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854 67 TIL B. L. CLARKE T. R. CUNNINGHAM	G. E. F M. G. 1	LUNDELL R. H. MÜLLER MELLON H. H. WILLARD	TECHINI
	the factor of	Concentration Internation of the International Concentration of the International Concentrational Conce	2
Systematic Polarographic Metal Analysis James J. Lingane	147	Chromatographic Determination of Carotene in Alfalfa L. W. Charkey and H. S. Wilgus, Jr.	184
Determination of Sulfur Dioxide in Dehydrated Foods A. N. Prater, C. M. Johnson, M. F. Pool, and G. Mackinney	153	Determination of Manganese after Oxidation to Tri- Dihydrogen Pyrophosphatomanganiate J. I. Watters and I. M. Kolthoff	187
Determination of Sodium in Potassium Hydroxide Dwight Williams and George S. Haines Refrective Index-Dw Substance Tables for Starch	157	Determination of Vitamin A and Carotenoids in Butterfat . F. P. Zscheile, R. L. Henry, J. W. White, Jr., H. A. Nash, C. L. Shrewsbury, and S. M. Hauge	190
Conversion Products J. E. Cleland, J. W. Evans, E. E. Fauser, and W. R. Fetzer	161	Adaptor for Angle Centrifuge Tests W. E. Baier	193
Determination of Zinc in Cyanide Brass-Plating Baths A. S. Miceli and I. O. Larson	165	Titrimetric Determination of Zinc	194
Determination of Sesamin	166	Determination of Total Phthalic Anhydride in Oil- Modified Alkyd Resins A. I. Goldberg	198
Determination of Camphor and Alcohol in Spirit of Camphor by Refractive Index and Specific Gravity		Determination of Total Phthalic Anhydride in Modified Alkyd Resins C. D. Doyle	200
Elmer M, Plein and Charles F. Poe	168	Constant-Level Float Valve Wilburn A. Boggs	201
Precision and Accuracy of Colorimetric Procedures as Analytical Control Methods	169	Hot Distilled Water Reservoir Wilburn A. Boggs	201
Flow Characteristics of Dispersions of Cotton and Regenerated Cellulose Rayon Fabrics in Cupram- monium Viola C. Jelinek	172	MICROCHEMISTRY Mineral Contamination Resulting from Grinding Plant Samples	202
Antimony Trichloride Reaction of Vitamin D Edgar M. Shantz	179	Glass Electrode Assembly for Titrating Micro- biological Vitamin Assays	
Versatile Liquid-Liquid Extractor W. D. Long	180	E. B. McQuarrie and H. J. Konen	205
Elimination of Nitrate Impurities from 30 Per Cent Hydrogen Peroxide E. C. Cantino	181	Chlorometry. Titrimetric Procedure Available for Microanalysis	206
Operating Procedure for Determining Heat of Combustion of Gasoline	182	Thiosulfate Washers in Alkoxy Microdetermina- tions E. P. White	207
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INDUSTRIAL AND ENGINEERING CHEMISTRY PUBLISHED BY

THE AMERICAN CHEMICAL SOCIETY Unalytical Edition

Systematic Polarographic Metal Analysis

Analysis of the Copper Group with the Aid of Electrolytic Separations

JAMES J. LINGANE

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Mass.

The best supporting electrolyte for the simultaneous polarographic determination of copper, bismuth, lead, and cadmium contains 0.4 M sodium tartrate, 0.1 M sodium hydrogen tartrate, and not more than 0.005% gelatin as a maximum suppressor. Concentrations of gelatin larger than 0.03% obliterate the bismuth wave. When one or more of the nobler members of the group predominates and thus interferes with the polarographic determination of the others, the interfering constituents may conveniently be removed by electrol-

ONE of the most attractive features of the polarographic method as applied to metal analysis is that relatively few physical separations are necessary, and interferences can be eliminated in many instances simply by proper choice of supporting electrolyte (2, 4). However, in a systematic scheme that provides for the detection and determination of a dozen or more metallic elements, a few preliminary group separations are a practical necessity; otherwise interferences become too numerous to be circumvented simply by changing supporting electrolytes.

It is fortunate that the hydrogen sulfide and ammonium sulfide groups of the classical qualitative analytical scheme happen to be at least as, or more, amenable to subsequent polarographic analysis than any other two combinations of the metals concerned, and separation into these groups will be employed in the systematic polarographic scheme that is being developed in this laboratory. Furthermore, in the analysis of the hydrogen sulfide group it is planned to follow classical procedure through one more stage and separate the sulfides by extraction with strongly alkaline sulfide solution into a copper group (copper, bismuth, lead, and cadmium) and a tin group (tin, antimony, and mercury), because this simple separation greatly facilitates subsequent polarographic determinations and creates a maximal number of opportunities for simultaneous determinations.

The general polarographic characteristics of the metals of the hydrogen sulfide group in various supporting electrolytes were discussed in the first paper of this series (4), which also described a simplified method of computing concentrations by the use of previously determined diffusion current constants. The present paper presents detailed information concerning optimum conditions for analysis of the copper group, and describes an electrolytic procedure for separating interferingly large amounts of the nobler members of the group from small amounts of the baser members prior to the determination of the latter.

OPTIMUM CONDITIONS FOR POLAROGRAPHIC ANALYSIS OF THE COPPER GROUP

The general characteristics of the waves of copper, bismuth, lead, and cadmium in a number of supporting electrolytes, and the technique of the polarographic measurements, have been discussed (4). When all members of the group are present an ysis with a mercury cathode at a carefully controlled potential, and the minor baser metals are then determinable in the residual solutions. A mercury cathode is uniquely advantageous for electrolytic separations because the optimum values of the cathode potential may be deduced reliably from the known polarographic characteristics of the metals to be separated. An apparatus and technique for performing such separations are described in detail, and the efficiency of the method is illustrated by typical examples.

WALTER J. MURPHY,

EDITOR

acidic tartrate solution is the only supporting electrolyte of those investigated in which their half-wave potentials differ sufficiently to permit their simultaneous determination. The use of a tartrate supporting electrolyte for the simultaneous determination of copper, bismuth, lead, and cadmium was recommended originally by Suchy (7), who published polarograms showing wellseparated waves of these metals in strongly alkaline as well as acidic tartrate media. The writer has never been able to duplicate the satisfactory polarograms from alkaline tartrate media reported by Suchy. According to the author's experience (4) copper and bismuth do not produce satisfactory waves in alkaline tartrate solutions although lead and cadmium do, and an acidic tartrate medium must be employed for the simultaneous determination of all members of this group. When all four metals are present the optimum pH range of the tartrate supporting electrolyte is between about 4 and 4.5.

At a pH equal to or smaller than that of a pure sodium hydrogen tartrate solution (ca. 3.6) the copper and bismuth waves tend to coalesce, and in solutions of pH much greater than about





Mixture of ca. 0.8 millimolar copper, bismuth, lead, and cadmium, in tartrate media of various pH values. Total concentration of sodium tartrate and sodium hydrogen tartrate was 0.5 M, and the pH values were (a) 5.5, (b) 4.5, (c) 4.1, and (d) 3.6.

5, the bismuth wave is not well developed when gelatin is used as a maximum suppressor. These facts are demonstrated by the series of polarograms in Figure 1.

Curve a was obtained with a solution that contained approximately 0.8 millimolar copper, bismuth, lead, and cadmium, in 0.5 M sodium tartrate containing 0.02 M sodium hydrogen tartrate, 0.1 M sodium chloride, and 0.005% gelatin as a maximum suppressor (pH 5.5). Curves b, c, and d were recorded after successive additions of a standard nitric acid solution, so that solution b contained 0.4 M tartrate ion and 0.1 M hydrogen tartrate ion (pH about 4.5), solution c contained 0.3 M tartrate ion and 0.2 M hydrogen tartrate ion (pH about 4.1), and solution d corresponded to 0.5 M sodium hydrogen tartrate (pH about 3.6). The decrease in the wave heights from a to d resulted from the dilution produced by the addition of the nitric acid, and not from a change in the diffusion current constants.

The half-wave potentials and other characteristics of the copper, lead, and cadmium waves are not altered very much by changes in pH between about 3.6 and 6 in these tartrate media, but the half-wave potential of bismuth undergoes a pronounced shift to a more positive value with decreasing pH. The halfwave potential of bismuth decreases from -0.31 volt at a pH of about 5.5 (curve a) to -0.17 volt at a pII of about 3.6 (curve d), whereas the half-wave potentials of the other metals decrease by only about 0.03 volt. Consequently, with decreasing pH below about 5 the bismuth and lead waves become better separated but the copper and bismuth waves approach coincidence. The best supporting electrolyte for the simultaneous determination of all four metals when they are present at about equal concentrations is one containing about 0.4 M tartrate ion and 0.1 M hydrogen tartrate ion, corresponding to curve b in Figure 1. In this supporting electrolyte, and in the presence of 0.005% gelatin (see below), the half-wave potentials of copper, bismuth, lead, and cadmium are, respectively, -0.09, -0.23, -0.48, and -0.64 volt vs. the saturated calomel electrode, and their diffusion current constants (4) are 2.37, 3.12, 2.37, and 2.34 microamperes per millimole per liter at 25° for $m^{2/3}t^{1/6} = 1$. These latter values may conveniently be used, instead of individual calibrations with known solutions in every case, to compute concentrations from observed diffusion currents (4).

For the determination of a small amount of copper in the presence of a very large amount of bismuth, a somewhat larger ratio of tartrate ion to hydrogen tartrate ion than 4 to 1 is preferable (curve a, Figure 1).

The concentration of gelatin used as a maximum suppressor has a very marked effect on the properties of the bismuth wave, as shown in Figure 2. Without gelatin (curve a) the bismuth wave shows a sharp maximum, although the other waves are fairly well developed. With 0.005% gelatin (curve b) all four waves are well defined, but with 0.01% gelatin the bismuth wave becomes flattened and a definite diffusion current plateau is not observed before the reduction of lead begins (curve c). With 0.03% gelatin (curve d) the bismuth wave is obliterated completely, and the diffusion currents of lead and cadmium are greatly suppressed. The suppressive effect of gelatin on the waves of other metals has been noted before (2). When bismuth is present the concentration of gelatin should not exceed 0.005%, and even if bismuth is absent it should not be larger than 0.01%. In spite of this one undesirable quality, gelatin remains one of the best and most generally applicable maximum suppressors when it is used with discretion.

Moderate concentrations (up to about 0.2 M) of sodium nitrate or sodium chloride, which may accumulate in practical analyses, have no appreciable influence on the properties of any of the waves when the total concentration of sodium tartrate and sodium hydrogen tartrate is 0.5 M. More than small amounts of potassium salts cannot be present in the acidic tartrate solutions because of the limited solubility (ca. 0.03 Min pure water) of potassium hydrogen tartrate.

When a large-e.g., 0.01 M-concentration of lead is added

Vol. 16, No. 3

to an acidic tartrate solution it partly precipitates, apparently as lead hydrogen tartrate. From measurements of the diffusion current of the lead in equilibrated solutions the solubility of the precipitate was found to be $1.77 \times 10^{-3} M$ at 25° C. in a solution containing 0.4 M sodium tartrate and 0.1 M sodium hydrogen tartrate. However, the precipitate readily forms supersaturated solutions which are quite stable, and it is possible to work with concentrations of lead up to about 5 millimolar if the polarographic measurements are made within about an hour after the solutions are composited. For example, in one instance a solution containing 9.1 millimolar lead ion was stable for over an hour and a half at 25° C. with nitrogen bubbling through it, but when precipitation was induced by seeding and scratching the glass wall of the cell it proceeded rapidly, and solubility equilibrium was attained after about 10 minutes.

COMBINATION OF ELECTROLYTIC SEPARATIONS WITH POLAROGRAPHIC ANALYSES

It is evident that a single polarogram from an acidic tartrate supporting electrolyte will suffice for the simultaneous determination of all members of the copper group when they are present at very nearly equal concentrations, but in actual practice such an ideal situation cannot be expected, and a generally applicable systematic scheme of analysis must provide for those instances where one or more of the group predominates and thus interferes with the determination of the others. The predomination of a less noble metal, such as lead, will not interfere with the determination of a more noble metal, such as copper, because the wave of the latter is well in advance of that of the former, and traces of copper can be determined in the presence of an excess of bismuth, lead, or cadmium. In general, when the concentrations increase in the order copper, bismuth, lead, cadmium, a complete analysis of the group can be achieved by simply recording four polarograms of the same solution with successively smaller galvanometer sensitivities, so as to magnify in turn the wave of each constituent to a value which will allow accurate measurement. In the opposite case, when the concentrations decrease in the order copper, bismuth, lead, cadmium, the larger waves of the nobler metals prevent accurate measurement, or in extreme cases even the detection, of the smaller waves of the baser metals, and it is then necessary to eliminate the waves of the nobler metals.

There are three possible methods that might be used to eliminate the interference of the intrinsically nobler metals: (1) physical separation by precipitation, distillation, extraction,



Figure 2. Influence of Gelatin

Mixture of ca. 0.8 millimolar copper, bismuth, lead, and cadmium, in acidic tartrate medium of pH 4.5. Concentrations of gelatin were (a) 0, (b) 0.005, (c) 0.01, and (d) 0.03%. March, 1944

or electrodeposition; (2) changing the supporting electrolyte so that the order of the waves is reversed (usually as a re-sult of complex ion formation); and (3) "compensation" of the large diffusion current of the nobler metal by the application of a controllable counter e.m.f. to the recording galvanometer, so that the sensitivity may be increased to record the wave of the baser minor metal (2, 5). All these methods have been used, although only the first two have real practical utility. The compensation method is attractive in principle, but has only limited practical application because large galvanometer oscillations persist when the nobler diffusion current is balanced out; such oscillations are only partly eliminated by "condenser damping" (5), and it is not advisable to reduce their magnitude by simply decreasing the drop time to a small value, because, as will be



Figure 3. Cell for Electrolytic Separations at Controlled Potential with a Mercury Cathode

shown in a forthcoming paper, the diffusion current deviates significantly from the Ilkovič equation when the drop time is less than about one second.

Of the physical methods of separation, precipitation methods have been the most popular, but they suffer from two disadvantages which in certain cases are serious. In the first place loss of the minor constituents by coprecipitation is an everpresent hazard, and secondly the introduction of the precipitating reagents frequently complicates the analysis of the solution remaining.

The author found that electrodeposition at controlled cathode potential constitutes an excellent and generally applicable means of separating metals prior to polarographic analysis. The electrogravimetric separation and determination of metals by controlled potential have been developed to a high degree of practical utility, chiefly by the excellent investigations of Sand and his collaborators (β), but have not hitherto been applied in conjunction with polarographic analysis.

The separation of metals by electrodeposition is not without disadvantages. From a theoretical viewpoint the objection may validly be raised that an "absolutely complete" separation can never be attained, chiefly because of the exponential relation between the concentration of a metal ion and the potential of the cathode on which it is depositing, and the fact that the cathode potential must necessarily be limited to prevent the codeposition of baser metals. However, this objection has only academic interest as far as the application of electroseparations to polarographic analysis is concerned, because complete separation is not required and it is only necessary to reduce the concentration of the interfering nobler metal to a value commensurate with that of the baser metal. Electroseparations also require special apparatus, which, however, is simple and easily available. These slight disadvantages are overshadowed by the fact that once the apparatus is assembled it can be applied to numerous separations, and by the further fact that separations are achieved rapidly with a minimum disturbance of the composition of the solution and without introducing extraneous reagents.

A mercury rather than a solid metal cathode has been used in the present investigation in order to capitalize on the fact that the current-voltage curves that are obtained polarographically with the dropping electrode provide all the information that is necessary about the potential to which the cathode must be controlled to affect electroseparations, and thus a laborious, empirical establishment of optimum conditions is avoided. Although mercury cathodes have long been used in electrogravimetric analysis, apparently they have not heretofore been employed in determinations or separations at a controlled cathode potential, since no reference to such usage is to be found in the comprehensive bibliography (up to 1936) published by Böttger (1), nor in Sand's monograph (6) published in 1940.

The cell used is shown in Figure 3. It has a capacity of about 75 cc., and is provided with a two-way stopcock in the bottom for the introduction and withdrawal of the cathode mercury from the reservoir, and for withdrawing the solution after electrolysis. The mercury pool cathode has an area of about 10 sq. cm. and the mercury-solution interface (not merely the solution) is kept in rapid motion by the propeller-type glass stirrer.

The necessity of providing efficient stirring cannot be overemphasized, because it is the factor which is chiefly responsible for the rate of deposition (current density) that can be obtained at a controlled potential. The stirring must be effective enough practically to eliminate concentration polarization at the mercury cathode, as otherwise the current density is more or less controlled by diffusion and is too small to permit separations in a reasonable time. It is not sufficient mercly to stir the solution, however vigorously. The stirrer should be placed so that its blades are partly immersed in the mercury as shown in Figure 3, and the rate of stirring adjusted so that the interface is set in rapid circular motion without being so violent that drops of mercury are thrown about. The stirrer blades should be propeller-shaped, and so inclined that they impel downward rather than upward. Under these conditions of stirring the surface of the mercury undergoes vigorous but smooth churning and the entire pool revolves.

The cathode mercury or amalgam can be used repeatedly, provided that the metals previously deposited in it are more noble than the metal being separated—for example, mercury which contains copper can be used subsequently for the separation of bismuth, or if it contains copper and bismuth it may be used later in the separation of lead. Conversely, the mercury cannot be re-used when it contains a metal that is less noble than the metal being separated. For instance, mercury which has previously been used to separate bismuth or lead cannot later be used to separate copper, because at the relatively positive potential at which copper is deposited (-0.15 to -0.17 volt) the bismuth or lead undergoes anodic dissolution and contaminates the solution (see Figures 1 and 2). To avoid the use of excessive quantities of mercury and its frequent purification, it is convenient to keep the used mercury separated in three lots: one containing only dissolved copper and used only for copper separations, the second containing only copper and bismuth for copper and bismuth separations, and the third containing copper, bismuth, and lead. By keeping these three portions of mercury in contact with solutions of mercurous nitrate in dilute nitric acid the concentration of dissolved metals is kept small, and the dilute amalgams can be re-used indefinitely.

The cell was provided at first with a platinum anode, but this proved unsatisfactory for separations of copper from bismuth in an acidic tartrate medium because the bismuth was partially oxidized at the anode (probably to Bi_2O_6) and precipitated. Attempts were made to prevent the oxidation of bismuth by adding small concentrations (0.05 M) of hydrazine sulfate or hydroxylamine hydrochloride to the solutions as anodic depolarizers, but, although oxidation of bismuth was thus eliminated, polarograms of the solutions after electrolysis showed spurious waves that interfered with the waves of the metals. A platinum anode is also undesirable because it introduces hydrogen ion into the solution and decreases its pH. These difficulties were finally circumvented by the use of a silver anode. This consists of No. 18 silver wire wrapped as a tight cylinder (area ca. 10 sq. cm.) around the stirrer shaft and spiraled up the shaft to the motor chuck, where it is held in place by a wrapping of copper wire. Electrical connection is completed by dipping the copper leading-in wire into a mercury pool in the top of the motor shaft. The bottom of the anode should be about 2 cm. above the stirrer blades to prevent it from shortcircuiting the mercury cathode when the latter is stirred.

The solution to be electrolyzed is provided with a moderate concentration of chloride ion (0.1 to 0.2 M), so that the anode functions as a silver-silver chloride electrode, whose working potential is about 1 volt less positive than that of a platinum (oxygen) anode. Oxidation of bismuth and alteration of the pH of the solution are thus avoided, and the only effect of the anode reaction is the removal of chloride ion from the solution in amount equivalent to that of the metal deposited in the cathode.

Silver chloride is insoluble in an acidic tartrate medium and it deposits on the anode as an adherent coat. This coating reduces the effective area of the anode and increases the cell resistance (indicated by the necessity of increasing the total applied e.m.f. to maintain a constant cathode potential as electrolysis proceeds), and hence it is advisable to remove it after each experiment by electrolytic reduction from a dilute sulfuric acid solution in conjunction with a platinum anode.



Figure 4. Electrical Circuit for Electrolytic Separations at Controlled Cathode Potential

A, ammeter (0 to 0.5 ampere). V, voltmeter G, galvanometer (0.01 microampere per mm.) S.C.E., saturated calomel reference electrode

The potential of the mercury cathode is measured continuously against a saturated calomel reference electrode during electrolysis, and controlled by changing the total e.m.f. applied to the cell. The salt bridge side arm from the calomel electrode is filled with a 3% agar gel saturated with potassium chloride, and its tip is constricted slightly to hold the gel in place. The tip of the bridge must be placed within about 1 mm. from the mercury cathode when the mercury is at rest (see Figure 3), so that the amount of ohmic potential drop that is necessarily included in the observed cathode potential will be negligible. The most satisfactory results are obtained when the tip is so adjusted that it actually becomes immersed slightly and trails in the mercury-solution interface when the stirrer is in motion, but it must not dip so deeply into the mercury that electrolytic contact with the solution is lost. Proper location of the tip can be tested by placing a dilute copper amalgam in the cell in contact with a copper solution, and, with the polarizing e.m.f. disconnected, comparing the observed cathode potential with and without stirring: the two readings should agree to 0.01 volt

The electrical comparing the observed cathode potential with and without stirring; the two readings should agree to 0.01 volt. The electrical circuit is diagrammed in Figure 4. The e.m.f. applied to the cell is regulated by a single 10-ohm radio-type potentiometer-rheostat (General Radio Company, Type 333-A) and it is read on the voltmeter (0 to 6 volts). The voltmeter is a convenience rather than a necessity. A 0 to 0.5-ampere ammeter, graduated to 0.01 ampere, is used to measure the current.

