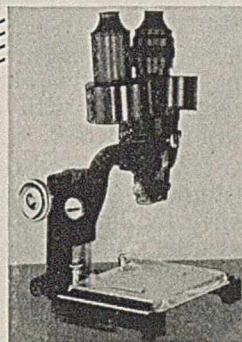


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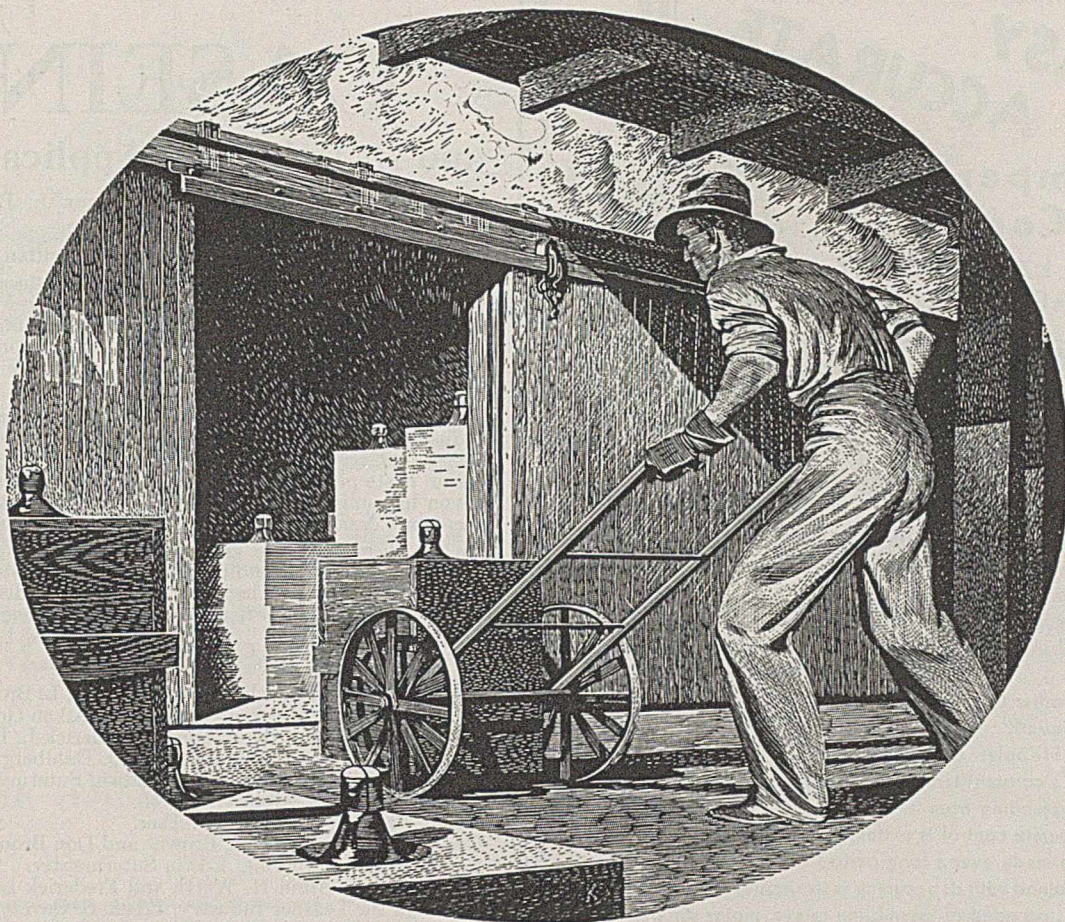
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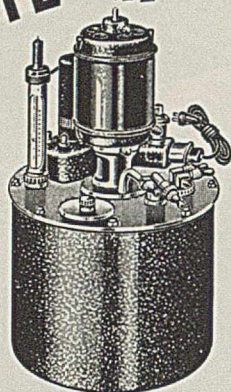
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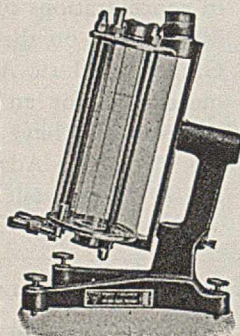
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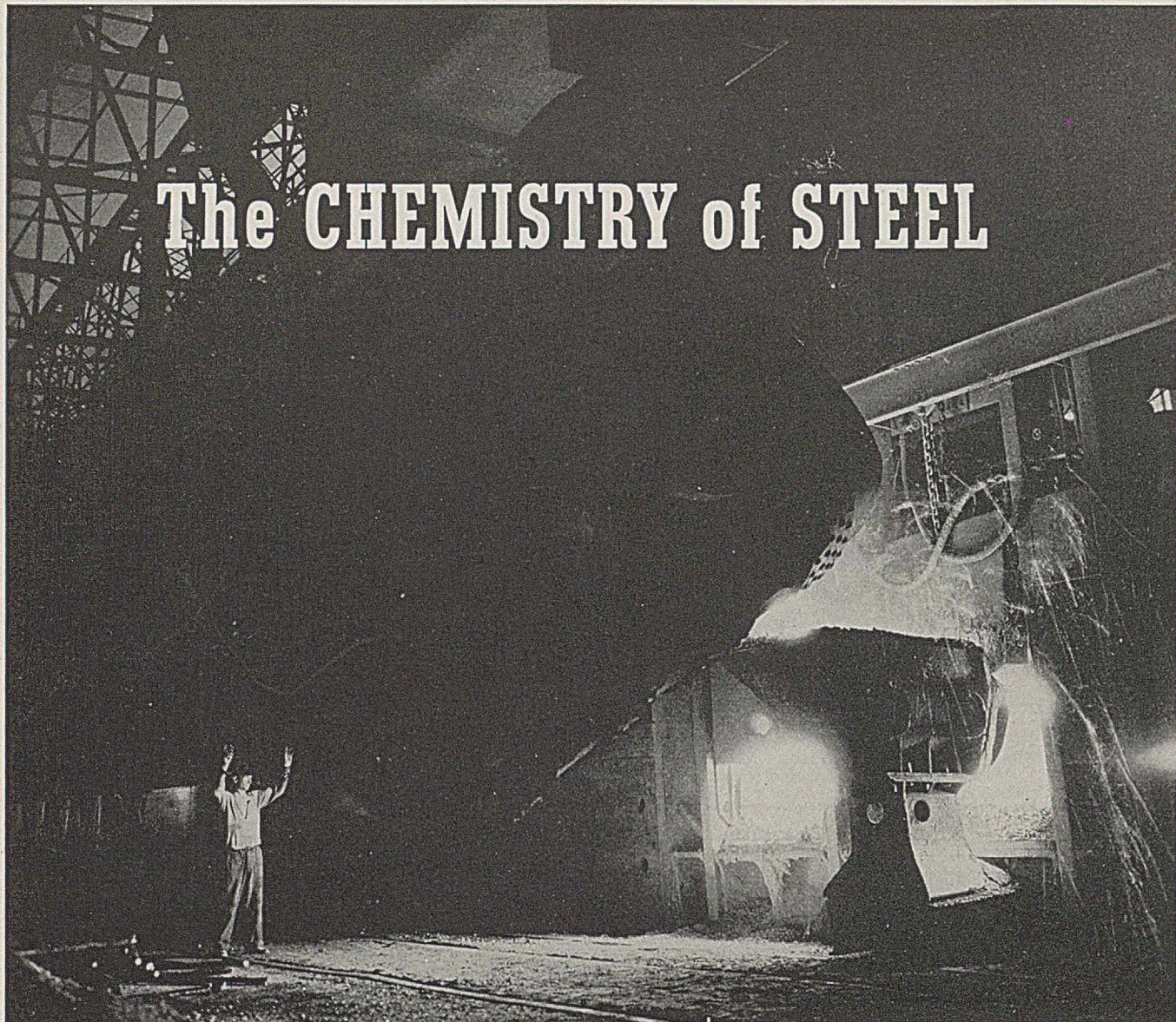
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