The potential of the cathode vs. the saturated calomel reference electrode may be measured with a potentiometer, but it is much more convenient and amply accurate to measure it with a highresistance voltmeter as recommended by Lassieur (3) and Sand (δ). The author employed an improvised high-resistance voltmeter assembled from a critically damped Leeds & Northrup box-type galvanometer in series with a 0 to 5-megohm adjustable resistance. The galvanometer had a sensitivity of 0.01 microampere per mm., and thus the series resistance was about 1 megohm when it was adjusted to produce a full-scale (100-mm.) deflection with an impressed e.m.f. of 1 volt. The resistance of the instrument is so much larger than that through the salt bridge (ca. 700 ohms) that the error due to iR drop through the latter is only about 0.07% and hence negligible. Since the resistance of this voltmeter is so large it can be calibrated directly against a Weston standard cell (through a tapping key) without damaging the latter. The instrument was calibrated to read from 0 to 1 volt, and the readings were precise and accurate to ± 0.01 volt.

Incidentally, the Sargent-Heyrovský polarograph can be used as a high-resistance voltmeter and thus made to serve a dual purpose. The instrument is set at maximum galvanometer sensitivity (ca. 0.003 microampere per mm.) and provided with an external resistance of about 3 megohms which is adjusted so that 100 mm. on the scale corresponds to 1 volt.

Gelatin must not be present during an electrolytic separation with the mercury cathode, because, as a result of its adsorption on the mercury surface, it causes the stirred mercury to disperse into droplets and erratic current readings result. The current density at a given value of the cathode potential was decreased considerably by even 0.01% of gelatin. Care must be observed in discontinuing the electrolysis to

Care must be observed in discontinuing the electrolysis to prevent resolution of the deposited metal from the cathode. With the circuit still closed the mercury reservoir is lowered to drain the mercury from the cell, while the cathode potential is maintained constant at the value used during the deposition. When the mercury recedes to a point just above the stopcock the latter is turned through 180 °C. to drain the last bit of mercury from the cell quickly. The loss of some solution during this last operation is of no consequence, because the subsequent polarographic analysis determines concentrations rather than absolute amounts of the metal ions remaining; the absolute amounts are computed from the concentrations and the volumetric stoichiometry involved in preparing the solutions for electrolysis.

Not the least of the advantages of electrolysis at a controlled potential is the fact that the current reading is a reliable criterion of the progress of the separation. In all the cases investigated the current finally dropped to less than 10 milliamperes from initial values ranging from 100 to 500 milliamperes, depending on the original concentration of the metal ion being deposited (compare Figure 6). Little is gained by continuing the electrolysis longer than 5 or 10 minutes after the current decreases to 10 milliamperes or less.

In the separations and polarographic determinations described below, the supporting electrolyte consisted of 0.4 M sodium tartrate plus 0.1 M sodium hydrogen tartrate plus 0.1 M sodium chloride (occasionally also 0.1 M sodium nitrate), and it is referred to simply as the "standard acidic tartrate supporting electrolyte". Electrolytic separations were performed at ambient room temperature in the presence of air, but the polarographic analyses were carried out at 25° C. after air was removed from the solutions with nitrogen.

SEPARATION OF COPPER. Maximum rapidity of electrolytic separation of two metal ions requires that the potential of the



Figure 5. Analysis of Copper Group with Copper Predominating Original solution contained, respectively, 100, 2.52, 2.00, and 2.32 millimolar copper, bismuth, lead, and cadmium, and polarograms were obtained at 25°C with the standard acidic tarbate supporting electrolyte of pH 4.5 containing 0.005% gelatin. (a) 1 to 20 dilution of original solution, with galvanometer sensitivity 0.340 microampere per mm. (b) Residual solution from electrolysis of a 1 to 5 dilution of the original solution with potential of mercury cathode between -0.13 and -0.16 volt vs. S.C.E. Galvanometer sensitivity 0.0680 microampere per mm. (c) Comparison solution containing same concentrations of bismuth, lead, and cadmium, as were present before electrolysis in solution to. Galvanometer sensitivity 0.0680 microampere per mm. Each curve starts at 0 volt, and each voltage mark corresponds to an increment of 0.15 volt. mercury cathode be maintained at a value sufficiently negative to yield the diffusion current of the first, but, to avoid codeposition, the potential must be more positive than that at which reduction of the second metal ion begins. Polarograms of solutions of copper and bismuth in the standard acidic tartrate supporting electrolyte indicate that the optimum potential range for the separation of copper from bismuth should be from -0.12 to -0.16 volt vs. the saturated calomel electrode, and this has been confirmed experimentally.

A typical experiment in which a large amount of copper was separated from small amounts of bismuth, lead, and cadmium is demonstrated by the polarograms in Figure 5. A stock solution, simulating the sort of solution that would result from the solution of the copper group sulfides in nitric acid, was prepared containing, respectively, 100, 2.52, 2.00, and 2.32 millimolar copper, bismuth, lead, and cadmium, as the nitrates in 0.5 M nitric acid. Curve a in Figure 5 is a polarogram of a 1/20 dilution of the stock solution in the standard acidic tatrate supporting electrolyte. The waves of bismuth, lead, and cadmium are scarcely detectable in the presence of the 40-fold excess of copper.

Fifty cubic centimeters of a 1/5 dilution of the stock solution—i.e., 0.02 *M* in respect to copper—in the standard acidic tartrate solution were subjected to electrolytic separation as described above with the potential of the mercury cathode maintained between -0.13 and -0.16 volt. The current-time curve for this separation is shown in Figure 6, and is typical of all those obtained in other cases. Following an initial rapid decrease during the first 3 minutes, during which a steady state of electrolysis was established, the current remained constant up to about 10 minutes, and then decreased rapidly and finally gradually approached zero. The solution became colorless after 25 minutes and the electrolysis was stopped after 40 minutes i.e., 10 minutes after the current had fallen below 10 milliamperes. A 20-cc. sample of the residual solution was treated with 0.5 cc. of a 0.2% gelatin solution, and its polarogram was recorded as curve *b* in Figure 5. The galvanometer sensitivity for curve *b* is approximately five times greater than that for curve *a*, and the original concentrations of the metal ions were four times as great.





In addition to the well-defined waves of bismuth, lead, and cadmium, a small wave due to residual copper is present in the polarogram of the solution after electrolysis (curve b in Figure 5). This small wave corresponds to only 0.09 millimolar copper compared to 20 millimolar before electrolysis. In other words, the electrolytic separation was 99.5% effective, which is satisfactory, considering the fact that the half-wave potentials of copper and bismuth differ by only 0.20 volt. Obviously the small amount of residual copper does not interfere with the waves of the other metals.

To establish the fact that the other metals, particularly bismuth, were not codeposited with the copper during the electrolytic separation, a comparison solution was prepared in the standard acidic tartrate medium containing the same concentrations of bismuth, lead, and cadmium—i.e., 0.504, 0.400, and 0.464 millimolar—as were present originally in the solution before electrolysis. The polarogram of a 20-cc. sample of this com-



Figure 7. Analysis of Copper Group with Bismuth Predominating
(a) Original solution containing 1.04 millimolar copper, 10.07 millimolar bismuth, 0.400 millimolar lead, and 0.465 millimolar cadmium, in acidic tartrate supporting electrolyte of pH 4.5 containing 0.005% gelatin. Galvanometer sensitivity 1.70 microamperes per mm. (b) Polarogram of solution a repeated with galvanometer sensitivity 0.0680 microampere per mm. (c) Solution remaining after electrolysis of solution a with potential of mercury cathode between --0.35 and --0.40 volt va. S.C.E. Galvanometer sensitivity 0.0680 microampere per mm.
(d) Comparison solution containing same concentrations of lead and cadmium s. In solution a. Galvanometer sensitivity 0.0680 microampere per mm.

parison solution plus 0.5 cc. of 0.2% gelatin is shown as curve c in Figure 5. A comparison of the waves of bismuth, lead, and cadmium, in curves b and c shows that no appreciable amounts of these metals were codeposited with the copper. It is evident that successful results could be obtained with a larger proportion of copper to bismuth, lead, and cadmium than in this experiment, and it should be possible to determine considerably less than 1 mole % of any of the three other metals in copper and its compounds.

When, in the separation of copper from bismuth, the cathode potential is allowed to exceed -0.16 volt, bismuth is codeposited to an extent dependent on how greatly this limiting potential is exceeded. For example, in another experiment identical with the above in all respects except that the cathode potential was maintained at -0.18 volt, 14% of the bismuth was lost.

In the separation of copper from lead the cathode potential may be as large as -0.40 volt, which permits a larger current and correspondingly shorter time of electrolysis (for a given amount of copper) than in the separation from bismuth. Conditions are even more favorable in the separation of copper from cadmium.

At a given value of the cathode potential the initial current is approximately proportional to the concentration of the metal ion being deposited, and consequently the time required for a complete electrolysis is roughly the same regardless of the concentration. For example, the separation of copper at a cathode potential of -0.16 volt required 30 to 40 minutes when the concentration of copper ranged from a few millimolar up to 0.05 M.

SEPARATION OF BISMUTH. The analysis of the copper group when bismuth predominates is exemplified by the polarograms in Figure 7.

A stock solution was prepared containing 1.04 millimolar copper, 10.07 millimolar bismuth, 0.400 millimolar lead, and 0.465 millimolar cadmium, in the standard acidic tartrate supporting electrolyte. Curve a in Figure 7 is a polarogram of a 20-cc. sample of this solution to which 0.5 cc. of 0.2% gelatin was added. The copper wave is clearly discernible before the large bismuth wave, but the lead and cadmium waves are barely detectable. The wave of this relatively very large concentration of bismuth shows a small rounded maximum, and hence it would have been better practice to dilute the solution five-or tenfold before recording its polarogram. In order to magnify the copper wave for accurate measurement, the galvanometer sensitivity was increased by a factor of 25 and curve b was recorded.



Figure 8. Analysis of Copper Group with Lead Predominating Figure 6. Analysis of Copper Group with Lead Predominating Original solution contained 5.05 millimolar copper, 2.52 millimolar bismuth, 50.3 millimolar lead, and 2.32 millimolar cadmium. Polarograms obtained at 25° C. from acidic tartrate supporting electrolyte of pH 4.5 containing 0.005% gelatin (a) 1 to 20 dilution of original solution, with galvanometer sensitivity 0.170 microampere per mm. (b) Polarogram of solution a repeated with galvanometer sensitivity increased to 0.0340 microampere per mm. (c) Solution remaining after electrolyzing a 1 to 5 dilution of the original solution, with potential of mercury cathode between -0.54 and -0.56 volt us. S.C.E. Galvanometer sensitivity 0.0340 microampere per mm. (c) Comparison solution containing same concentration of cadmium as solution or before electrolysis. Galvanometer sensitivity 0.0340 microampere per mm.

A 50-cc. sample of the original solution was electrolyzed as described previously to remove the copper and bismuth. The electrolysis was started with the potential of the mercury cathode at -0.35 volt, and was gradually allowed to increase to -0.40volt and then held constant at this value until the electrolysis The electrolysis was continued for 40 minutes, during which time the current dropped from an initial value of 150 to 3 mil-liamperes. A 20-cc. sample of the residual solution was then treated with $0.5 \cdot cc$. of 0.2% gelatin, and curve c in Figure 7 was recorded at a relatively great galvanometer sensitivity. Only a trace (0.02 millimolar) of bismuth remained in the solution, and the separation was 99.8% complete.

Curve d (Figure 7) is the polarogram of a comparison solution containing the same concentrations of lead and cadmium (0.400and 0.465 millimolar) as were present in the original solution. By comparing curves c and d it is evident that no detectable amounts of lead or cadmium were lost during the deposition of the copper and bismuth.

The separation of bismuth from lead and cadmium is so complete that it should be possible to determine a few tenths of a per cent of the latter metals in bismuth and its compounds.

SEPARATION OF LEAD. A typical example of the analysis of the copper group with lead predominating is furnished by the polarograms of Figure 8.

A stock solution was prepared containing 5.05 millimolar copper, 2.52 millimolar bismuth, 50.3 millimolar lead, and 2.32 millimolar cadmium in 0.5 N nitric acid. A 1/20 dilution of this solution was prepared in the standard acidic tartrate medium, a 20-cc. sample was treated with 0.5 cc. of 0.2% gelatin, and polarograms a and b of Figure 8 were recorded. Curve a at the lower galvanometer sensitivity shows the waves of all four metals distinctly. Curve b was recorded at an increased gal-vanometer sensitivity to magnify the waves of copper and bismuth to measurable magnitudes.

A 50-cc. sample of a 1/5 dilution of the stock solution in A 50-cc. sample of a 1/5 dilution of the stock solution in the acidic tartrate supporting electrolyte was prepared and electrolyzed to remove copper, bismuth, and lead. When this solution was prepared a considerable proportion of the lead slowly precipitated as coarse crystals of lead hydrogen tartrate. The precipitate caused no trouble and gradually dissolved as electrolysis proceeded. The potential of the mercury cathode was maintained between -0.54 and -0.54wold the ontimum values indicated by the polenorement of lead volt, the optimum values indicated by the polarograms of lead and cadmium. The initial current was 100 milliamperes, it decreased to 8 milliamperes after 28 minutes, and the electrolysis was discontinued after 35 minutes. A 20-cc, sample of the residual solution was treated with 0.5 cc. of 0.2% gelatin, and curve c of Figure 8 was recorded. This polarogram shows that the residual solution contained a small amount of lead (0.24 millimolar), but since its wave is smaller than that of the cad-

mium it does not interfere with the measurement of the latter. By continuing the electrolysis for a somewhat longer time a more complete separation could doubtless be obtained, but this will be necessary only when the concentration of cadmium is very small.

Curve d in Figure 8 is a comparison solution containing the same concentration of cadmium (0.465 millimolar) as in the original solution, and by comparing this curve with curve bit is evident that no cadmium was lost during the deposition of the lead.

CONCLUDING REMARKS

In the application of the foregoing methods it is most convenient if the size of sample taken for analysis corresponds to not less than about 5 mg. nor more than about 500 mg. of any member of the copper group in a final volume of 100 cc.

Standard procedures may be used to prepare a solution of the sample, to remove silver and mercurous ions as the chlorides, to precipitate the hydrogen sulfide group, and to separate the copper and tin groups. The procedures described by Swift (8) are particularly suitable for these preliminary separations.

The washed copper group sulfides are dissolved in dilute nitric acid, and, after boiling to remove hydrogen sulfide and oxides of nitrogen, the solution is diluted to a known volume-e.g., 100 cc. An aliquot portion of this "copper group solution" is then made up to a known volume in the standard acidic tartrate medium with 0.005% gelatin (after either partial neutralization or addition of dilute nitric acid as required to provide a ratio of tartrate to hydrogen tartrate ion of 4 to 1). Polarograms of this solution are then recorded, and from those waves that are of measurable height the corresponding concentrations are computed with the aid of the known diffusion current constants as already described (4).

Those electrolytic separations dictated by the first polarogram are then carried out and the residual solutions are analyzed as described above. It is most convenient to use separate aliquot portions of the original copper group solution in the acidic tartrate supporting electrolyte for these separations. It is also advisable to perform separations of the nobler constituents, and polarographically test for the baser metals in the residual solutions, even though waves of the latter were not observed on the original polarogram, because traces of a baser metal may be completely masked by large amounts of a nobler metal (see Figure 5). Furthermore, such separations should be performed one at a time. For example, an original polarogram might show large copper and lead waves but no detectable bismuth wave if only a very small amount of bismuth were present. In such a case the cathode potential during the separation should not be more negative than -0.16 volt, so that only copper will be removed and any bismuth can be detected and determined from the polarogram of the residual solution.

The combination of electrolytic separations with polarographic analysis is obviously capable of general application in a systematic scheme of metal analysis, and it should prove useful for various special alloy analyses. Further examples of the utility of the method will be described in forthcoming papers.

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Determination of Sulfur Dioxide in Dehydrated Foods

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Details are presented of a rapid direct titration method for determining sulfur dioxide in dehydrated foods. The reliability of the method has been established by recovery of added sulfur dioxide and by comparison with distillation and polarographic methods.

A Control measure in the application of sulfite solutions to vegetables intended for dehydration, a simple method for determining the sulfur dioxide content has become necessary. The method proposed here has been designed for inspection and field work with a minimum of equipment but is also well adapted to laboratory research. It has been compared with other chemical methods and also the polarographic method.

The methods of Monier-Williams (10), an official A.O.A.C. method, and of Nichols and Reed (11) involve distillation of the sulfur dioxide into neutral hydrogen peroxide or standard iodine solution. Simultaneously with the publication of the Monier-Williams report, there appeared a series of reports on the determination of sulfur dioxide by a British committee and other contributors (2). The committee method, which includes rapid distillation of the sulfur dioxide into an iodine solution, is of limited application. The Nichols and Reed method, employing iodine, has been widely used in California on dried fruits.

The distillation methods are time-consuming and not well adapted to field work. In addition, with cabbage, onions, and other vegetables having a high volatile-sulfur content, abnormally high values are obtained on the unsulfited controls when the distillate is absorbed in iodine.

To eliminate many of the objectionable features of the distillation methods, direct titration of an aqueous extract either with or without preliminary clarification has been proposed. Liberation of bound sulfur dioxide by alkaline treatment forms the basis of the method, first described by Ripper (12). One may use the double titration technique in which one sample is titrated for total reducing substances and the other is treated to remove sulfur dioxide from the reaction. It can be oxidized to sulfate, or removed by formation of an addition complex. The latter method is preferable, in the authors' opinion, because there is less possibility of drastic change in the other constituents of the food, and the two titrations differ only with respect to one component—sulfur dioxide.

Two recent papers, one by Iokhel'son and Nevstrueva (3) and another by Bennett and Donovan (1), describe direct titration methods. In the former the dehydrated food material is treated with alkali solution to liberate the "bound" sulfur dioxide; the extract is clarified and then titrated with iodine to yield the total reducing substances. A similar sample is treated with formaldehyde to react with the sulfur dioxide present. Titration of this sample yields reducing substances other than sulfur dioxide, which is then calculated from the difference between the two titrations. This method, involving clarification, is time-consuming. The Bennett and Donovan procedure was developed for citrus juices which are used directly without extraction or clarification, and acetone is used instead of formaldehyde. Unfortunately, data on proper conditions for wider applicability of the method are not included.

The method described here is an adaptation of these direct titration procedures. The specific optimum conditions have been determined for each step of the analysis. For convenience, this modified Bennett-Donovan procedure is referred to as the direct titration method.

PREPARATION OF SAMPLE

Considerable care must be used in preparing the sample. A representative sample must be ground or subdivided into suffi-

ciently fine particles so that the solutions used will leach out all the sulfur dioxide. In the distillation methods the boiling process effectively disintegrates the tissue, even though relatively large pieces are placed in the still. The direct titration methods depend upon leaching action without heating and require the sample to be finely subdivided before analysis. Preferably a mill such as the Wiley mill with a 2-mm. screen should be used, in which the sample is ground until practically all has passed through the 2-mm. screen. A food grinder designed for preparing vegetable purees can be used, provided certain conditions as to load and time of grinding are adhered to, so that practically all the material passes a 10-mesh screen and at least 60% passes a 20-mesh screen. For the samples reported in this paper adequate subdivision was obtained by 1.5 minutes of grinding at high speed with a 30-gram charge of dehydrated shredded cabbage or a 100-gram charge of dehydrated diced carrots or potatoes. If large pieces of material are left unground, low results are obtained in the assay.

Dried fruits have physical characteristics different from those of dried vegetables and must be handled differently. By passage through a kitchen food chopper, followed by soaking and grinding in a food blender, it is possible to prepare uniform, finely divided suspensions of dried fruits for analysis. The presence of any lumpy material not finely divided will generally yield low analytical results.

ALKALINE LIBERATION OF BOUND SULFUR DIOXIDE

For each assay an 8-gram sample of the ground dehydrated material was suspended in 400 ml. of water, 5 ml. of 5 N sodium hydroxide were added, and the mixture was allowed to stand for 20 minutes. The amount of alkali needed is not critical in itself, but must be accurately measured. The quantity indicated gives a mixture sufficiently alkaline to release the bound sulfur dioxide, while four times as much yields the same result. The length of time necessary to liberate the sulfur dioxide was determined by comparing results over periods up to 60 minutes (Table I). No significant variation in sulfur dioxide liberation was found after 10 minutes up to 60 minutes. Twenty minutes was chosen as a convenient time.

Table 1. Effect of Time of Alkali Treatment on Liberation of Sulfur Dioxide

Length of Alkali	Suprairy off	Sulfur Dioxide	
Treatment	Cabbage	Carrota	Potatoes
Min.	P.p.m.	P.p.m.	P.p.m.
0 (no alkali treatment)	2020	1880	1410-
ALL MANUS DIE DE	2520	2060	
5	2860	2260	1960'
10	3020	2380	2100
20	3060	2400	2040
30	3060	COMPANY STREET,	27 62 725
40	3060	2400	2020
50	3040	not be they also do	USET MOTIFICS
60	3120	2400	2040

FORMATION OF ACETONE-SULFUR DIOXIDE COMPLEX

The effects of pH, acctone concentration, and reaction time on the formation of the complex were determined.

To study the effect of pH on the formation and stability of the complex, 8-gram samples in 400 ml. of water were treated with alkali for 20 minutes, acidified to different pH levels, treated, with 40 ml. of acetone, allowed to stand 10 minutes, and titrated with 0.05 N iodine solution. Minimum iodine titers represent reducing substances other than sulfur dioxide and indicate maximum binding of the sulfur dioxide. Table II shows that, maximum binding occurs in cabbage and carrots between pH.

Table II. E	Effect of	oH on	Stability	of A	cetone	Complex
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	0	.05 N Iodine Require	d
рН	Debydrated cabbage Ml.	Dehydrated carrots Ml.	Dehydrated potatoes Ml.
1.0	5.20	1.50	0.60
$1.5 \\ 2.0 \\ 2.0$	4.40 4.00 4.20	0.90	0.40
3.0	4.20	0.90	0.40
4.0	4.50 5.20	1.00 3.10	0.40 1.60
6.0	8.40	4.00	7.00

2 and 3, whereas in potatoes the range is extended to pH 4. For safe general applicability, the range of pH 2 to 3 was chosen.

Kolthoff and Furman (4, 7) observe that the addition compound is unstable in strongly acid solution, and state that the optimal pH for addition is about that of a bisulfite solution that is, 4.0. Their discussion is concerned with the determination of aldehyde or ketone in the presence of excess sulfite, whereas the reverse is the present objective. Experimentally, with the foods tested, a pH range from 2 to 3 was found most suitable. This range offers the additional advantage of a good end point; the starch-iodine end point is less satisfactory with an excess of acetone at pH 4.

The same pH range was found to be optimum for analysis of dried fruits. It is necessary, therefore, to maintain this pH during the acetone treatment and titration. A similar range is desirable for the formaldehyde complex.

To determine the amount of acid required to neutralize the alkaline digestion mixture and yield a pH in the proper range, buffer curves were drawn in which pH was plotted for the mixture to which successive increments of 5 N acid were added. Dehydrated cabbage, carrots, and potatoes all gave the same curve, as might be anticipated under these conditions, and required 7.5 ml. of 5 N hydrochloric acid. Dehydrated apples, apricots, and peaches gave a curve slightly different from that obtained with vegetables and required only 6 ml. of the 5 N acid. The amount of acid required to bring the alkaline digestion mixture to the pH range of 2 to 3 should be determined for each commodity. Because the optimum pH range is in a region where the pH is affected considerably by added acid, it is necessary to measure the alkali and acid accurately with pipets or dispensing burets rather than with graduated cylinders.

Concentrations of acetone up to 33% by volume have been recommended for binding the sulfur dioxide (1, 8). In high concentration, acetone interferes with the development of the color of the starch-iodine end point. By varying the amount of acetone used, it has been found that quantitative binding of the sulfur dioxide occurs under the conditions of the analysis at concentrations of acetone of 10% by volume or even slightly less. With 10% acetone present, satisfactory end points can be obtained, provided sufficient starch is added.

In the pH range indicated, the reaction between the acetone and the sulfur dioxide is complete in approximately 5 minutes. Standing for longer periods, up to 2 hours, was without further effect. For convenience of operation when several samples were being run, a 10-minute interval was ådopted.

Many substances will react with sulfur dioxide to form stable complexes. Formaldehyde does not interfere with the color at the starch end point and yields satisfactory results with some commodities. In some cases the end point is easier to follow with formaldehyde than with acetone. However, formaldehyde consistently yields results 5 to 10% higher with cabbage than does acetone.

As noted by Kolthoff and Furman (4, 7) the analysis hinges upon two factors: the dissociation constants, K, of the salts of the bound sulfurous acid and the speed of establishment of equilibrium. The K for the formaldehyde complex is theoretically preferable $(1.2 \times 10^{-7} \text{ at } 25^{\circ} \text{ C})$, compared with 4×10^{-3} for acetone).

The working conditions are in the range 10^{-3} M for bisulfite, and M for acetone. It is thus possible to calculate that a titration error caused by incomplete binding is of the order of 0.4%. However, as the titration approaches completion, the equilibrium has been destroyed, and differences in the speed of the reverse reaction may be responsible for the divergences between acetone and formaldehyde. This would imply that the formaldehyde value would be more nearly correct, but this in turn would suggest an error in the Monier-Williams value. The reasoning is not entirely satisfactory because the divergence is not uniform for all commodities but is most pronounced with cabbage. Glyoxal, which is now commercially available in a 30 to 40% solution, may prove satisfactory, although the details have not been worked out.

Because of acetone interference at the starch end point, other indicators were tried. Methylene blue was found satisfactory but no better than the starch as finally used. By using a large amount of starch, 10 ml. of 1% solution per titration, and a minimum amount of acetone, about 10% by volume, it was possible to obtain satisfactory end points.

Table III. Replicate Analyses of Samples

Debydrate Samples	d	P.p.m. SO2	Average
Cabbage A Cabbage I Cabbage I Cabbage I Cabbage I Carrots A Carrots I Potatoes A Potatoes I	A 4 B 11 C 19 D 30 E 33 A 23 A 10 B 20	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	397 1230 1308 3068 3312 2396 2264 159 2071

ANALYTICAL PROCEDURE

The determination is best carried out in a 600-ml. tall-form beaker with the aid of a slow-speed stirrer carrying a propeller with broad blades having a steep pitch. With this type of stirrer, thorough mixing is obtained without beating air into the mixture. If a stirrer is not available the determination can be carried out in a 1-liter Erlenmeyer flask or even a quart fruit jar, which is shaken during the analysis.

Two 8-gram samples (=10 mg.) of the dehydrated product are transferred to the titration vessels; 400 ml. of water and 5 ml. of 5 N sodium hydroxide are added to each and the mixtures are stirred. After 20 minutes the mixtures are acidified with 5 N hydrochloric acid—7.5 ml. for cabbage, carrots, or potatoes, or 6 ml. for dried apricots, apples, or peaches. To one of the samples 40 ml. of acetone are added, while the other sample is titrated at once with 0.05 N iodine solution using 10 ml. of 1% soluble-starch solution. It is important that the acidified sample be titrated at once before recombination occurs. The end point is reached when, with vigorous stirring or shaking, a blue color flashes throughout the entire mixture and persists for a few seconds. The acetone-treated mixture is titrated similarly after standing for 10 minutes.

The end points in the titrations are fleeting. In the samples containing acetone this is particularly true because the complex continuously yields a small amount of sulfur dioxide by dissociation. When no acetone is present, the end point is more persistent but even then it is not permanent. With these socalled flash end points, quantitative results can be obtained. However, in cases where the available equipment will not grind the sample fine enough, it is possible arbitrarily to standardize the method against the Monier-Williams method by choosing a more permanent end point for the titration carried out in the absence of acetone.

Reagent blanks must be determined by a similar set of titra-

Table IV.

Surgen and Surgen	Sulfited Cat	bage and Car	rot Suspension	Land by Diel
SO: Originally Present, A Mg.	SO2 Added Mg.	SO: Found (Total), B Mg.	SO: Recovered, B - A Mg.	Recovery %
		Cabbage		
10.33 10.33 10.33	19.21 19.21 19.21	26.82 27.04 27.26	16.49 16.71 16.93	85.8 87.0 88.1 Av. 87.0
10.33 10.33	37.80 37.80	45.10 45.30	34.77 34.97	92.0 92.5 Av. 92.2
10.33 10.33	75.15 75.15	80.05 80.40 Carrots	69.72 70.07	92.8 93.3 Av 93.0
18.02 18.14 18.14	19.91 19.93 19.93	37.30 37.46 37.15	19.28 19.32 19.01	96.8 96.8 95.4 Av. 96.3
18.02 18.02 18.14	39.95 39.95 38.75	$56.50 \\ 56.40 \\ 56.05$	38.48 38.38 37.91	96.3 96.0 97.8 Av. 96.7
18.02 18.02 18.14	78.30 78.30 77.15	95.28 94.90 94.00	77.26 76.88 75.86	98.7 98.2 98.4 Av. 98.4

Recovery of Sulfur Dioxide Added to Dehydrated

tions without food material and subtracted from the corresponding titration values. The difference between the two corrected titers multiplied by 200 yields sulfur dioxide in parts per million.

For material with a high starch content, such as potatoes, the titration is continued until the mixture has developed a deep blue color. During the titration some iodine is adsorbed on the small solid potato particles, causing them to be blueblack. This is removed slowly and represents only a very small amount of the total iodine used. It does, however, impart a gray cast to the mixture which is not to be mistaken for the true end point. By addition of iodine until a deep blue color is reached, correct and consistent values are obtained.

ANALYTICAL RESULTS

The reproducibility of results with the proposed method was checked by repeated assays of sulfited dehydrated cabbage, carrot, and potato samples (Table III). Accuracy was checked both by recovery of added sulfur dioxide and by comparison with other methods. In addition to the methods of Monier-Williams and Nichols and Reed, which were used for comparison, check determinations were carried out with the aid of the dropping mercury electrode (5, 6).

To determine the recovery of added sulfur dioxide, standard amounts of sodium metabisulfite solution were added to suspensions of dehydrated sulfited cabbage and carrots. These samples were analyzed before and after the addition of the sulfite solution. Very erratic results were obtained under these conditions, the deviations being considerably greater than those encountered in actual analytical practice. Plant material contains compounds that exert a protective action and inhibit the destruction of sulfur dioxide by oxidation or other reactions. Samples of sulfured commodities ready for analysis contain the sulfur dioxide in a form which is protected and not readily susceptible to loss in handling; in samples to which sulfite solutions have just been added the sulfur dioxide is stabilized only after an appreciable lapse of time. It was found that the addition of 0.1% of sodium pyrophosphate decahydrate to the sodium metabisulfite solution led to consistent recovery data. The literature on the inhibitors of sulfur dioxide destruction, other than sodium pyrophosphate, has been reviewed by Monier-Williams (10) and by Mitchell, Pitman, and Nichols (9).

Table IV lists the data obtained on the recovery of sodium metabisulfite solution stabilized with sodium pyrophosphate when added to dehydrated cabbage and carrots. In each case, an 8-gram sample was taken and the regular analysis performed except that the indicated amounts of metabisulfite solution were added to 400 ml. of suspension before addition of alkali.

The data in Table IV show fair recovery in cabbage and good recovery in carrots. Even though these commodities were both sulfured before dehydration and contained appreciable sulfur dioxide, in the case of cabbage there was a consistent loss of added sulfur dioxide. This loss probably would not appear during routine analysis of samples which have been dehydrated after sulfuring, because the loss would have occurred during the processing.

Representative data comparing the direct titration method with the distillation methods for several commodities are given in Table V.



Figure 1. Measurements with Dropping Mercury Electrode Supporting electrolyte: (1) 0.1 N hydrochloric acid; (2) plus 0.243 mg. of SO2 per 50 ml.; (3) plus 0.486 mg. of SO2 per 50 ml.; (4) plus 0.972 mg. of SO2 per 50 ml.; (5) plus 1.944 mg. of SO2 per 50 ml.

Table V. Comparison of Methods of Sulfur Dioxide Analysis

Commodity	Titration		Williams		Reed	
	- California		P.p.7	1. SO:		
Dehydrated cabbage A, not sulfited	100	10000	60	68	320	520
Dehydrated cabbage B, sulfited	372	413	464	468	640	840
Dehydrated cabbage C, sulfited	2310	2450	2560	2480	2632	2570
Dehydrated cabbage D, sulfited	4490		4580	4570	4500	4340
Dehydrated carrots A, not sulfited	0	0	20	20	0	0
Dehydrated carrots B, sulfited	2520	2620	2610	2690	2380	2420
Dehydrated carrots C, sulfited	6260	6220	6390	6460	6300	6320
Dehydrated onions A, not sulfited	86	86	153	121	850	840
Dehydrated onions B, sulfited	445	414	759	644	1490	1550
Dehydrated potatoes A, not sulfited	20	20	-10	40	0	0
Dehydrated potatoes B, sulfited	42	83	142	146	0	60
Dehydrated potatoes C, sulfited	249	314	300	322	180	220
Dehydrated potatoes D, sulfited	853	687	752	732	660	660
Dehydrated potatoes E, sulfited	2160	2225	2295	2305	2090	2100
Dried apples sulfited	3055		2960	2930	2615	2555
Dried apricots A, sulfited	1605	1 12.11	1663	1700	1520	1500
Dried apricots B, sulfited	884	884	914	909	680	886
Dried peaches sulfited	1685	and and	1705	1735	1600	1555
The second s						

MEASUREMENTS WITH DROPPING MERCURY ELECTRODE

Most of the methods of determining sulfur dioxide content depend upon general oxidation or neutralization reactions and are not specific. To obtain data specific for the molecular species involved, a polarographic method employing the dropping mercury electrode was used. Kolthoff and Miller (6) have reported results on pure aqueous solutions of sulfurous acid.

A simple manual dropping mercury electrode was used (5). A number of capillaries were prepared by drawing out capillary tubing with a 0.25-mm. bore. One having a drop time of about 2 seconds was finally chosen and used in all these studies, since it gave the maximum values of diffusion current that still maintained approximate linearity with concentration. Measured at -0.6 volt in 0.1 N hydrochloric acid, the values for use in the Ilkovič equation (5) were as follows:

> t = 2.33 sec. m = 1.83 mg. sec.⁻¹ $m^{2/3} t^{1/6} = 1.72 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$

Preliminary experiments led to the choice of 0.1 N hydrochloric acid as the supporting electrolyte. To calibrate the apparatus, 0.1 N hydrochloric acid was introduced into the electrolysis cell and swept free of dissolved oxygen with a stream of nitrogen. The gas flow was then diverted to flow over the surface of the solution, aliquots of dilute sodium bisulfite solution were in-troduced to make a final volume of 50 ml., the mixture was stirred carefully to avoid incorporating oxygen, and the current-voltage data were recorded.

Representative data are plotted in Figure 1, which includes the current-voltage curves for pure aqueous solutions of sodium bisulfite in 0.1 N hydrochloric acid and, in the upper left corner, a graph showing the relation between the current (sum of diffusion and residual currents) at -0.6 volt and the concentration of sulfur dioxide.



- 5.6.7.8.

Three drops of 1% gelatin solution were added to suppress maxima in pure solutions. Maximum suppressors were not necessary in suspensions of vegetable material. All voltages were measured with a saturated calomel half-cell as the reference electrode. Typical curves obtained with cabbage and carrot suspensions are given in Figure 2.

As shown in the figures, the half-wave potential for sulfur dioxide is the same in pure aqueous solutions as in cabbage or carrot suspensions. Under the conditions used there were no interfering waves in the dehydrated vegetable suspensions. Good

Table VI.	Sulfur Dioxide	Found by D	ropping Mercu	y Electrode
and by Dire	ect Titration of S	ulfited Dehy	drated Cabbage,	Carrots, and
		Potatoes	-	a file of

122 - 1 - 1 - 2 - 2 - 2 - 2 - 2 - 2 - 2	Sulfur	Dioxide
Commodity	Direct titration	Mercury electrode
	P.p.m.	P.p.m.
Cabbage Carrots Potatoes A Potatoes B	1104,1070 489,499 687,653 2160,2225	$\begin{array}{c} 1100, 1050, 1060\\ 483, \ 465\\ 675, \ 690\\ 2140, 2150 \end{array}$

Table VII. Recovery of Sulfite Added to Unsulfited Dehydrated Cabbage Suspensions

	(Dropping mercury electrode dat	a)
SO ₂ Added	SO ₂ Found	Recovery
Mg.	Mg.	%
0.486	0.465	95.7
0.486	0.485	99.8
0.972	0,930	95.7
0.972	0.920	94.6
0.972	0.925	95.2

recovery of sulfur dioxide added to cabbage and carrots is shown in curves 3 and 7, respectively, of Figure 2, which resemble curve 3 in Figure 1. Additional recovery data for cabbage are presented in Table VII. A typical curve showing the effect of acetone is included in Figure 2. The conditions represented by curves 4 and 5 differ only in that for the latter they include the addition of acetone. With acetone present, sulfited cabbage yields the same curve as the unsulfited cabbage and the supporting electrolyte. The use of acetone or other binding agent is unnecessary in the polarographic procedure. The curve is included here to demonstrate the completeness of reaction between sulfurous acid and acetone.

In analyses of dehydrated vegetables 1 gram of the material was weighed into the electrolysis vessel and 48 ml. of water were added. Larger amounts of dried material may be used, provided the suspensions produced are not too viscous to work with conveniently. The distilled water used had been swept free of oxygen by passing a vigorous current of nitrogen through it for 30 minutes. One-half milliliter of 5 N sodium hydroxide was added, the suspension was allowed to stand 10 to 30 n in-utes, and 1.5 ml. of 5 N hydrochloric acid were added. Measurements of the diffusion current were commenced immediately.

No oxygen wave has been noted during analysis of samples of sulfited dehydrated vegetables. This is to be expected, considering the well-known ability of sulfur dioxide to remove oxygen quantitatively under alkaline conditions. Loss of sulfur dioxide is minimized by the use of oxygen-free water and avoidance of vigorous agitation which might incorporate oxygen. With material that has not been previously treated with sulfite, it is of course necessary to remove dissolved oxygen by bubbling a stream of inert gas through the suspension.

Results obtained by the dropping mercury electrode as compared with the direct titration method are given for dehydrated cabbage, carrots, and potatoes in Table VI. Recovery of sulfite added to dehydrated cabbage is shown in Table VII.

DISCUSSION

From the data presented, it is concluded that the direct titration method gives reproducible results and has an accuracy comparable with that of the distillation methods, especially in the range of 500 to 4000 p.p.m. of sulfur dioxide. It has the advantage of requiring less time than the distillation methods, and very little equipment. It can be mastered readily by an inexperienced analyst and should prove helpful for inspection and control laboratories and field stations. The results obtained by the direct titration and distillation methods are in agreement with those obtained with the dropping mercury electrode, which yields data specific for sulfur dioxide under the conditions used.

In addition, the direct titration procedure is capable of providing information not obtainable by the distillation methods. For example, omission of the alkali in the two titrations will yield the free sulfur dioxide, and the sulfur dioxide present in the bound form can then be estimated by determining the total as described above. The determination will not be precise, because a measurable time will be needed to leach out the sulfur dioxide from the food particles, and the equilibrium in the suspension may have shifted appreciably from that in the dehydrated material.

The various methods yield results that show general agreement. Results by the Nichols-Reed method disagree with those by the other methods on cabbage and onions, when the total sulfite is low. On cabbage at higher sulfite levels, the results closely approximate those obtained by the other procedures. Fresh unsulfited cabbage may yield iodine-reducing distillates which, calculated as sulfur dioxide, are equivalent to 2000 to 4000 p.p.m. on the dry basis. Most of the natural reducing material is lost during dehydration; in control-dried cabbage, for example, analogous figures vary from 300 to 1000 p.p.m. This material does not affect the Monier-Williams or the direct titration values, which are therefore preferred for these commodities.

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Determination of Sodium in Potassium Hydroxide

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Sodium is separated from potassium by extraction of perchlorates with isopropanol and is precipitated from the alcoholic filtrate with a magnesium uranyl acetate reagent containing a relatively high concentration of uranium. The method is rapid and economical, and requires no temperature control during precipitation. Recovery of sodium is 94% complete and accurate results are obtained by means of an empirical factor. The limit of uncertainty of the method under the best conditions was found to be $\pm 0.009\%$ for a sample analyzing 0.082% sodium hydroxide; under routine laboratory conditions it was ±0.018% for a sample analyzing 0.085% sodium hydroxide.

THE sodium content of potassium hydroxide has been deter-mined in this laboratory for a number of years by separation of most of the potassium as the perchlorate, followed by precipitation of the sodium with magnesium uranyl acetate. Two procedures have been used: (1) separation of the potassium in aqueous solution followed by precipitation of the sodium with the Caley-Foulk reagent (3); (2) separation of the potassium in isopropanol solution followed by precipitation of the sodium with a reagent having a higher concentration of uranium than that recommended by Caley and Foulk.

The use of the reagent recommended by Caley and Foulk has a number of disadvantages. Precipitation is slow and requires mechanical stirring for a half hour for completion. A very large excess of dilute reagent is used. This increases the cost and exaggerates solubility effects. As a result of the latter, close temperature control and saturation of the reagent with sodium are required.

The Calcy-Foulk reagent contains 35 times as much magnesium as uranium, expressed in terms of an equivalent quantity of sodium. It was found that the characteristics of the reagent could be improved by increasing the uranium concentration fourfold at the expense of a slight decrease in the concentration of the magnesium. Only a relatively small volume and a slight excess of this reagent, calculated on the basis of the uranium, are required. Temperature effects are negligible, owing to the low solubility of sodium in this reagent. Prolonged agitation is not required and precipitation is complete in a few minutes (in a few seconds in most cases).

This reagent has been used for the precipitation of sodium from both alcoholic and aqueous solutions and is equally satisfactory in both media. Relatively small amounts of potassium interfere and for this reason it is necessary to utilize an organic solvent for separating most of the potassium from the sodium prior to precipitation of the sodium. Of the solvents tested for this purpose, 99% isopropanol is the most satisfactory. Isopropanol is also the most satisfactory solvent tested for transferring and washing the precipitate. The precipitate is weighed after drying at 110° C.

REAGENTS

MAGNESIUM URANYL ACETATE. Dissolve 160 grams of uranyl acetate dihydrate, 180 grams of magnesium acetate tetrahydrate, and 45 grams of glacial acetic acid in 750 ml. of distilled water by heating to about 70° C. with stirring. Cool to 25° C., dilute to 1 liter, and filter before using. The specific gravity of this reagent should be 1.169 = 0.005 at $25^{\circ}/15^{\circ}$ C.

ISOPROPANOL, 99%, supplied by the Carbide and Carbon Chemicals Corporation as the anhydrous grade. PERCHLORIC ACID, 70 to 72%, C.P.

PROCEDURE

Weigh a 1-gram portion of solid potassium hydroxide or 2 grams of a liquid sample into a 180-ml. tall-form beaker and dilute to about 10 ml. Add a drop of phenolphthalein and neutralize by the dropwise addition of 70% perchloric acid, adding 1.0 ml. of acid in excess of the neutral point. Evaporate carefully, to avoid spattering, on a hot plate until dense white fumes of chloric acid appear and then fume 0.5 minute more. After a little experience the perchloric acid fumes can readily be distinguished from the less dense water vapor. The whole evaporation should be performed at such a temperature that spattering will not occur; 15 minutes is about the minimum time in which this can safely be accomplished.

After the evaporation is completed, cool the beaker and contents to room temperature in a stream of water, and extract the precipitate with successive 5-ml. portions of isopropanol. Caution should be exercised at this point to avoid the danger of adding organic matter to hot perchloric acid. The extraction can best be accomplished by adding the isopropanol from a small fine-tipped wash bottle up to a predetermined mark upon the side of the beaker. Stir the mixture thoroughly, breaking up any large lumps of solid material, and decant as much of the liquid and as little of the solid as possible through a Gooch cru-cible containing a disk of Whatman No. 40 filter paper. (Whatman No. 40 disks, 21 mm. in diameter, to fit No. 3 Coors Gooch crucibles, may be obtained from H. Reeve Angel and Co., New York.) Repeat this operation three more times, transferring the precipitate to the crucible with the last 5-ml. portion. Rinse the beaker into the crucible once with a fine jet of isopropanol and wash down the sides of the crucible similarly, using a minimum of alcohol. Transfer the contents of the suction flask to a dry 180-ml. tall-form beaker and rinse the flask with a minimum of isopropanol. The volume of the beaker contents should be about 25 ml. at this point.



Figure 1. Effect of Potassium in Alcoholic Solution

Precipitate the sodium by adding 10 ml. of the magnesium uranyl acetate reagent slowly to the alcoholic solution with swirling. Continue to swirl for 20 seconds. Allow the precipitate to stand for 10 minutes or longer and filter through a tared Gooch crucible containing a disk of Whatman No. 40 filter paper. Transfer the precipitate and rinse the beaker with four or five small portions of isopropanol. Wash down the sides of the crucible with isopropanol, using no more than 25 ml. for the entire transfer and washing operation. Remove the crucible carefully, wipe off the outside, dry 5 minutes at 105° to 110° C., cool, and weigh. Calculate per cent sodium hydroxide as follows:

 $\frac{\text{Grams of ppt.} \times 0.0261 \times 100}{\text{Grams of sample} \times 0.94} = \% \text{ NaOH}$

EXPERIMENTAL

The reagent recommended by Caley and Foulk (3) contains 42.5 grams per liter of uranyl acetate dihydrate, 250 grams per liter of magnesium acetate tetrahydrate, and 60 grams per liter of glacial acetic acid. From 1 to 5 ml. of solution containing up to 50 mg. of sodium are mixed with 100 to 500 ml. of the reagent and stirred vigorously for 30 to 45 minutes at 20° C. Because of the appreciable solubility of sodium in this reagent and the large volume used, it is necessary to saturate the reagent prior to use and store at a temperature above 20° C. The uranium content of the reagent is equivalent to 0.77 mg. of sodium per ml., while the magnesium content is equivalent to 27 mg. per ml. It seemed desirable, therefore, to make the uranium and magnesium content more nearly equivalent. It was found that solutions could be prepared which contained 180 grams per liter of each salt, but that uranyl acetate precipitated from this solution upon stirring at 20° C. For this reason, 160 grams per liter of uranyl acetate tetrahydrate were chosen as the maximum practical concentration.

The concentration of magnesium acetate tetrahydrate must be maintained somewhat below 250 grams per liter in order to permit the required amount of uranyl acetate to dissolve. Some of the experimental work was performed with a reagent containing 160 grams per liter of the magnesium salt, but a batch prepared from a reagent labeled $Mg(C_2H_3O_2)_2.xH_2O$ resulted in low recoveries of sodium and apparently contained only about 130 \$0.04. In view of the extremely high potassium-sodium ratio in caustic potash, the possibility of determining sodium without a prior separation of the potassium appeared remote. However, the advantages of such a procedure were so great that it was considered advisable to investigate this possibility. Conditions were found which prevented the precipitation of potassium in the absence of sodium, but the same conditions resulted in large positive errors in the recovery of added sodium. Moreover, when the sodium magnesium uranyl acetate was dissolved and reprecipitated under the same conditions as before, the weight of the second precipitate bore no relationship to the amount of sodium present. Thus, the direct determination of sodium in caustic potash by either one or two precipitations as the triple acetate appears to be unsatisfactory.

Having eliminated the direct determination of sodium in the presence of potassium, the procedure resolved itself into two parts: (1) separation of a large portion of the potassium and (2) precipitation of the sodium. The simplest procedure for the separation of the potassium would involve acidifying the sample with perchloric acid, removing the precipitated potassium perchlorate by filtration of the cold aqueous solution, and precipitating sodium in the filtrate. To determine the effect of the potassium remaining in this filtrate varying amounts of potassium perchlorate were added to portions of sodium perchlorate, equivalent to 4.0 mg. of sodium. The volume of each solution was adjusted to 5 ml. and the sodium precipitated with 10 ml. of magnesium uranyl acetate. The data obtained indicated that potassium perchlorate in excess of 70 mg. would probably interfere under these conditions. The solubility of potassium perchlorate in water is such that it appeared impractical to reduce the concentration below this level.

Table I. Solubil	ities of Sodium	and Potassium	Perchlorates
Solvent	NaClO: G./25 ml.	KClOs G./25 ml.	NaClO4 KClO4 Ratio X 10 ⁻²
Methanol Ethanol Isopropanol Isopropanol, 91%	7.81 3.02 0.62 0.81	$\begin{array}{c} 0.0207 \\ 0.0025 \\ 0.0015 \\ 0.0064 \end{array}$	3.8 12.1 4.1 1.3

Barber and Kolthoff (2) separated potassium from sodium with ammonium perchlorate in 72% ethanol and precipitated the sodium from the aqueous solution after evaporating the alcohol. Willard and Diehl (7) list the solubilities of sodium and potassium perchlorates in several alcohols and mixed solvents. The high sodium perchlorate-potassium perchlorate solubility ratios indicated the possibility of separating the sodium from the potassium by extraction, prior to the sodium determination. In pursuance of this, the approximate solubilities of sodium and potassium perchlorates in several solvents were determined. To avoid separation of the solvents, the study was limited to alcohols which were miscible with the magnesium uranyl acetate reagent. The alcohols were technical materials and were used without further purification. They are described by the supplier as follows: methanol, not less than 99.85% by weight; ethanol, absolute; isopropanol, approximately 91% by volume and isopropanol, not less than 99.4% by volume. The following procedure was used.

To 100-ml. portions of the alcohols was added excess of the finely pulverized salt. After heating to 50° C. to hasten dissolution the mixtures were agitated vigorously for 2 hours at 25° C. The excess salt was allowed to settle, the supernatant liquid was filtered, 25-ml. portions of the filtrate were evaporated to dryness in tared weighing bottles, and the residue was weighed.



The data obtained (Table I) indicate that ethanol gives by far the most favorable ratio of solubility of sodium perchlorate to potassium perchlorate, while methanol and 99% isopropanol give about equal ratios. Dilution of isopropanol to 91% substantially decreased the ratio. This suggested the desirability of making the separation in an essentially anhydrous medium.

The effect of potassium in alcoholic solutions was determined by precipitating 10 mg. (13.3 mg. were used in some tests) of sodium from 25 ml. of the alcohol. To simulate actual working conditions 0.75 ml. of 70% perchloric acid was added to each solution. The data presented in Figure 1 show that ethanol is entirely unsatisfactory as a solvent for the precipitation. If methanol is used as the solvent, the amount of potassium perchlorate which may be present without causing appreciable interference is about twice the solubility of potassium perchlorate in methanol, while the corresponding value for 99% isopropanol is forty-fold. It follows that isopropanol is the most satisfactory solvent for the separation and precipitation of the sodium.

Since the complete removal of perchloric acid was impractical, the maximum amount which could be tolerated was determined. The data obtained, shown graphically in Figure 2, indicate that amounts up to 1.0 ml., and probably more, do not interfere in any of the three alcohols tested. Positive errors were obtained at intermediate acid concentrations when using ethanol as the solvent. While the cause of this anomalous behavior was not ascertained, it may be due to variations in the degree of solvation.

A 30-minute stirring period was utilized in all the experimental work described above to ensure complete precipitation of the sodium magnesium uranyl acetate. To determine the possibility of shortening the stirring period, 3.0 mg. of sodium, 2.0 mg. of potassium, and 0.5 ml. of 70% perchloric acid were dissolved in 25 ml. of 99% isopropanol; 10 ml. of magnesium uranyl acetate were added and the solutions were agitated for varying periods. The data obtained are presented in Table II and indicate that precipitation is complete after 10 seconds of swirling. A 20second swirling period was adopted to provide a safety factor. Subsequent experience with the routine application of the method indicated that better precision was obtained by allowing the precipitate to stand 10 minutes, after swirling and before filtering.

The customary wash solution used for sodium magnesium uranyl acetate is 95% ethanol, shaken and maintained in contact with an excess of the precipitate. This and other solvents were tested as wash solutions by determining the solubility losses dur-

ing washing. Five 0.65-gram portions of the triple acetate precipitate, corresponding to about 10 mg. of sodium, were washed in Gooch crucibles with successive 25-ml. portions of the various solutions. Table III shows that methanol is unsatisfactory as a wash solution; 95% ethanol in contact with excess precipitate and 91% isopropanol are about equally satisfactory; 99% isopropanol is somewhat superior to the last two; and the solubility of the precipitate in acctone is negligible. However, acetone was found to precipitate the reagent, leaving considerable residue in the beaker. Thus, although acetone is excellent for washing the precipitate prior to drying, it is not satisfactory for transferring or washing the precipitate free of excess reagent. For this reason, 99% isopropanol was selected as the most satisfactory wash solution considered. The precipitate may be dried at 105° to 110° C. or by aspirating air through it. If the latter method is used, the precipitate should be washed with a small volume of acetone to take advantage of its higher vapor pressure and to reduce the time required to

evaporate the solvent completely.

Caley and Foulk (3) found that the precipitate formed in aqueous solutions is solvated with 6.5 molecules of water. Schoorl (6) and Caley and Rogers (4) found independently that magnesium uranyl acetate which has been precipitated from aqueousethanolic solutions is solvated with ethanol as well as water. The authors' experience with the precipitate from aqueous solutions showed that it readily attained constant weight at temperatures up to 120° C., lost weight slowly at 150° C., rapidly at 180° C., and quickly blackened at 200° C. On this basis a portion of the precipitate from isopropanol solution was dried at 145° to 150° C. for an extended period. The data, plotted in Figure 3, show a marked change in the rate of loss in weight after 6 hours, the continued loss in weight being attributed to decomposition of the molecule. Extrapolation of the curve indicates a rapid loss of 9.4 or 9.5%, depending upon whether decomposition is assumed to begin immediately upon heating or not until desolvation is complete. The isopropanol content of portions of

Table II. Effect of Tin	ne of Agitation	
(3.0 mg. of Na	added)	
Agitation	Sodium Found ^a Mg.	Error Mg.
Stirred mechanically 30 min. Stirred mechanically 15 min. Swirled manually 60 sec. Swirled manually 60 sec. Swirled manually 5 sec. Swirled manually 5 sec. Swirled manually 2 sec.	3.02 3.04 3.01 3.07 3.09 2.89 2.85	$\begin{array}{r} +0.02 \\ +0.04 \\ -0.01 \\ +0.07 \\ +0.09 \\ -0.11 \\ -0.15 \end{array}$
^a After subtracting blank of 0.11 mg.		

Table III. Solvent Action of Wash Solutions on Sodium Magnesium Uranyl Acetate

	117-1-1-1	L	oss of Precipit	tat-	
Washing	Methanol, 99.85%	Ethanol, 95% ^a	Isopropanol, 91% Gram/25 ml	Isopropanol, 99%	Acetone
1 2 3 4 5 Av.	0.076 0.089 0.096 0.087	0.004 0.003 0.001 0.003 0.0028	0.006 0.003 0.001 0.002 0.001 0.0033	0.001 0.001 0.001 0.001	0.000 0.000 0.000 0.001 0.0003
^a Maintain	ed in contact	with sodi	um magnesiu	m uranyl acet	ate precip



the precipitate was determined by oxidation with dichromate in sulfuric acid solution, followed by titration of the excess dichromate with ferrous sulfate using diphenylamine sulfonic acid as the indicator. The recovery of known amounts of isopropanol was 95% complete under the conditions used. The isopropanol content found on duplicate portions of the precipitate was 1.04 and 1.06%. By difference, the water content is 8.4%. These data correspond to a precipitate containing 7 molecules of water and 0.3 molecule of isopropanol and having a molecular weight of 1534. Thus, the theoretical factor for converting to sodium is

To determine the volume of isopropanol required to extract the sodium perchlorate from the potassium perchlorate, synthetic samples containing added sodium equivalent to 0.87% of sodium hydroxide were carried through the procedure except that varying volumes of isopropanol were used. Extraction with 10 ml. of isopropanol resulted in the recovery of 0.86%, and 0.88% was recovered when 30 ml. was used. These data indicate that the sodium is readily extracted and that 20 to 25 ml. should be adequate for routine use.

To determine the accuracy of the procedure, a sample of lowsodium potassium hydroxide was prepared by a method similar to that of Richards and Mueller as described by Archibald (1). c.p. potassium oxalate was recrystallized from water and a hot saturated solution prepared. This was placed in a large porcelain evaporating dish and electrolyzed, using a mercury pool as cathode and a platinum disk as anode. The contents were cooled by immersing the dish in ice water. When the mercury began to solidify, the supernatant liquid was discarded and the amalgam washed three times with intermittent electrolysis until the wash water was free of oxalate ion. Distilled water was added to the amalgam and the current reversed to hasten the formation of the potassium hydroxide. The aqueous solution was then evaporated in a porcelain casserole to 48% potassium hydroxide and stored in a hard-rubber bottle to avoid sodium contamination.

The purified potassium hydroxide was diluted so that 10 ml. were equivalent to a 2-gram sample of 45% potassium hydroxide. To 10-ml. portions of this solution were added varying portions of standard 0.1 N sodium hydroxide and the solutions were analyzed. Duplicate portions containing no added sodium were found to contain 0.003% sodium hydroxide. This was considered to be a blank determination and was subtracted from the actual analyses shown in Table IV.

These data show preponderantly negative errors with fairly consistent recoveries of about 94% of the added sodium. This indicates that the method is best applied to the determination of small amounts of sodium where the absolute errors observed are less serious. However, by means of an empirical factor for converting the weight of the precipitate to per cent sodium hydroxide, the accuracy can be made equal to the precision of the method, which is shown to be very good.

The precision of this procedure was determined under the best conditions and under routine conditions as described by Moran (5). Assuming random distribution and applicability of the normal law integral, 68.3% of all analyses would be expected to lie within the range of the average of a group of analyses plus or minus the standard deviation for an infinite group. Similarly, 99.7% of all analyses should lie within the range of the average plus or minus three times the standard deviation for an infinite group. The latter range has been termed the limit of uncertainty, LU (5). The precision under the best conditions, LU_1 , was determined by the analyses of 10 portions of a homogeneous sample (Table V). The LU_1 of =0.009% in a sample analyzing 0.082% sodium hydroxide is considered satisfactory. The pre-

Table V.	Precision of	Method under Best (Conditions, LU1
	Analysis No.	NaOH, %	Deviation from Average, %
	1 2 3 4	0.083 0.083 0.086 0.075	+0.001 +0.001 +0.004 -0.007
	5 6 7	0.083 0.083 0.085	+0.001 +0.001 +0.003
in any distance	8 9 10	0.081 0.082 0.082	0.000 0.000
Standard de Standard de LU_1	eviation of grou eviation of infin	ip lite group	±0.0028 ±0.0030 ±0.009

Table VI. Precision of Method under Routine Conditions, LU2

Analysis	mple printes prinklike	NaOH,	Deviation from Average,
IN O.	Date	%	%
1	May, 1941	0.088	+0.003
2	May, 1941	0.087	+0.002
3	June, 1941	0.086	+0.001
4	June, 1941	0.087	+0.002
5	July, 1941	0.077	-0.008
6	July, 1941	0.087	+0.002
7	August, 1941	0.074	-0.011
ð	August, 1941	0.099	+0.014
10	September, 1941	0.085	0.000
10	October 1041	0.085	0.000
12	October 1941	0.094	+0.009
13	November 1941	0.050	-0.003
14	November 1941	0.082	-0.001
15	December, 1941	0.076	-0.009
16	December, 1941	0.085	0.000
17	Innuary 1049	0.076	0.000
18	Jenuery 1042	0.070	-0.005
19	January 1942	0.020	
20	February 1942	0.084	-0.001
21	February, 1942	0.086	+0.001
22	March, 1942	0.094	+0.009
23	March, 1942	0.089	+0.004
24	April, 1942	0.087	+0.002
25	April, 1942	0.090	+0.005
26	May, 1942	0.088	+0.003
27	May, 1942	0.084	-0.001
28	June, 1942	0.088	+0.003
29	June, 1942	0.090	+0.005
30	July, 1942	0.086	+0.001
31	July, 1942	0.085	0.000
32	August, 1942	0.075	-0.010
24	September 1049	0.075	-0.010
25	September 1049	0.080	-0.005
36	October 1942	0.087	10.002
37	October, 1942	0.089	+0.002
38	November, 1942	0.090	+0.005
39	November, 1942	0.088	+0.003
40	December, 1942	0.088	+0.003
41	December, 1942	0.085	0.000
Av	tim need me politin		0.085
Standard de	viation of group		*0.0058
Standard do	vistion of infinite group		±0.0059
LU1	From Promp		=0.018

0.0150.

cision under routine conditions, LU_2 , was determined from analyses on the same sample over a period of 20 months. These data, representing 41 analyses by seven different analysts and shown in Table VI, indicate an LU_2 of $\pm 0.018\%$ and an average of 0.085% sodium hydroxide. This LU_2 represents a rigorous test of the analytical method and the LU_2 - LU_1 ratio of 2 to 1 is considered normal and as indicating the effect of personal, seasonal, and other variations.

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Refractive Index—Dry Substance Tables for Starch **Conversion Products**

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The refractive index of starch hydrolyzate sirups has been found to measure their dry substance content, provided the ash and dextrose equivalent are also known. All commercial corn sirups are marketed with essentially the same ash content, largely a function of the dextrose equivalent. Thus with the dextrose equivalent known, refractive indices are readily defined in terms of dry substance. Fortunately the correction for dextrose equivalent is small and

STARCH conversion products for the purposes of this paper are defined as corn sirups and Nos. "70" and "80" corn sugar sirups, made by the simple hydrolysis of starch by acid. This definition automatically excludes dual conversion sirupsacid followed by enzymic hydrolysis and interconversion sirups made by chemical treatment on an acid hydrolyzate. Of the products mentioned, corn sirup is the only one which reaches the trade as a sirup. The "70" and "80" sugars reach the consumer in the form of crystallized chips or billets. However, these products are sirups in the factory, and since the moisture at chipping is essentially the moisture at pouring, refractive index tables for these products are valuable for manufacturing control.

Corn sirup is the thick, viscous, substantially colorless sirup obtained from the incomplete hydrolysis of starch. It is sold on the basis of Baumé and dextrose equivalent and in the trade is often referred to as corn sirup unmixed or, more simply, C.S.U. The Baumé (commercial) will run from 42° to 47°, the greater part being 43°. Dextrose equivalent (D.E.) is defined within the industry as the percentage of reducing sugars calculated as dextrose, expressed on a dry substance basis. Under this general classification, commercial sirup falls roughly into four groups: brewers' body sirup, 25 to 35; standard confectioners' sirups, 40 to 45; extra sweet sirups, 50 to 57; and dual conversion sirup (acid plus enzyme), 60 to 70 D.E. The names of the first three groups are general, in that there is considerable interchange in the use of these sirups.

The employment of Baumé as the basis for the sale of corn sirup follows a natural custom for liquids or sirups. The hydrometer, which has always been used, has been standardized at 15.56° C. (60° F.). However, a Baumé test on commercial sirups at this temperature is impossible because they are too viscous. To eliminate this difficulty, an arbitrary method of linear. Likewise, the temperature correction, above 14% dry substance, is substantially linear. The precision of this method of determining dry substance is essentially the precision of a four-place refractometer. Tables are presented covering refractive index-dry substance for the usual commercial products from 0 to 90% dry substance and refractive index-commercial Baumé, since all corn sirup is marketed on a commercial Baume basis.

Baumé determination was adopted years ago and is still in use. The sirup under test is heated to 140° F. (60° C.) and Baumé reading obtained with a hydrometer standardized at 60° F. To the observed reading at 140° F. is added 1.00° Bé. which was originally purported to reduce the reading to 37.78° C (100° F.). This method for the sale of corn sirup is designated as commercial Baumé and expressed as commercial Baumé = Baumé (140°/60° F.) + 1.00° Bé. Although this procedure simplifies the test, it introduces other difficulties (5), so that the Baume test requires considerable skill in order to obtain results of a fine degree of precision. Since the Baumé scale is used as a measure of the dissolved solids or dry substance in a sirup, this relationship is of particular interest to manufacturers and users. Tables giving this relationship have been presented (5). However, determinations of Baumé as outlined above and of dry substances are laborious and time-consuming. A more rapid test for Baumé or dry substance has been desired for a long time. Refractive index has been proposed and the Abbe refractometer has been suggested for its case of manipulation and speed of operation.

HISTORICAL

A few tables have been published on the refractive index-dry substance relationship for starch conversion products. Most of these lack definition through a failure to define adequately the dextrose equivalent of the product (9). More recently a table has been published in Germany (6) but only the abstract has reached this country. The fault with such tables as have been prepared rests upon (1) inadequate methods for determination of dry substance, (2) failure to define the dextrose equivalent which in turn depends upon the dry substance, and (3) failure to recognize that the refractive index for a given dry substance is also a function of the dextrose equivalent.

Adequate methods for the determination of dry substance in starch conversion products (3, 4) have enabled more accurate

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sible.

data to be obtained for the dextrose equivalent. Thus a refractive index table became a matter of the collection of sufficient data. These data have been compiled and in use in this laboratory for six years. The original data have been extended to a complete range of starch conversion products and a wide range of temperatures. Although this would at first appear to necessitate extended tables, considerable simplification was pos-

MATERIALS

The materials used were commercial products and typical of each class:

	D.E.	Ash	Crude Protein, Dry Basis
Brewers' body sirup	32.8	0.25	0.04
Confectioners' corn sirup	42.0	0.28	0.04
High conversion corn sirup	55.0	0.30	0.04
(extra sweet corn sirup)			
"70" sugar	82.0	0.41	0.07
"70" sugar	89.0	0.61	0.07
"80" sugar	90.7	1.22	0.08
"70" sugar "80" sugar	89.0 90.7	0.61 1.22	0.07 0.08

With the exception of the "S0" sugar, the ash content of the others is essentially proportional to the dextrose equivalent, which proved advantageous for plotting refractive index vs. dextrose equivalent. Of the materials mentioned above, those of 42.0, 55.0, 89.0, and 90.7 D.E. were either diluted or concentrated for a series of sirups covering the complete range of dry substance from 0 to 90%. The method used for this procedure has been published (δ). The products of 32.8 and 82.0 D.E. were used in the concentrated ranges of 70 to 90% dry substance. In addition, the refractive index-dry substance-Baumé relationship was determined for specific Baumés on innumerable samples ship was determined for specific Baumés on innumerable samples of finished factory products and on similar samples manufac-tured by competitors during the six years the tables have been in use.

METHODS OF ANALYSIS

MOISTURE. The determination of moisture in corn sirup and corn sugar has been previously described (3, 4, 5). The methods used were as follows:

Com Sirup. Filter-Cel method (diatomaccous silica, Johns-Manville Hy-Flo), vacuum oven at 100°C.; alternative methods, toluene distillation and benzene distillation.

Corn Sugar. For 80 to 92 D.E., Filter-Cel method, vacuum oven at 80° C.; alternative, benzene distillation.

oven at 80° C.; alternative, benzene distillation. BAUMÉ BY HYDROMETER. Baumé determination has been previously described (5). The Corn Industries Research Foun-dation's official referee hydrometers manufactured by Wm. Hiergesell & Sons, New York, N. Y., were used. The sirup under test was poured into the cylinder (37.5 \times 5.6 cm., 15 \times 2.25 inch, Pyrex, without lip). The cylinder was sealed with dual stoppers, the bottom stopper being placed within 1.25 cm. (0.5 inch) of the sirup surface and the top stopper closed the cylinder. The cylinder was placed in the water bath (140° F.), so that water extended to within 2.5 cm. (1 inch) of the top. At the same extended to within 2.5 cm. (1 inch) of the top. At the same time, distilled water was added to a second cylinder, the test hydrometer inserted in it, and the cylinder placed in the water bath. After the sirup was freed of air, the cylinder was placed on a higher shelf, so that the surface of the sirup extended about 1.25 cm. (0.5 inch) above the water after the hydrometer was immersed. The dual stoppers were removed from the cylinder. The test hydrometer was removed, dried, and immersed in the The hydrometer was read in approximately 10 minutes. sirup. To the reading obtained was added the correction necessary from a previous comparison of the hydrometer with one certified

by the National Bureau of Standards. BAUME BY PYCNOMETER. A pycnometer in the form of a sphere with standard taper joints of Pyrex was designed and used. The apparent specific gravities by pycnometers on various con-centrations of corn sirup, employing the correction whereby the apparent specific gravity of pycnometers could be translated to hydrometer readings, were compared with actual readings by hydrometers in the same sirup and found to agree within 0.01° B6.

REFRACTIVE INDEX. Apparatus. Water bath, 120-liter (32-gallon), lagged, equipped with stirrer and metastic mercury regulator with sensitivity of 0.02° C. Water was transferred from bath to refractometer by means of a pump, with capacity of 37.85 liters (10 gallons) per minute. Light source, 60-watt frosted Mazda bulb.

Zeiss sugar refractometer, new model with rotating compen-sator, standardized at 20.0° C., Serial No. 54,128. The new model Zeiss sugar refractometer consists of a circular casing, con-

taining the mechanism, mounted on an upright stand. The height of stand is such that the ocular is at a convenient height for reading when the instrument is placed on a table. The fixed prism of the double prism is anchored in the casing and so placed that the inner surface of the prisms are placed horizontally, side by side, when the hinged prism is folded back for cleaning or recharging: The telescope, carried on a stout radial arm, is almost wholly enclosed, only the ocular protruding. In making observations, the eye looks horizontally into the

ocular. The image in the ocular presents the following appear-ance: In place of the usual cross lines, the field of view shows after 1n place of the usual cross lines, the held of view shows a linear mark, on the right of which is the percentage scale rang-ing from 0 to 50% in 0.2% and from 50 to 95% in 0.1%. On the left is a scale graduated in refractive indices, ranging from 1.330 to 1.540, graduated to the third decimal, the fourth decimal being estimated. The fact that reading is taken in the field of view ensures a considerable saving of time. The rotating com-pensator furnishes a means of rendering the boundary line be-tween the bright and dark portions of the field, sharp and free tween the bright and dark portions of the field, sharp and free of color fringes where white light illumination is employed and in addition renders the colorless boundary line exactly coincident in position with the sodium line—that is, the reading obtained with white light furnishes the refractive index, n_D , for sodium light

Although any suitable refractometer may be used for making dry substance-Baumé determinations of starch conversion products, the authors have preferred the Zeiss sugar type because of the case of cleaning and charging of samples. The instrument is rugged and has been used in many factories as a control instrument.

The range of the scale extends from n_D 1.300 to n_D 1.540, while the percentage readings range from 0 to 95%. The percentage scale is divided into fifths per cent from 0 to 50% and into tenths from 50% upwards. The refractive index scale reads to the third desired limit, while the fourth desired is actimated decimal direct, while the fourth decimal is estimated.

The constancy and precision of the refractometer were checked periodically. Distilled water and the test block supplied by the manufacturer for this particular instrument were employed at 20.0° C. For temperatures above and below 20° C., distilled water was used and the refractive index thus obtained compared to the value given in the International Critical Tables. During the past six years, the refractometer was found to check and in any case did not deviate more than one in the fourth place from these known refractive indices, which was deemed within the

The question of what refractometer temperature to use as the standard for the heavy commercial corn sirups (Baumé over 40°) was given considerable attention. The temperature chosen was 45° C, based on the following considerations:

1. Speed in transfer and closing of the prisms is essential. The thick viscous corn sirups present difficulties. However, their viscosities decrease sharply with increasing temperature (2) and the proportional decrease is very small above 43.33° C. (110°F.)

2. Most corn products and candy factory laboratories become warm in the summertime and those in the midwest often attain temperatures of 100° F. or more. The relative humidity is also high. If the refractometer temperature is less than room temperature, there is a tendency for the prisms to fog. This condensed moisture hinders the reading and also effects a dilution of the sample (7, 8).

The refractometer is already in use in many candy factories 3. as an instrument to measure the degree of cooking of starch jellies and the temperature used is generally 45° C. Therefore 45° C. enables such plants to measure the refractive index of corn sirup

with existing temperature control (1). Numerous studies were made to determine if any change took place in the sample when maintained at 45° C. The method usually employed was to introduce a sample at a low tempera-ture and obtain a series of readings. The temperature was then elevated to 45° or 50° C, and held there for periods up to several hourse while predings were the temperature. The batt was hours while readings were taken at intervals. The bath was hours while readings were taken at intervals. The basis were cooled down to the original temperature and another series of index readings was taken at intervals. The results at the high temperature were found to be constant and the readings at the low temperatures before and after heating checked precisely. Hence it was concluded that the use of the refractometer at 15° C resulted in poloss of precision if the transfer of the sample 45° C. resulted in no loss of precision if the transfer of the sample to the refractometer and the closing of the prisms were carried

out with dispatch. PROCEDURE. The method of applying the sirups to the re-fractometer is important and practice is the best directive.

Table I. Dry Substance-Refractive Index

	Dext	20.00 rose Equi)° C. valent an	d Ash	Dextr	45.00 ose Equi)° C. valent an	d Ash
Dry Substance	42.00 0.28%	55.00 0.30%	89.00 0.61%	90.7 1.22%	${}^{42.00}_{0.28\%}$	55.00 0.30%	89.00 0.61%	90.7 1.22%
$\begin{array}{c} 0.00\\ 1.00\\ 2.00\\ 3.00\\ 4.00\\ 5.00\\ 6.00\\ 7.00\\ 8.00\\ 9.00 \end{array}$	$\begin{array}{r} 1.3330\\ 1.3344\\ 1.3359\\ 1.3374\\ 1.3389\\ 1.3404\\ 1.3419\\ 1.3435\\ 1.3450\\ 1.3466\end{array}$	$\begin{array}{r} 1.3330\\ 1.3344\\ 1.3359\\ 1.3374\\ 1.3389\\ 1.3404\\ 1.3419\\ 1.3435\\ 1.3450\\ 1.3466\end{array}$	$\begin{array}{r} 1.3330\\ 1.3344\\ 1.3359\\ 1.3373\\ 1.3388\\ 1.3403\\ 1.3418\\ 1.3433\\ 1.3448\\ 1.3448\\ 1.3463\end{array}$	$\begin{array}{r} 1.3330\\ 1.3344\\ 1.3359\\ 1.3374\\ 1.3388\\ 1.3403\\ 1.3403\\ 1.3418\\ 1.3433\\ 1.3448\\ 1.3464\end{array}$	$\begin{array}{r} 1.3298\\ 1.3312\\ 1.3327\\ 1.3341\\ 1.3356\\ 1.3371\\ 1.3386\\ 1.3401\\ 1.3410\\ 1.3432\\ \end{array}$	$\begin{array}{r} 1.3298\\ 1.3312\\ 1.3327\\ 1.3341\\ 1.3356\\ 1.3371\\ 1.3386\\ 1.3401\\ 1.3416\\ 1.3431 \end{array}$	$\begin{array}{r} 1.3298\\ 1.3312\\ 1.3326\\ 1.3340\\ 1.3355\\ 1.3369\\ 1.3384\\ 1.3399\\ 1.3414\\ 1.3429\end{array}$	$\begin{array}{r} 1.3298\\ 1.3312\\ 1.3326\\ 1.3340\\ 1.3355\\ 1.3369\\ 1.3384\\ 1.3399\\ 1.3414\\ 1.3429\end{array}$
10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00	$\begin{array}{c} 1.3482\\ 1.3498\\ 1.3514\\ 1.3531\\ 1.3547\\ 1.3563\\ 1.3580\\ 1.3597\\ 1.3614\\ 1.3632\end{array}$	$\begin{array}{r} 1.3482\\ 1.3497\\ 1.3513\\ 1.3530\\ 1.3546\\ 1.3562\\ 1.3579\\ 1.3595\\ 1.3612\\ 1.3629\end{array}$	$\begin{array}{r} 1.3479\\ 1.3494\\ 1.3510\\ 1.3526\\ 1.3542\\ 1.3558\\ 1.3574\\ 1.3590\\ 1.3606\\ 1.3623\end{array}$	$\begin{array}{r} 1.3479\\ 1.3495\\ 1.3510\\ 1.3526\\ 1.3542\\ 1.3558\\ 1.3574\\ 1.3590\\ 1.3607\\ 1.3623\end{array}$	$\begin{array}{r} 1.3447\\ 1.3463\\ 1.3479\\ 1.3495\\ 1.3511\\ 1.3527\\ 1.3544\\ 1.3560\\ 1.3576\\ 1.3593\end{array}$	$\begin{array}{r} 1.3447\\ 1.3462\\ 1.3478\\ 1.3478\\ 1.3510\\ 1.3520\\ 1.3520\\ 1.3542\\ 1.3558\\ 1.3575\\ 1.3592\end{array}$	$\begin{array}{r} 1.3444\\ 1.3459\\ 1.3475\\ 1.3490\\ 1.3506\\ 1.3521\\ 1.3537\\ 1.3553\\ 1.3569\\ 1.3585\end{array}$	$\begin{array}{r} 1.3444\\ 1.3459\\ 1.3475\\ 1.3490\\ 1.3506\\ 1.3521\\ 1.3537\\ 1.3553\\ 1.3569\\ 1.3585\end{array}$
$\begin{array}{c} 20.00\\ 21.00\\ 22.00\\ 23.00\\ 24.00\\ 25.00\\ 26.00\\ 27.00\\ 28.00\\ 29.00\\ \end{array}$	$\begin{array}{r} 1.3649\\ 1.3666\\ 1.3684\\ 1.3701\\ 1.3719\\ 1.3737\\ 1.3755\\ 1.3774\\ 1.3792\\ 1.3811 \end{array}$	$\begin{array}{r} 1.3646\\ 1.3663\\ 1.3681\\ 1.3698\\ 1.3716\\ 1.3733\\ 1.3751\\ 1.3769\\ 1.3788\\ 1.3806\end{array}$	$\begin{array}{c} 1.3640\\ 1.3656\\ 1.3673\\ 1.3690\\ 1.3707\\ 1.3725\\ 1.3742\\ 1.3759\\ 1.3777\\ 1.3794 \end{array}$	$\begin{array}{c} 1.3640\\ 1.3656\\ 1.3673\\ 1.3690\\ 1.3707\\ 1.3725\\ 1.3742\\ 1.3759\\ 1.3777\\ 1.3794 \end{array}$	$\begin{array}{r} 1.3610\\ 1.3627\\ 1.3645\\ 1.3662\\ 1.3680\\ 1.3698\\ 1.3715\\ 1.3733\\ 1.3751\\ 1.3770\\ \end{array}$	$\begin{array}{r} 1.3608\\ 1.3625\\ 1.3642\\ 1.3659\\ 1.3677\\ 1.3694\\ 1.3712\\ 1.3729\\ 1.3747\\ 1.3765\end{array}$	$\begin{array}{c} 1.3602\\ 1.3618\\ 1.3635\\ 1.3652\\ 1.3669\\ 1.3686\\ 1.3703\\ 1.3720\\ 1.3737\\ 1.3754\end{array}$	$\begin{array}{r} 1.3602\\ 1.3618\\ 1.3635\\ 1.3652\\ 1.3652\\ 1.3685\\ 1.3685\\ 1.3602\\ 1.3719\\ 1.3737\\ 1.3755\end{array}$
$\begin{array}{c} 30.00\\ 31.00\\ 32.00\\ 33.00\\ 34.00\\ 35.00\\ 35.00\\ 37.00\\ 38.00\\ 39.00 \end{array}$	$\begin{array}{r} 1.3829\\ 1.3848\\ 1.3867\\ 1.3866\\ 1.3906\\ 1.3925\\ 1.3945\\ 1.3964\\ 1.3984\\ 1.4004 \end{array}$	$\begin{array}{r} 1.3824\\ 1.3843\\ 1.3862\\ 1.3860\\ 1.3899\\ 1.3919\\ 1.3938\\ 1.3957\\ 1.3977\\ 1.3997\end{array}$	$\begin{array}{r} 1.3812\\ 1.3830\\ 1.3848\\ 1.3866\\ 1.3885\\ 1.3903\\ 1.3922\\ 1.3941\\ 1.3959\\ 1.3978\end{array}$	$\begin{array}{r} 1.3812\\ 1.3830\\ 1.3848\\ 1.3860\\ 1.3885\\ 1.3903\\ 1.3921\\ 1.3940\\ 1.3959\\ 1.3978\end{array}$	$\begin{array}{r} 1.3788\\ 1.3806\\ 1.3825\\ 1.3844\\ 1.3863\\ 1.3882\\ 1.3901\\ 1.3921\\ 1.3940\\ 1.3960\end{array}$	$\begin{array}{r} 1.3783\\ 1.3802\\ 1.3820\\ 1.3839\\ 1.3857\\ 1.3876\\ 1.3895\\ 1.3914\\ 1.3934\\ 1.3953\end{array}$	$\begin{array}{c} 1.3772\\ 1.3789\\ 1.3807\\ 1.3826\\ 1.3844\\ 1.3862\\ 1.3880\\ 1.3899\\ 1.3917\\ 1.3936\end{array}$	$\begin{array}{r} 1.3773\\ 1.3790\\ 1.3808\\ 1.3826\\ 1.3844\\ 1.3863\\ 1.3881\\ 1.3899\\ 1.3918\\ 1.3937 \end{array}$
$\begin{array}{c} 40.00\\ 41.00\\ 42.00\\ 43.00\\ 44.00\\ 45.00\\ 45.00\\ 46.00\\ 47.00\\ 48.00\\ 49.00 \end{array}$	$\begin{array}{c} 1.4024\\ 1.4044\\ 1.4065\\ 1.4086\\ 1.4107\\ 1.4128\\ 1.4149\\ 1.4170\\ 1.4192\\ 1.4213\end{array}$	$\begin{array}{c} 1.4016\\ 1.4036\\ 1.4057\\ 1.4077\\ 1.4097\\ 1.4118\\ 1.4139\\ 1.4160\\ 1.4181\\ 1.4202 \end{array}$	$\begin{array}{c} 1.3997\\ 1.4016\\ 1.4036\\ 1.4055\\ 1.4074\\ 1.4094\\ 1.4114\\ 1.4134\\ 1.4154\\ 1.4174 \end{array}$	$\begin{array}{r} 1.3997\\ 1.4016\\ 1.4035\\ 1.4055\\ 1.4055\\ 1.4074\\ 1.4094\\ 1.4113\\ 1.4133\\ 1.4154\\ 1.4174\end{array}$	$\begin{array}{c} 1.3980\\ 1.4000\\ 1.4020\\ 1.4041\\ 1.4061\\ 1.4082\\ 1.4103\\ 1.4124\\ 1.4145\\ 1.4167\\ \end{array}$	$\begin{array}{c} 1.3973\\ 1.3993\\ 1.4012\\ 1.4032\\ 1.4053\\ 1.4073\\ 1.4093\\ 1.4114\\ 1.4135\\ 1.4156\\ \end{array}$	$\begin{array}{c} 1.3955\\ 1.3974\\ 1.3993\\ 1.4012\\ 1.4031\\ 1.4051\\ 1.4071\\ 1.4090\\ 1.4110\\ 1.4131\\ \end{array}$	$\begin{array}{c} 1.3955\\ 1.3974\\ 1.3993\\ 1.4011\\ 1.4032\\ 1.4051\\ 1.4071\\ 1.4091\\ 1.4111\\ 1.4131\\ \end{array}$
$\begin{array}{c} 50.00\\ 51.00\\ 52.00\\ 53.00\\ 54.00\\ 55.00\\ 55.00\\ 56.00\\ 57.00\\ 58.00\\ 59.00\\ \end{array}$	$1.4235 \\ 1.4257 \\ 1.4257 \\ 1.4301 \\ 1.4324 \\ 1.4346 \\ 1.4369 \\ 1.4392 \\ 1.4415 \\ 1.4438 \\ \end{array}$	$1.4224 \\ 1.4245 \\ 1.4267 \\ 1.4288 \\ 1.4310 \\ 1.4333 \\ 1.4355 \\ 1.4378 \\ 1.4400 \\ 1.4423 \\ \end{array}$	$\begin{array}{c} 1.4195\\ 1.4215\\ 1.4236\\ 1.4256\\ 1.4256\\ 1.4278\\ 1.4299\\ 1.4320\\ 1.4341\\ 1.4363\\ 1.4384 \end{array}$	$1.4195 \\ 1.4215 \\ 1.4235 \\ 1.4256 \\ 1.4277 \\ 1.4298 \\ 1.4320 \\ 1.4341 \\ 1.4362 \\ 1.4384$	$\begin{array}{c} 1.4189\\ 1.4210\\ 1.4232\\ 1.4254\\ 1.4276\\ 1.4298\\ 1.4321\\ 1.4344\\ 1.4367\\ 1.4390\\ \end{array}$	$1.4177 \\ 1.4199 \\ 1.4220 \\ 1.4242 \\ 1.4264 \\ 1.4286 \\ 1.4308 \\ 1.4331 \\ 1.4354 \\ 1.4376 \\ \end{array}$	$\begin{array}{c} 1.4151\\ 1.4171\\ 1.4192\\ 1.4212\\ 1.4233\\ 1.4254\\ 1.4275\\ 1.4296\\ 1.4318\\ 1.4339\end{array}$	$\begin{array}{c} 1.4151\\ 1.4171\\ 1.4192\\ 1.4212\\ 1.4233\\ 1.4254\\ 1.4275\\ 1.4296\\ 1.4317\\ 1.4339\\ \end{array}$
$\begin{array}{c} 60.00\\ 61.00\\ 62.00\\ 63.00\\ 64.00\\ 65.00\\ 66.00\\ 67.00\\ 68.00\\ 69.00\\ \end{array}$	$1.4462 \\ 1.4486 \\ 1.4510 \\ 1.4534 \\ 1.4558 \\ 1.4582 \\ 1.4607 \\ 1.4631 \\ 1.4656 \\ 1.4681 \\ 1$	$1.4446 \\ 1.4469 \\ 1.4493 \\ 1.4516 \\ 1.4516 \\ 1.4564 \\ 1.4588 \\ 1.4612 \\ 1.4637 \\ 1.4662 \\ \end{array}$	$1.4406 \\ 1.4428 \\ 1.4450 \\ 1.4473 \\ 1.4495 \\ 1.4518 \\ 1.4518 \\ 1.4540 \\ 1.4563 \\ 1.4587 \\ 1.4610 \\ 1$	$\begin{array}{c} 1.4406\\ 1.4428\\ 1.4450\\ 1.4473\\ 1.4495\\ 1.4518\\ 1.4518\\ 1.4540\\ 1.4563\\ 1.4587\\ 1.4610\\ \end{array}$	$1.4413 \\ 1.4437 \\ 1.4461 \\ 1.4485 \\ 1.4509 \\ 1.4534 \\ 1.4558 \\ 1.4583 \\ 1.4608 \\ 1.4633 \\ 1$	$1.4399\\1.4422\\1.4446\\1.4469\\1.4493\\1.4517\\1.4541\\1.4565\\1.4589\\1.4614$	$\begin{array}{c} 1.4361\\ 1.4383\\ 1.4405\\ 1.4427\\ 1.44427\\ 1.4449\\ 1.4471\\ 1.4494\\ 1.4517\\ 1.4540\\ 1.4563\end{array}$	$\begin{array}{r} 1.4361\\ 1.4383\\ 1.4405\\ 1.4427\\ 1.4450\\ 1.4472\\ 1.4450\\ 1.4472\\ 1.4495\\ 1.4518\\ 1.4541\\ 1.4564\end{array}$
$\begin{array}{c} 70.00\\ 71.00\\ 72.00\\ 73.00\\ 74.00\\ 75.00\\ 76.00\\ 76.00\\ 78.00\\ 79.00 \end{array}$	$1.4707 \\ 1.4733 \\ 1.4759 \\ 1.4785 \\ 1.4811 \\ 1.4837 \\ 1.4863 \\ 1.4803 \\ 1.4890 \\ 1.4917 \\ 1.4944$	$1.4687 \\ 1.4712 \\ 1.4737 \\ 1.4762 \\ 1.4788 \\ 1.4814 \\ 1.4839 \\ 1.4865 \\ 1.4892 \\ 1.4918 \\ 1$	$\begin{array}{r} 1.4633\\ 1.4657\\ 1.4681\\ 1.4705\\ 1.4729\\ 1.4754\\ 1.4778\\ 1.4802\\ 1.4827\\ 1.4827\\ 1.4852 \end{array}$	$1.4633 \\ 1.4657 \\ 1.4657 \\ 1.4681 \\ 1.4705 \\ 1.4729 \\ 1.4753 \\ 1.4778 \\ 1.4802 \\ 1.4802 \\ 1.4827 \\ 1.4852 \\ \end{array}$	$1.4658 \\ 1.4683 \\ 1.4709 \\ 1.4735 \\ 1.4761 \\ 1.4787 \\ 1.4813 \\ 1.4840 \\ 1.4867 \\ 1.4895 \\ \end{array}$	$\begin{array}{r} 1.4639\\ 1.4663\\ 1.4688\\ 1.4714\\ 1.4740\\ 1.4765\\ 1.4791\\ 1.4816\\ 1.4843\\ 1.4869\\ \end{array}$	$\begin{array}{r} 1.4587\\ 1.4610\\ 1.4634\\ 1.4657\\ 1.4681\\ 1.4706\\ 1.4730\\ 1.4754\\ 1.4778\\ 1.4803 \end{array}$	$\begin{array}{r} 1.4587\\ 1.4610\\ 1.4633\\ 1.4657\\ 1.4880\\ 1.4704\\ 1.4728\\ 1.4753\\ 1.4778\\ 1.4802 \end{array}$
80.00 81.00 82.00 83.00 84.00 86.00 86.00 86.00 87.00 88.00 89.00	$1.4971 \\ 1.4998 \\ 1.5026 \\ 1.5054 \\ 1.5082 \\ 1.5110 \\ 1.5138 \\ 1.5166 \\ 1.5195 \\ 1.5224 \\ 1$	$\begin{array}{r} 1.4944\\ 1.4971\\ 1.4098\\ 1.5025\\ 1.5053\\ 1.5080\\ 1.5108\\ 1.5135\\ 1.5163\\ 1.5191 \end{array}$	$\begin{array}{r} 1.4876\\ 1.4901\\ 1.4927\\ 1.4953\\ 1.4978\\ 1.5004\\ 1.5030\\ 1.5056\\ 1.5083\\ 1.5109\end{array}$	$1.4877 \\ 1.4902 \\ 1.4927 \\ 1.4953 \\ 1.4979 \\ 1.5005 \\ 1.5031 \\ 1.5057 \\ 1.5083 \\ 1.5110 \\ 1$	$\begin{array}{c} 1.4922\\ 1.4949\\ 1.4976\\ 1.5004\\ 1.5031\\ 1.5059\\ 1.5087\\ 1.5115\\ 1.5143\\ 1.5172\\ \end{array}$	$\begin{array}{c} 1.4896\\ 1.4922\\ 1.4949\\ 1.4975\\ 1.5002\\ 1.5030\\ 1.5058\\ 1.5085\\ 1.5113\\ 1.5140\\ \end{array}$	$\begin{array}{c} 1.4828\\ 1.4853\\ 1.4878\\ 1.4903\\ 1.4929\\ 1.4955\\ 1.4981\\ 1.5008\\ 1.5034\\ 1.5060\\ \end{array}$	$\begin{array}{r} 1.4827\\ 1.4852\\ 1.4878\\ 1.4904\\ 1.4929\\ 1.4955\\ 1.4981\\ 1.5007\\ 1.6033\\ 1.5059\end{array}$
90,00	1. 5252	1 5910	1 5136	1 5130	1 5909	1 5167	1 5007	1 5000

Experience has been that dilute sirups up to 35° Bé. may be applied best by means of a dropping pipet controlled by a rubber bulb and that for Baumés above 35° , the sirup can be applied most conveniently by glass rods with fire-polished ends.

The procedure followed in obtaining a series of refractive indices over a temperature range was as follows:

After a satisfactory transfer of the sample, the readings were commonly taken by lowering the bath temperature to the lowest point and working upward. The bath was equipped with electrical heating coils and a steam inlet. Readings were made only after the precision thermometer on the refractometer had shown a constant reading for at least 5 minutes. In many instances, observations were continued for long periods to establish whether or not the earlier reading coincided with the latter, thus establishing equilibrium in the sirup or eliminating the possibility of mutarotation. Each sample was subjected to a series of transfers until successive readings agreed exactly in the fourth place. The transfers were made at room temperature or slightly higher, and the refractometer was adjusted to the desired temperature by the circulating water from the bath. It was found particularly advisable to transfer the lighter samples at room temperature or slightly higher, for if the circulating water is much below room temperature, the open prisms tend to fog by condensation of atmospheric moisture.

If it is desired to obtain refractive indices on heavy Baumé corn sirup at temperatures below 45° C., special precautions must be followed in handling the refractometer. The sirup should be applied warm and then cooled to the desired temperature. After the refractive index has been obtained, the prisms must be warmed before attempting their release. The seal of the prisms with heavy corn sirup at low temperatures is so great that they may be seriously damaged if a cold separation is attempted.

METHOD OF PLOTTING GRAPHS

The average number of refractive index-dry substance determinations for the four sirups—42.00, 55.00, 89.00, and 90.7 D.E.—was ninetcen. Preliminary plotting had shown that the temperature differential in the range 18° to 50° C. could be considered a linear function for concentrations above 14% dry substance. For concentrations below 14% dry substance, the temperature relationship deviated from a linear function and approached that of water, with which it coincided at zero dry substance. Consequently, these four sirups were used for the master graphs at two temperatures: 20° and 45° C. The method of plotting was that of D.E. vs. factors (δ). The factors for each experimental dry substance were obtained as follows:

For 20° C.: Observed refractive index - 1.3330 dry substance For 45° C.: Observed refractive index - 1.3298 dry substance

The factors obtained ranged between 0.01300 and 0.02000. The graph obtained used dry substance as the ordinate, each millimeter equaling 0.10% D.S., and factors as the abscissas, each millimeter equaling 0.00002 factor value. The points were located on the graph paper by means of a hand lens and marked with the fine point of a drawing compass. The resulting curve drawn through the points in each case was of small, uniform curvature. From the four master curves, factor values were obtained for each dry substance and the refractive index was computed for these data.

The calculated values, when compared to the experimental data, gave the following results for each curve: Approximately 45% of comparative values were identical; approximately 40% differed by 0.0001 refractive index, this difference being equally divided between plus and minus values; approximately 10% differed by 0.0002 refractive index, again equally divided between plus and minus values; the remainder differed by 0.0003 to 0.0004 and were confined to the high dry substances range of 84 to 88%. Sirups of this dry substance are very viscous and the experimental technique is very difficult for the refractometer, Baumé, and moisture determinations. Several independent tests were always made at this range of dry substance in an attempt to "tie down" the refractive index-dry substance relationship. With ordinary plotting—i.e., refractive index vs. dry substance—it was difficult to distinguish valid data and the trend. The method of factors vs. dry substance clearly distinguished the valid data and defined the trend of the curve.

The resulting refractive index-dry substance data for the dry substance range of 0 to 90% and at temperatures of 20° and 45° C. appear in Table I.

Table II. Increase in Refractive Index Caused by 0.61% Added

0.0000
0.00005 0.00010 0.00015 0.00020 0.00025 0.00035 0.00035 0.00035

REFRACTIVE INDEX-DRY SUBSTANCE-DEXTROSE EQUIVALENT RELATIONSHIP

As stated earlier, the ash contents of the three sirups 42.00, 55.00, and 89.00 D.E. were essentially proportional $\left(\frac{\operatorname{ash content}}{\mathrm{D.E.}} = K\right)$ to the dextrose equivalent and any variation of the ash from this norm was less than the experimental error in measurement on a four-place refractometer. To obtain the effect of the dextrose equivalent on the refractive index, the values for the refractive index-dry substance for these three sirups were plotted in the following manner:

Refractive index was used for the ordinates, each millimeter equaling 0.0002, and dextrose equivalent for the abscissas, each millimeter equaling 0.20. Thus a cross plot of the three values would give the refractive index-dry substance relationship for a given dry substance value. The curve through the three points was found to be a straight line which did not deviate more than 0.0001 in refractive index values within the experimental limitations of the refractometer and the mechanics of plotting. The

time for each dextrose equivalent was extrapolated to 30.00 and 92.00 D.E. From these data, the refractive indices for a 32.8 D.E. sirup were calculated for high dry substance values and compared to the experimental refractive index for the same sirup. The results were the same in most cases, with a deviation not greater than 0.0001 refractive index at any chosen value, again within the limitations of the refractometer and the graph paper. The same was true for the interpolated refractive index for 83.4 D.E. as compared to the experimental values. The facts indicate that the refractive indexdry substance-dextrose equivalent relationship can be obtained for any desired dextrose equivalent from these curves.

EFFECT OF ASH

The ash in starch conversion products is largely sodium chloride (δ). In Table I essentially identical values for refractive index were obtained for the sugar sirups 89.00 D.E., ash 0.61% and 90.7 D.E., ash 1.22%. This was pure coincidence, for the refractive index decreases with increasing dextrose equivalent and increases with increasing ash. However, if both sugar sirups are reduced to an ash-free dextrose equivalent basis, and recalculation made for the 89.00 D.E., 0.61% ash, to place it on the same dextrose equivalent basis as the 90.7 D.E., 1.22% ash, this calculated sugar would have the values 91.2 D.E., ash 0.61%. The refractive index of such sugar values can be obtained easily for all dry substance values shown above. The refractive index-dry substance values for this sugar in comparison to the values for the sugar sirup 90.8 D.E., ash 1.22%, immediately measures the effect of 0.61% ash for all dry substance values between 0 and 90%. A table for a sugar sirup of 91.2 D.E., ash 0.61%, has been constructed and the effect of ash content of 0.61% on the refractive index is given in Table II.

Since these data record the effect of one ash value for a complete range of dry substance, it is at once apparent that a complete set of ash corrections can be prepared with reasonable precision if at least one cross plot of ash effect can be obtained for a high dry substance value. This is based on the assumption that the effect of ash is independent of the dextrose equivalent of the sirup.

A regular corn sirup was chosen to determine the effect of ash (sodium chloride) because of ease of moisture determination (5)and these former data may be consulted for the exact procedure. Briefly, a corn sirup substantially ash-free was prepared and salt was added to the sirup in increasing amounts. Two concentrations were so chosen that values above and below the desired constant dry substance were obtained with the corresponding refractive indices. A straight line cross plot for a fixed dry substance value was made in terms of refractive index. The values for a 76.34 D.S. sirup with increasing salt additions are given in Table III.

REFRACTIVE INDEX-COMMERCIAL BAUME

Corn sirup is sold on a Baumé basis. This test requires special skill if reliable data are to be obtained. Therefore, a table giving the refractive index-commercial Baumé relationship is even more important from the standpoint of commerce than the re-

Table III. Increase in Refractiv	ve Index with Increasing Ash
(76.34 D.S. sirup, refra Ash-Dry Substance Basis	ctive index at 45° C.) Increase in Refractive Index
$\begin{array}{c} 0.00\\ 1.00\\ 2.00\\ 3.00\\ 4.00\\ 5.00\\ 6.00\\ 7.00\\ 8.00 \end{array}$	$\begin{array}{c} 0,00000\\ 0,00042\\ 0,00086\\ 0,00130\\ 0,00174\\ 0,00218\\ 0,00250\\ 0,00250\\ 0,00268\\ 0,00274 \end{array}$

Table IV. Commercial Baumé-Refractive Index

(Refractive indices of corn sirups and corn sugar sirups of various commercial Baumé values) Dextrose Equivalent-Ash										
В6.	30.00 0.28	35.00 0.28	42.00 0.28	45.00 0,28	50.00 0.30	55.00 0.30	60.00 0.30	65.00 0.30	82.00 0.41	89.00 0.61
	Refractive Index at 45.00° C.									
$\begin{array}{r} 40.00\\ 41.00\\ 42.00\\ 43.00\\ 44.00\\ 45.00\\ 46.00\\ 47.00 \end{array}$	1.47741.48251.48781.49331.49861.50411.50981.5155	$1.4773 \\ 1.4824 \\ 1.4877 \\ 1.4931 \\ 1.4985 \\ 1.5040 \\ 1.5097 \\ 1.5154 \\$	$\begin{array}{r} 1.4771\\ 1.4822\\ 1.4875\\ 1.4929\\ 1.4983\\ 1.5038\\ 1.5095\\ 1.5152\end{array}$	$\begin{array}{c} 1.4770\\ 1.4821\\ 1.4874\\ 1.4928\\ 1.4982\\ 1.5037\\ 1.5094\\ 1.5151\end{array}$	1.47691.48201.48731.49271.49211.50361.50331.5150	$1.4768 \\ 1.4820 \\ 1.4873 \\ 1.4926 \\ 1.4980 \\ 1.5036 \\ 1.5092 \\ 1.5149$	$\begin{array}{r} 1.4767\\ 1.4818\\ 1.4871\\ 1.4924\\ 1.4978\\ 1.5034\\ 1.5090\\ 1.5148\end{array}$	1.47661.48171.48691.49231.49771.50331.50891.5147	$\begin{array}{r} 1.4762\\ 1.4813\\ 1.4865\\ 1.4919\\ 1.4973\\ 1.5029\\ 1.5085\\ 1.5143\end{array}$	$\begin{array}{r} 1.4760\\ 1.4811\\ 1.4863\\ 1.4916\\ 1.4971\\ 1.5027\\ 1.5083\\ 1.5142\end{array}$
			R	efractive	Index at	20.00° C				
$\begin{array}{r} 40.00\\ 41.00\\ 42.00\\ 43.00\\ 44.00\\ 45.00\\ 46.00\\ 47.00 \end{array}$	$\begin{array}{c} 1.4825\\ 1.4876\\ 1.4928\\ 1.4928\\ 1.5037\\ 1.5093\\ 1.5148\\ 1.5208\end{array}$	$\begin{array}{c} 1.4824\\ 1.4875\\ 1.4927\\ 1.4927\\ 1.4980\\ 1.5035\\ 1.5092\\ 1.5147\\ 1.5206\end{array}$	$\begin{array}{c} 1.4821\\ 1.4872\\ 1.4925\\ 1.4978\\ 1.5033\\ 1.5089\\ 1.5145\\ 1.5204 \end{array}$	$\begin{array}{c} 1.4820\\ 1.4871\\ 1.4924\\ 1.4977\\ 1.5032\\ 1.5088\\ 1.5144\\ 1.5203\end{array}$	1.48191.48701.49231.49761.50311.50871.51431.5202	$1.4818 \\ 1.4869 \\ 1.4921 \\ 1.4975 \\ 1.5030 \\ 1.5086 \\ 1.5142 \\ 1.5201 \\$	1.4817 1.4868 1.4920 1.4973 1.5029 1.5084 1.5141 1.5200	$\begin{array}{r} 1.4815\\ 1.4866\\ 1.4918\\ 1.4918\\ 1.5027\\ 1.5082\\ 1.5139\\ 1.5198\end{array}$	$\begin{array}{c} 1.4810\\ 1.4862\\ 1.4913\\ 1.4967\\ 1.5022\\ 1.5077\\ 1.5135\\ 1.5193 \end{array}$	1.48081.48591.49111.49651.50201.50751.51321.5191

tractive index-dry substance table. Such a table was constructed by the following procedure:

The refractive index was obtained at two temperatures, 20.00° and 45.00° C., for the dry substance corresponding to the commercial Baumés 40 to 47 according to the accepted values for this relationship (δ). The three master graphs, 42.00, 55.00, and 89.00 D.E., were employed. These data were plotted on millimeter paper employing refractive index as the ordinate, each millimeter equaling 0.0002 refractive index, and as abscissa, the dextrose equivalent, each millimeter equaling 0.10 D.E. Thus each set of points represented one Baumé and a straight line was found to be the best curve through these points. The deviation of points from the straight line was not greater than 0.0001 refractive index—i.e., within the limits of the refractometer and the graph paper. The curve was extrapolated to 30.00 and 92.00 D.E. The extrapolated values for 32.8 D.E. were either equal to or not greater than 0.0001 refractive index from the experimental values for the sirup, as were also the interpolated values for the 83.4 D.E. sugar sirup. From the graph of these values, tables of refractive index-commercial Baumé for a range of dextrose equivalents have been calculated (Table IV). A column of values is also given for the corn sugar sirup—90.7 D.E., 1.22% ash—which, because of its ash content, is not covered by the above method of graphing but is of interest because such a corn sugar sirup is typical of that required for an "80" sugar.

SUMMARY

The refractive index of starch conversion products decreases with increasing dextrose equivalent. The effect of ash (sodium chloride) is to increase the refractive index. The decrease of

refractive index with increasing dextrose equivalent is proportional to the increase in dextrose equivalent if the ash content of the products is also proportional to the dextrose equivalent.

The temperature-refractive index relationship is linear within the range 18° to 45° C. when the concentration exceeds 14% dry substance and within the limits of precision of a four-place instrument.

Tables are presented covering the refractive index-dry substance relationship for starch conversion products typical of commerce, and refractive index-commercial Baumé for typical commercial products of varying dextrose equivalents.

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Determination of Zinc in Cyanide Brass-Plating Baths

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HE large number of papers on the determination of zinc which have appeared during the past 8 years attest to the widespread need for rapid and reliable analytical procedures for this determination. Of the many methods available for the determination of zinc, only two appear to meet the demands placed on control methods. A control method does not long survive unless it is inherently reliable, rapid, and inexpensive. The two methods found to possess these qualities are: (1) the ferroevanide titration using diphenylbenzidine as internal indicator (2) with ferric ion held in solution as the pyrophosphate complex (1), and (2) electrodeposition (5). Where electrolytic equipment is largely tied up by copper determinations, the determination of zinc by ferrocyanide titration is designated. The application of this method to cyanide brass-plating solutions is discussed below. The application of the electrolytic determination of zinc will be discussed in a later paper. Recently (4) the polarograph has been successfully employed for determination of the copperzinc ratio of electrodeposited brass. The authors do not as yet report its use in the determination of copper and zinc in the brass-plating bath.

PROCEDURE

Centrifuge until clear a portion of the cyanide brass-plating solution to be analyzed, pipet 10 ml. into a 180-ml. electrolytic beaker, add dropwise 10 ml. of concentrated hydrochloric acid, and heat until clear. If the solution is not heated until clear, the ferrocyanides initially precipitated by the acid will not complctely redissolve in the next step. Cool and carefully add 7 ml. of a mixture consisting of 3 volumes of concentrated nitric acid and 2 volumes of concentrated sulfuric acid. Evaporate to sulfur trioxide fumes, finally heating over an open flame to cause copious fuming. This step appears essential to assure complete destruction of ferrocyanides and of organic matter. Cool the residual moist salts, wash the beaker sides, add 1 ml. of 1 to 1 nitric acid, and remove copper by electrodeposition.

After the removal of copper, add 3 drops of 5% ammonium

persulfate solution to oxidize any ferrous iron to the ferric state. Evaporate to 25 ml. to destroy excess persulfate. Cool, rinse beaker walls, add 2 grams of sodium pyrophosphate to form the ferric iron complex, and finally, 5 ml. of concentrated ammonia. At this point the solution should be alkaline. If not, make just alkaline to phenolphthalein. Neutralize the solution with 1 to 1 altaine to phenophinatchine and a null in excess. Warm the solution to 40° to 45° C. At this stage commence vigorous mechanical agi-tation of the solution. This is essential for the rapid response of the indicator to ferrocyanide additions. Add 3 drops of 1% dithe indicator to ferrocyanide additions. Add 3 drops of 1% di-phenylbenzidine in sirupy phosphoric acid and 3 drops of 0.2%potassium ferricyanide. The latter addition causes the formation of the violet oxidation product of diphenylbenzidine. Titrate to a permanent end point, using a 0.025 molar solution of potassium ferrocyanide containing 0.3 gram of potassium ferricyanide per liter. The ferricyanide in the titrating solution is essential for obtaining reproducible results and for maintening good indi obtaining reproducible results and for maintaining good indi-cator reactivity.

LIMITATIONS AND ERRORS

The successful functioning of the internal indicator requires careful control of the solution composition. However, the determination is not subject to all the limitations cited in the literature. Nitrates can be present to the extent of 0.5 ml. of concentrated nitric acid per 50 ml. of solution. This makes readily possible the use of small amounts of nitric acid as cathode depolarizer in the electrodeposition of copper. The indicator functions properly in a solution containing 4.5 grams of ammonium sulfate, 6 ml. of 1 to 1 sulfuric acid, and at least 20 mg. of zinc ion per 50 ml. of solution. These proportions must be maintained in order to preserve the sensitivity of the indicator. Samples containing less than 20 mg. of zinc ion may require the addition of known amounts of standard zinc chloride solution prepared from metallic zinc.

To determine the effect of extraneous substances in concentrations higher than those encountered in the analysis of a typical plating solution, a standard zinc chloride solution was used.

End Point Ml. of 0.025 M Potassium Ferrocyanide Effect on Indicator Color Change Substance (Plus Blank) Blank (21.6 mg. of Zn++ in approximately 50 ml. of soln.) Yellow-green end point color change 8.85 10 mg. of Pb++ 10 mg. of As+++ 10 mg. of Sb+++ 10 mg. of Sn++ 10 mg. of Al+++ 8.85 8.85 8.85 8.85 8.85 8.85 No effect No effect No effect No effect Slightly slower color change 20 mg. of Fe⁺⁺⁺ (as pyrophosphate complex) 40 mg. of Fe⁺⁺⁺ (as pyrophosphate complex) 50 mg. of Fe⁺⁺⁺ (as pyrophosphate complex) 10 mg. of Ni⁺⁺ 8.85 Blue-green end point 8.85 Blue-green end point 8.85 Blue-green end point (Ni precipitated as the ferrocyanide) 15.05 10 mg, of M⁺⁺ 10 mg, of Mg⁺⁺ 10 mg, of Ca⁺⁺ 10 mg, of SiO₃⁻⁻ 20 mg, of SiO₃⁻⁻ 4 ml, of 1 to 1 HNO₃ 1.5 ml, of 1 to 1 HNO₃ 1.3 ml, of 1 to 1 HNO₃ 10 mg, of Magnus cleaner⁴ 10 mg, of Magnus cleaner⁶ 10 mg, of action details 10 mg, of action deta 8.85 No effect No effect 8.85 No effect No effect Color change slow No change No change 8.85 9.15 8.90 8.85 8.85 8.80 8.85 Color change less sharp Color change less sharp No effect No color or end point 3

Table I. Effect of Extraneous Substances on Diphenylbenzidine

An alkaline cleaner with about 10% silicate and 0.5% phosphate.
Similar to Durodex but containing a small amount of scap.
The three types of inhibitors used are thought to be:

a piperidine derivative.
a sulforated primary or secondary aromatic amine.
an aldehyde-aromatic amine reaction product.

Each titration sample was prepared by pipetting 10 ml. of standard zinc chloride solution into a 180-ml. electrolytic beaker, adding 4 grams of ammonium sulfate, 6 ml. of 1 to 1 sulfuric acid, and finally the extraneous material to be tested. The resulting solu-tion was diluted to 50 ml., heated to 45 °C., and titrated with the ferrocyanide solution.

A common source of indicator trouble arises from the presence of small amounts of surface-active organic matter in the solution. Reference to Table I shows that such material is capable of preventing completely the formation of the colored form of the indicator and must as a consequence be destroyed before proceeding to the zinc titration. Certain common inorganic ions in concentrations as high as 0.2 mg. per ml. of solution do not interfere significantly with the titration. The end point is unaffected and

the color change remains sharp, though slight changes in hue may result. A silicate-ion concentration above 0.5 mg. per ml. renders the color change slow and less distinct. In the absence of iron the end point color is yellow-green; in the presence of iron, bluegreen. A few trials with solutions of known zinc content will familiarize the analyst with the various stages of the color changes before and at the end point. However, a few hints will aid (3).

With the initial addition of 3 drops of ferricyanide, a violet color should develop. Lack of color at this point indicates serious divergence from the suggested procedure. A new sample is indicated. With the addition of 0.025 molar potassium ferrocyanide (containing 0.3 gram of potassium ferricyanide per liter), the initial violet changes to blue. As the titration proceeds, the blue color fades to a light shade of blue. At a few milliliters from the end point, this light blue will change through blue-green, then yellow-green, and finally attains a light violet color. The color transitions obtained following the light blue stage depend on the rate at which ferrocyanide is added, on the temperature, and on the rate of stirring. Some stages in the color change may not appear. The color at about 2 ml. from the end point should, however, be violet. Enough time must be allowed for the development of the violet complex, which at 40° to 45° C. is a very sensitive and mobile indicator.

If sufficient time is allowed for its development after each increment of ferrocyanide, the end point can be approached with certainty and precision. The titration requires 5 to 10 minutes. Starting with clear bath solution, the determination of both copper and zinc requires an average of 1.5 hours. A distinct advantage of the suggested procedure is that no transfers are required, the analysis being started and finished in the same vessel.

ACKNOWLEDGMENTS

The labor of sifting, by laboratory trials, the present method from among the many methods reported in the literature fell also upon other members of the Motor Products Development Laboratory staff. The authors wish to acknowledge the help of V. F. Felicetta, C. A. Ihrcke, R. E. Mosher, and J. H. Sinclair. They wish also to thank the United States Rubber Company for permission to publish this work.

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Determination of Sesamin

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A method for the quantitative determination of sesamin in sesame oil is based upon measurement of the greenish-yellow color produced by sesamin when it is allowed to react with a mixture of perchloric acid and hydrogen peroxide.

SESAME oil, a vegetable oil extensively used in Europe and Asia for culinary purposes, has commanded but little attention in this country, and the number of published American investigations (?) on it is small. In a large measure this is probably because it is an imported oil and is not an important article of our commerce.

In 1940 Eagleson (1, 3) showed that the toxicity to houseflics of a kerosene solution of pyrethrins was considerably increased by the addition of a small amount of sesame oil. The oil

alone in kerosene was without effect and was the only one of 42 animal and vegetable oils tested (2) that produced synergism. By fractional distillations of sesame oil Haller et al. (5) showed that the principle responsible for this synergistic effect is sesamin, one of the components of the nonsaponifiable fraction and a characteristic constituent of the oil. Sesamin is a substituted bicyclodihydrofuran and is not very reactive chemically. It can also be removed from the oil by extraction with 90% acetic acid, or by adsorption (6) on charcoal or clay, from which it can be removed by elution with suitable solvents.

Besides sesamin, sesame oil contains sesamolin, which on treatment with mineral acid yields sesamol, a phenol. This compound is responsible for several of the color tests (8, 9)used to identify sesame oil. Its value as a synergist with pyrethrum is not known.





Figure 1. Standard Reference Graph

With the curtailment of pyrethrum imports due to the war, the discovery that sesame oil containing sesamin could save part of the pyrethrins in insectidical compositions has assumed considerable importance. The addition of 5% of sesame oil to a solution of pyrethrins in kerosene (2) or dichlorodifluoromethane (4) saves about 50% of pyrethrum.

To be effective as a synergist with pyrethrum, sesame oil must contain sesamin, but the minimum quantity needed has not yet been determined because the sesamin content is variable, and no quantitative method has been proposed for its detection and estimation. Whether the variability is due to variation in the seed or to removal of more or less of the sesamin in the process of refining the oil also remains to be determined.

This paper proposes a method for the determination of sesamin, based upon the observation that a mixture of perchloric acid and hydrogen peroxide gives a greenish-yellow color with any vegetable oil containing sesamin. The color persists for about 6 minutes and this allows ample time for measurement. A curve is established, from which the sesamin content of unknown solutions is read directly, by measuring the color produced by standard solutions of pure sesamin dissolved in sesaminfree sesame oil. The color is measured in this laboratory in an Aminco photoelectric photometer employing a No. 46 blue filter (optical centroid at about 460 millimicrons) and water as a blank to balance the photometer at 100% transmission. (Formation of bubbles of oxygen, after 10 to 15 minutes, in reagent-refined kerosene mixture precludes its repeated use as the blank.) By carrying out the following procedure for preparing the standards and the reagent and for developing the color, it is believed that reasonably accurate results may be obtained.

PROCEDURE

PREPARATION OF REAGENT. Caution must be exercised in handling the following reagents, since they are extremely corrosive. Add, with shaking, 2 ml. of 30% hydrogen peroxide to 4 ml. of 70 to 72% perchloric acid maintained at 15° to 20° C. A mixture that is prepared below 10° C. gives erratic transmission values. This amount of reagent suffices for one reading only. The reagent must be made up fresh for each reading not more than 10 minutes before use. If allowed to stand longer, it oxidizes rapidly and also gives erratic values. PREPARATION OF STANDARD SOLUTIONS. The sesamin-free

sesame oil used in the standard solutions is prepared by dis-solving 100 grams of sesame oil in 100 ml. of petroleum ether (b.p. 30° to 60° C.) and extracting it in a separatory funnel about six times with 20-ml. portions of 90% acetic acid, or until a test portion of the oil shows no color in the reagent described above. The petroleum ether solution of the oil is washed free of acid with metar and then drived oran acidium suffets. The ail of acid with water and then dried over sodium sulfate. The oil

is recovered in 97% yield by removing the solvent completely under reduced pressure.

The pure sesamin used in the standard solutions may be obtained by washing the combined acetic acid extracts once with 25 ml. of petroleum ether and then removing almost all the acetic acid under reduced pressure, at 15 to 20 mm., 60° to 80° C. The residue crystallizes when 5 to 10 ml. of hot 95% ethanol are added. The sesamin is filtered from the cold solution and purified by several recrystallizations from ethanol. The sesamin used in these determinations melted at 121–122° C. (corrected). All samples of refined sesame oil tested in this laboratory were found by acetic acid extraction to contain approximately 1% of sesamin by weight.

One hundred milligrams of pure sesamin, ground in a mortar to a fine powder, are made up to 10 grams with the sesamin-free sesame oil and dissolved with slight warming. Aliquots of 1000, 750, 500, 250, and 100 mg. of this solution are made up to 10 ml. with refined kerosene in separate volumetric flasks. (In these experiments the kerosene used was Deobase.) These standard sesame oil solutions therefore contain 1.00, 0.75, 0.50,

DEVELOPMENT AND MEASUREMENT OF COLOR. One milli-liter of the standard solution is pipetted into a small, dry centrifuge tube. The 6 ml. of freshly prepared reagent are added, and the tube is closed quickly with a clean, tight-fitting rubber stopper. After being shaken vigorously for 30 seconds, the tube is centrifuged for 2 minutes to clear the resulting emulsion, and then the contents are carefully poured into a clean, dry photom-eter test tube. The aqueous layer, at the bottom of the tube, shows a color ranging from faint yellow to dark greenish yellow, depending upon the amount of sesamin present. The color is measured in the photometer excepts 5 minutes after the recent measured in the photometer exactly 5 minutes after the reagent is added. The procedure is repeated on each of the other standard solutions. As shown in Figure 1, the results are plotted on semilogarithmic paper as per cent transmission against concentration of sesamin, providing a standard graph for reference of all analyses made on the same instrument with the same reagents.

To determine the sesamin content of a sample of unknown oil, usually 500 mg. of oil are diluted to 10 ml. with refined kero-sene. The 500-mg. sample is ideal for any oil containing from

0.25 to 1.75% of sesamin. It is probably best to keep the transmission readings between 80 and 28% by adjustment, if necessary, of the size of sample taken. A 1-ml, aliquot of this solution is pipetted into a dry centrifuge tube and the procedure outlined above for develops ing the adaption the standard solutions is followed exactly. The ing the color in the standard solutions is followed exactly. The percentage of light transmission is measured in the photometer and is referred to the standard graph. The concentration of sesamin contained in the aliquot of the kerosene solution is read from the standard graph, and the percentage of sesamin in the university in a standard graph. the unknown oil is calculated as follows:

Per cent of sesamin $= \frac{\text{concentration of sesamin} \times 10}{\text{milligrams of unknown oil}} \times 100$

PRECISION OF METHOD

The curve shown in Figure 1 is drawn through 6 points, each of which is the average of 10 measurements. The standard deviations of the transmission readings tended to increase with the readings themselves, the largest deviation, $\pm 2.5\%$, occurring at 65% transmission. Allowance for this trend and for the curvature of the standard line indicates that the standard error of the final result is practically constant, and that it amounts to about $\pm 0.05\%$ of sesamin when the result of a single determination on an unknown is read from a curve established from 10 replicates.

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Determination of Camphor and Alcohol in Spirit of Camphor by Refractive Index and Specific Gravity

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N EARLIER investigations the authors accomplished the analysis of spirit of camphor by means of 2,4-dinitrophenylhydrazine (1) and the optical activity of camphor (2). The method presented here uses the two physical constants, refractive index and specific gravity, and is applicable to synthetic camphor as well as the natural product.

Schoorl (3) and Weber (4) used physical constants for the analysis of spirit of camphor official in the Dutch and German Pharmacopoeias, respectively. However, their works are not applicable to analysis of the United States Pharmacopoeial product because the preparations in the Dutch and German Pharmacopoeias contain 10% (by weight) camphor and about 60% (by weight) alcohol. The composition of those spirits therefore varies considerably from that of the U.S.P. product.

EXPERIMENTAL

Samples of camphor were obtained from widely different sources over a period of 10 years. Each sample was purified at least twice by sublimation. The first 10% and the last 5% of the sample were rejected each time.

Several solutions containing varying percentages of camphor and of alcohol were prepared from each sample. The solutions studied were made to contain from 7.5 to 11.5% (weight to volume) camphor and from 70 to 90% (by volume) alcohol by the method described in a previous communication (2).

by the method described in a previous communication (2). The refractive indices of the solutions were determined at 20° C. with a Valentine, Abbe-type refractometer and the specific gravities were determined with a 25-cc. pycnometer at 20° C.

From the refractive indices and the specific gravities of about 100 solutions a chart (Figure 1) was constructed in which the ordinates represent the refractive indices and the abscissas represent the specific gravities. By connecting the points as

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plotted, several four-sided figures were formed and divided into smaller units in order to facilitate the use of the chart. Greater accuracy can be obtained with an enlarged chart with additional subdivisions. The more nearly horizontal lines represent camphor percentages from 7.5 to 11.5 and the more nearly vertical lines represent alcohol percentages from 70 to 90.

	Table	I. Ana	lysis of N	latural (Camphor		
Camphor Present %	Alcohol Present %	Refrac- tive Index	Specific Gravity	Cam Deter- mined %	vari- ation %	Alc Deter- mined %	ohol Vari- ation %
% 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7.85 7.92 8.90 8.90 9.35 9.40 9.35 9.80 9.80 9.80 10.00	% 70.00 87.93 90.00 77.00 73.00 78.00 74.00 88.00 87.50 83.00 87.50 85.00 70.00 85.31 85.31 85.31 85.31 85.31 85.31	$\begin{array}{c} 1.3719\\ 1.3715\\ 1.3708\\ 1.3726\\ 1.3727\\ 1.3726\\ 1.3724\\ 1.3738\\ 1.3738\\ 1.3739\\ 1.3739\\ 1.3739\\ 1.3742\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3751\\ 1.3751\\ 1.3751\\ 1.3751\\ 1.3751\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3743\\ 1.3757\\$	0.8780 0.8237 0.8153 0.8503 0.8695 0.8695 0.8297 0.8538 0.8658 0.8479 0.8365 0.8194 0.8365 0.8300 0.8300 0.8360 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8465 0.8285 0.8280 0.8285 0.8287 0.8285 0.8285 0.8285 0.82572	% 7.50 7.41 7.49 7.60 7.75 7.90 8.74 8.74 8.74 8.74 8.74 8.74 8.87 9.58 9.58 9.58 9.58 9.58 9.58 9.58 9.58	$\begin{array}{c} & & & \\$	% 70.00 87.80 89.97 79.75 85.94 78.08 85.94 73.08 85.94 73.08 85.94 73.98 80.00 82.47 83.19 87.52 84.87 69.97 74.00 79.90 79.89 80.64 85.20 85.2	$\begin{array}{c} & & & \\$
$ \begin{array}{r} 10.90 \\ 11.00 \\ 11.00 \\ 11.10 \\ 11.50 \\ 11.50 \\ 11.50 \\ \end{array} $	82.00 75.00 84.00 87.00 70.00 85.00	$ 1.3756 \\ 1.3764 \\ 1.3754 \\ 1.3746 \\ 1.3764 \\ 1.3758 $	0.8375 0.8601 0.8300 0.8188 0.8730 0.8257	$ \begin{array}{r} 10.77 \\ 11.10 \\ 10.96 \\ 11.09 \\ 11.58 \\ 11.55 \\ \end{array} $	$\begin{array}{r} -0.13 \\ +0.10 \\ -0.04 \\ -0.01 \\ +0.08 \\ +0.05 \end{array}$	82.12 74.85 84.20 86.86 70.00 85.11	+0.12 -0.15 +0.20 -0.14 0.00 +0.11

The chart was used for the analysis of samples of spirit of camphor of known composition. The refractive index and specific gravity of each solution were determined. The point of intersection on the chart found from these two constants was located by reference to the respective ordinate and abscissa. From this point of intersection the percentage of alcohol was determined by following along the nearly vertical lines from the point of intersection to the outside of the four-sided figure, either top or bottom. The percentage of camphor was determined by following the nearly horizontal lines to the outside, either right or left. For example, the refractive index of 1.3740 and the specific gravity of 0.8500 may be selected. After the point of intersection has been found, the alcohol content may be read as 79.29% and the camphor content as 8.92%.

Thirty-three samples of spirit of natural camphor of known composition were analyzed by use of a chart similar to Figure 1; the results are given in Table I. The determined values are in accord with the theoretical values. The camphor content shows variations from -0.15 to +0.18% and the alcohol content from -0.25 to +0.20%.

Since synthetic camphor is now used to a considerable extent, several samples of spirit were prepared with the synthetic product col-
		Table II.	Analy	sis of Sy	nthetic	Camphe	or	
	phor	in the second	Refrac-		Can	phor	Alo	ohol
	Pres-	Alcohol	tive	Specific	Deter-	Vari-	Deter-	Vari-
NO.	ent	Fresent	Index	Gravity	mined	ation	minea	ation
	%	%			%	%	%	%
1	10.00	85.56	1.3741	0.8275	9.92	-0.08	85.50	-0.06
1	10.00	85.56	1.3742	0.8279	9.98	-0.02	85.35	-0.21
1	10.00	85.56	1.3741	0.8277	9.90	-0.10	85.48	-0.08
2	10.15	77.00	1.3754	0.8549	10.15	0.00	77.00	0.00
2	10.00	85.66	1.3743	0.8278	10.08	+0.08	85.34	-0.22
2	10.40	84.00	1.3749	0.8321	10.33	-0.07	83.88	-0.12
0	9.70	79.00	1.3749	0.8001	9.70	+0.00	10.01	-0.09
2	10.00	88.00	1.0744	0.0470	10 03	-0.02	85 QA	-0.13
2	0 30	84.00	1 3730	0.8230	0 31	10.03	83 08	-0.02
4	10.00	85 54	1 3744	0 8277	10 17	+0.01	85 33	-0.21
L.	11 10	81 00	1 3763	0 8405	11 22	+0.12	80.93	-0.07
	8 00	80.00	1 3730	0 8486	8 00	0.00	80 15	+0.15
5	10 00	85.56	1 3742	0.8277	10.00	0.00	85.45	-0.11
3	10.90	80.00	1.3760	0.8447	10.85	-0.05	80.00	0.00
6	10.00	85.40	1.3743	0.8284	10.03	+0.03	85.18	-0.22
6	10.00	80.00	1.3751	0.8407	10.00	0.00	79.90	-0.10
6	10.50	85.60	1.3746	0.8250	10.54	+0.04	85.70	+0.10
7	10.00	85.40	1.3742	0.8286	9.91	-0.09	85.20	-0.20
7	10.00	86.00	1.3741	0.8250	10.07	+0.07	85.97	-0.03
7	9.70	79.00	1.3749	0.8501	9.75	+0.05	78.91	-0.09
8	10.00	85.40	1.3742	0.8286	9.91	-0.09	85.20	-0.20
8	10.50	85.60	1.3745	0.8250	10.45	-0.05	80.77	+0.17
8	9.70	79.00	1,3750	0.8600	9.82	+0.12	18.18	-0.22
							10 × 1 × 1 × 1	or the state

lected from eight different sources; Table II shows the results of the analyses. Again these are in accord with the theoretical values.

SUMMARY

A chart has been constructed from which the percentages of alcohol and camphor in spirit of camphor may be determined when the refractive index and specific gravity of the spirit are known. Analyses of different samples of spirit of camphor, whether prepared from natural or synthetic camphor, by the proposed method show close agreement with the theoretical values.

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Precision and Accuracy of Colorimetric Procedures as Analytical Control Methods

Determination of Aluminum

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A colorimetric procedure for the determination of aluminum, calculated and represented as aluminum trioxide and involving the formation of the red complex by the interaction of the aluminon reagent and the aluminum ion, has been developed to meet the special requirements in the rapid analysis of leach liquors in pilot-plant operations. The factors influencing color intensities have been investigated and the requisite techniques for a precision and an accuracy of a control character are described. Employing these techniques in the analysis of an aliquot of the leach liquor, precision and accuracy studies as applied to ordinary and refined laboratory techniques have been made on typical analytical data. Statistical reasoning based on the standard deviation is applied to the acquired data. Applying ordinary laboratory techniques, the average precision, measured by the average deviation of the single results from the mean, is of the order of 1% or 10 parts per 1000, while the overall accuracy is of the order of 1 to 3%.

NUMEROUS literature references (7, 8, 12) and recently published books (3, 6, 17) describe in detail the procedures involved in colorimetric determinations. Although the colorimetric method has been used for the rapid estimation of small quantities of many inorganic substances, not a great deal of emphasis has been placed on the precision and accuracy that might be expected in its use as an analytical control method. In quality control work, speed is so essential that precision and accuracy are often sacrificed; however, since intelligent conclusions in plant operations have to be based on the analytical data, it is essential to ascertain the precision and accuracy of the control methods.

Recent investigations in this laboratory have been concerned with the colorimetric procedures involving aluminum, titanium, silicon, and sodium. The procedures are, for the most part, adaptations of previously published methods; however, as a matter of convenience, deviations from standard procedures are necessarily made from time to time, and the subsequent effects of the variables on precision and accuracy are briefly considered. Statistical reasoning based on the standard deviation is applied to the acquired data (1). The purpose of this investigation is therefore twofold: to describe satisfactory laboratory techniques in colorimetric procedures as applied to aluminum and to evaluate the precision and accuracy that might be expected in routine analyses.

The usual procedure in the colorimetric determination of aluminum involves the formation of the red complex by the interaction of the ammonium salt of aurin tricarboxylic acid (aluminon) and the aluminum ion in a carefully buffered solution (3). In the investigation of aluminum in plants, Winter, Thrun, and Bird (15) conclude that maximum color is obtained in the presence of 10% ammonium acetate when the solution is maintained at a temperature of 80° C. for 10 minutes and pH 4 (approximately). In the presence of 25 ml. of both ammonium acetate and annonium chloride, they find that the dye changes color at about pH 7. Roller (10) states that the red color which aluminum ion gives with aurin tricarboxylic acid is much more sensitive if made at about pH 6.3 instead of in alkaline solutions as recommended by Yoe and Hill (16). The latter authors, investigating the procedure under different experimental conditions, cite five factors that affect the test for aluminum with aluminon: time, temperature, volume, concentration, and the presence of other ions. Lampitt, Sylvester, and Belham (5) suggest the use of glycerol to stabilize the lake formed. Thrun (13) has investigated the use of protective colloids in colorimetric determination of certain metals as lakes of dyes and recommends the use of a gum arabic solution.

The colorimetric method presented here for the determination of aluminum, calculated and represented as aluminum trioxide, has been developed at this station to meet the special requirements in the rapid analysis of leach liquors in pilot-plant operations. The sample taken for analysis must be free from inter-

	(0.04 mm	(ALO)	
	(0.04 mg. (DI 211203)	
	Rea	ding	
Test Tube	No. 1	No. 2	Average
1	185	185	185
2	185	185	185
3	185	186	186
4	184	186	185
50	161	166	164
184	173	168	170
284	159	157	158
384	183	178	181
484	158	158	158
584	163	163	163
1b	187	186	187
2h	183	186	185
ãb	184	187	186
4b	184	187	186
56	185	187	180
00	100	101	180

fering ions, which include ferric iron, beryllium, and chromium, since these form a lake similar to that formed by aluminum. Certain variations may be introduced to eliminate these interferences. Chromium lake, for instance, in acetate solution is rapidly decomposed by the addition of ammonia and ammonium carbonate (6). Several procedures may be followed for eliminating interfering iron (4, 9). Phosphate, if present in appreciable quantities, prevents the formation of aluminum lakes.

ANALYTICAL PROCEDURE

REAGENTS. Composite Solution. Dissolve 154 grams of ammonium acetate, 5 ml. of concentrated hydrochloric acid, 0.400 gram of ammonium salt of aurin tricarboxylic acid and 1 gram of gum arabic in water, and dilute to 1000 ml. Dissolve each reagent in a minimum quantity of distilled water, and add the ingredients of the composite in the order named. The aluthe ingredients of the composite in the order named. minon reagent, weighed out to the nearest milligram, dissolves readily in cold water. To make accurate dilutions, the solution of gum arabic must be cautiously added: otherwise persisting foams will greatly alter the liquid level. The composite solution determined are accurate with any expected to the light. deteriorates with age, especially when exposed to the light; it therefore, must be protected from light when stored. Standard Aluminum Solution. Dissolve 4.74 grams of alu-

mium chloride hexahydrate in 1000 ml. of water (1 ml. = 1 mg. of aluminum trioxide) and standardize gravimetrically (2). Working Standard. Dilute 5 ml. of the standard to 500 ml.

(1 ml. = 0.01 mg. of aluminum trioxide). PROCEDURE. Discharge an aliquot of the previously diluted and

acidified leach liquor (10 ml. of liquor and approximately 15 ml. of concentrated hydrochloric acid in 250 ml.), of an amount estimated to contain 0.01 to 0.06 mg. of aluminum trioxide, into a 25-ml. calibrated blood-sugar test tube by means of a pipet, add distilled water to the 12.5-ml. mark, and thoroughly mix the contents. Add 10 ml. of the composite solution by means of an au-tomatic pipet and sufficient water to bring the meniscus to the 25-ml. mark. Mix the contents of the tube well and place in a boiling water bath for precisely 10 minutes. Cool the tube and contents in running tap water for 5 minutes, mix again, and determine the color absorption with the Klett-Summerson photoelectric colorimeter. A filter of range 500 to 570 millimicrons is employed, since a spectrophotometric study of the color in question shows a maximum absorption at 530 m μ in the red complex.

Since absorption of the red color is not a linear function of the aluminum trioxide concentration, a calibration curve must be established. Quantities of the working standard, equivalent to 0.01, 0.02, 0.03, 0.04, 0.05, and 0.06 mg. of aluminum trioxide, are discharged into blood-sugar test tubes, and the lakes are formed in the usual manner.

Procedures for the gravimetric analysis of aluminum involve the use of a modification of the quinolate method (2).

From the standpoint of accuracy, ease of manipulation, and rapidity of technique, preliminary investigations indicated that the method of dilution was entirely satisfactory. Calibration of twenty blood-sugar test tubes resulted in an average precision of 0.2% or 2 parts per 1000. No detectable difference in colorimeter reading could be observed in comparing procedures involving pipets, burets, and 25-ml. blood-sugar test tubes.

In an investigation on the factors influencing color intensities, certain anomalous results were obtained in establishing the standardization curve (Table I). Even though these tubes were

thoroughly cleaned with chromic acid cleaning solution, it is apparent that only new tubes gave reproducible results. The previous history of the remainder of tubes was unknown. Table II shows the effects of chemically clean test tubes on the reproducibility factor. Tubes in Series I of this table were cleaned with chromic acid cleaning solution; tubes of Series II were cleaned by treating successively with chromic acid, water, ethyl alcohol, benzene, and water; and tubes of Series III were treated with hot chromic acid, water, and alkaline cleaning mixture (14) and rinsed thoroughly with distilled water. Thus, to obtain reproducibly accurate results the test tubes must be chemically clean. In all subsequent colorimetric measurements, new tubes only are used, and these are cleaned, using the procedure as established for Series III.

The length of time in the boiling water bath has a marked effect on the color intensity, as shown in Figure 1. The technique of heating at water-boiling temperatures is employed to increase greatly the rate of color development, and since the color intensity varies with the time, the tubes in all of these investigations were heated precisely 10 minutes.

Table II. Cleaning Effects on Blood-Sugar Test Tubes (0.04 mg of Al-O-)

(0.04 mg. 01	111104/	
C	olorimeter Readi	ngs
Series I	Series II	Series III
203	196	190
192	188	188
169	173	185
172	178	187
175	180	185
163	170	183
187	186	182
188	188	183
167	169	183
169	170	183
previous history unk	nown,	
	C Series I 203 192 169 175 163 187 187 188 167 169 previous history unk	Colorimeter Réadi Colorimeter Réadi Series I Series II 203 196 192 188 169 173 172 178 175 180 163 170 187 186 188 188 169 170 previous history unknown.

The effect of varying quantities of composite on the color intensity is shown in Figure 2. Since the quantity of composite added influences the color intensity, exactly 10 ml. of the aluminon reagent were added from an automatic pipet.

Since the temperature of the sample and reagents is a factor in this method, a control of $\pm 5^{\circ}$ C. of the solution temperature at the time of standardization should be maintained. Several degrees above and below that at which the curve is established result in no serious error. High temperatures promote color development, with attendant high aluminas, while lower temperatures have the opposite effect.

In the preparation of the composite solution, quantitative and qualitative techniques were applied to several sources of the re-



agent. To reproduce the values of previously established standardization curves fairly accurately, it became necessary to weigh out the material on a quantitative basis. An Eastman product appeared to give fairly consistent values. Taylor-Austin (12), recognizing the variations in the color produced by the method, suggests a restandardization whenever a fresh supply of the solid reagent is put into use. Scherrer and Smith (11) state that a satisfactory reagent may be synthesized. However, in view of these variabilities and the fact that the composite undergoes a marked change on standing, even when protected from light, the prime necessity of carrying along a standard in routine analysis cannot be overemphasized. It is common practice in this laboratory to establish a new curve when it is observed that the reading of the standard, when compared with the curve, is in error by an amount greater than 4 or 5%. In the desired concentration range, 0.04 mg. of alumina per 25 ml., this represents 6 or 7 scale divisions. For close control work, especially if the curve has not been determined recently, moderate success has been realized by evaluating the scale divisions in the desired concentration range in terms of milligrams of alumina; thus, by running a standard in the concentration range of the unknown, one can calculate the alumina from the colorimeter reading. Obviously, since the milligrams per unit vary over different parts of the curve as well as for different curves, no permanent values should be assessed to each unit.

PRECISION AND ACCURACY

The precision and accuracy of the colorimetric method are conveniently studied by applying the techniques considered in the foregoing paragraphs to the analysis of a leach solution. An initial investigation was concerned with a factor of reproducibility of results. For this purpose two leach liquors, previously acidified and diluted (10 ml. in 250 ml.) were divided into five portions each, and a 1-ml. aliquot (2 ml. in 250 ml.) of each sample was taken for the measurement. The alumina content, recalculated by applying an appropriate factor for dilution (125), was measured over a period of several weeks. Table III, representing ordinary and refined laboratory techniques, shows what might be expected in the way of precision for 10 typically representative

That No.	
1030 190.	
$Mg./ml.$ d $(d^2 \times$	106)
Precision of Method under Ordinary Conditions	
1 5.11 -0.063 396	39
2 5.23 +0.057 324	19
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	59 19
5 5.11 -0.063 396	<u>.</u>
6 5.25 +0.077 593	29
7 5.14 -0.033 100 8 5.14 -0.033 100	39
9 5.14 -0.033 100	39
10 5.19 +0.017 28	39
Av. = X 5.173 $\Sigma d^2 = 24210 \times 10^{-10}$)~4
1/2d1 - +0.040 -	
	010
$\overline{X} = a\sigma = 5.173 \pm 0.053 \ (P_s = 0.99, 10 \text{ observations})$	
Av. of gravimetric data = 5.114 mg. (Al ₂ O ₃) per ml.	
Precision of Method under Best Conditions	
1 5.11 +0.018 33	24
2 5.08 -0.012 14	14
3 5.11 +0.018 33	24
5 5.08 -0.012 14	14
6 5.08 -0.012 14	14
7 5.14 +0.048 230	04
9 5.09 -0.002 48	4
10 5.12 +0.028 78	34
$Av. = \overline{X}$ 5.092 $\Sigma d^2 = 7369 \times 10^{-10}$	-6
$\overline{\Sigma d^2}$	
$\sqrt{10} = \pm 0.027 =$	Ø10
$\overline{X} = a\sigma = 5.092 \pm 0.029 (P_A = 0.99, 10 \text{ observations})$	
Av. of gravimetric data = 5.124 mg. (Al ₂ O ₃) per ml.	



Figure 2. Effect of Varying Quantities of Composite on Color Intensity

values. The method of evaluating the factor of precision is that derived from consideration of results set up by A.S.T.M. (1). As shown in the table, the numerical results are based on the fact that 99 in 100 limits are used and that these results are based completely on the evidence contained in 10 determinations. The accuracy of the method is determined by making a comparison with gravimetric results; gravimetric data for 10 different leach liquors are given in Table IV.

	Table IV. And	alysis of Leach L	iquors.	
	Accuracy of method	l under ordinary c	onditions	
Test No.	Gravimetric Mg./ml.	Colorimetric Mg./ml.	pH	Error %
1 2 3 4 5 6 7 8 9 10	$\begin{array}{r} 4.113\\ 3.468\\ 3.640\\ 3.589\\ 3.637\\ 3.926\\ 3.831\\ 3.855\\ 3.732\\ 3.977\end{array}$	4.23 3.43 3.70 3.63 3.65 3.93 3.97 3.82 3.62 3.97	6.0 6.0 6.0 6.0 6.0 6.0 6.0 6.0	<12 >L <10 31 30

DISCUSSION

The expression, $P_s = 0.99$ (statistical probability), cited in Table III implies that a value for a was chosen such that, in 99 chances out of 100, one might expect the ranges bounded by the computed limits to include, of the universe sampled, the objective average, \overline{X}' .

From the data in Table III, it is apparent that the colorimetric method should give an average precision, measured by the average deviation of the single results from the mean, of approximately 1%, or 10 parts per 1000. On the basis of the gravimetric value, this represents an accuracy of 1.1%, or 11 parts per 1000. The precision and accuracy are increased by employing refined techniques. In this case special attention was given to temperature control, accurate aliquoting and pipetting, and precise establishment of the standardization curve. However, to attain this precision and accuracy, speed was materially sacrificed. In this case, the average precision becomes 0.6% or 6 parts per 1000. When compared with the gravimetric value, this represents an accuracy of 0.6% or 6 parts per 1000.

The accuracy of the colorimetric method is best judged from the data in Table IV. It is apparent that the accuracy of the method is of the order of 1 to 3%; however, in routine work an occasional 4% error has been observed. In view of the fact that the accuracy is inextricably tied in with the standardization curve, the importance of precise establishment of the calibration curve cannot be overemphasized. If the curve were recently established, then the accuracy and precision become nearly identical if put on the basis of a single analysis. This necessarily follows, since the method involves an empirical comparison against a calibration curve. It is obvious that a higher degree of accuracy will be obtained if, in the preparation of the solution for the colorimetric determination, the concentration of the unknown is approximately adjusted so as to fall in the range above 0.04 mg. per 25 ml.

A further consideration of Table IV reveals the fact that the leach liquors, having been previously acidified with approximately 15 ml. of concentrated hydrochloric acid, when aliquoted to the correct concentration in the presence of excess ammonium acetate, yield a reproducible pH (6.0).

Undoubtedly, colorimetric procedures may be applied for the determination of any element in any given amount by taking suitable aliquot portions for the measurement of the final color; however, applying such a procedure the degree of accuracy will fall markedly as the amount of sample, represented by the aliquots, becomes smaller and smaller. Application of the colorimetric process as a method of analytical control must be decided in terms of the effective range of accuracy by the individual analyst after carefully considering the problem at hand.

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Flow Characteristics of Dispersions of Cotton and Regenerated Cellulose Rayon Fabrics in Cuprammonium Their Significance in Fluidity Calculations

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Flow-pressure and fluidity-velocity gradient graphs were used to determine the flow properties of cuprammonium dispersions of cellulose fabrics and to evaluate the method of calculating the fluidity values. The limits of application of the kinetic energy and velocity gradient adjustments were determined for cellulose-cuprammonium dispersions, under experimental conditions very similar to those recommended by the American Society for Testing Materials. The viscometer and buret consistometer were compared in the Auldity technique.

THE fluidity determination of cellulose dispersed in cuprammonium reagent is an important technique used in the study of cotton and regenerated cellulose rayon fabrics. It is a sensitive method for measuring the extent of degradation of cellulose. A linear relationship between fluidity values and service (11, 12) has been demonstrated in serviceability studies of cotton and rayon fabrics which have been subjected to wear and laundering. Raw cotton fibers dispersed in the cuprammonium solvent exhibit a lower fluidity than deteriorated cellulose.

The purpose of this study was to investigate the flow characteristics of cuprammonium dispersions of cotton and regenerated cellulose rayon fabrics over a wide range of fluidity values. The flow properties of cellulose-cuprammonium dispersions heretofore have been studied only in limited scope. It is important to

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know which cellulose-cuprammonium dispersions are true viscous liquids and which exhibit anomalous flow properties. This information is fundamental in calculating the fluidities of these liquids.

The flow characteristics of the cellulose-cuprammonium dispersions were determined by means of flow-pressure and fluidityvelocity gradient graphs. As a result of the study of the flow properties of these dispersions, the limits of application of the kinetic energy and velocity gradient adjustments were determined. A comparison was made of the fluidity values obtained with the viscometer and the buret consistometer, and the appropriate instrument for the cellulose-cuprammonium fluidity determination was found to be dependent on the flow characteristics of the dispersion.

VISCOMETERS AND METHODS OF CALCULATION OF FLUIDITY VALUE

Two types of capillary tube viscometers are ordinarily used in the fluidity determination of cellulose-cuprammonium dispersions. Figure 1, A, shows the type of viscometer which delivers one or two volumes of liquid, and is recommended by the National Bureau of Standards (10), the American Society for Testing Materials (1), and the British Fabrics Research Committee (7). B is essentially the buret consistometer of Herschel and Bulkley (3) with attach the constant of the constant of the start of the B is essentially the buret consistent of (δ) and permits the (δ) with attachments described by Conrad (δ) and permits the table of quantities in one determination. The discharge of a number of quantities in one determination. buret consistometer is used in the Bureaus of Human Nutrition and Home Economics (13) and Agricultural and Industrial Chem-istry (6), U. S. Department of Agriculture.



- 1. Body of viscometer, 10 = 0.25 mm. inside
- diameter Capillary discharge tube, 0.88 ± 0.02 mm. Inside diameter, 25 ± 0.5 mm. length Steel plunger Rubber stopper Flanged rubber tube 2.

- Clips Glass capillary Metal hooks for rubber bands Metal collar õ
- Body of consistometer, 10 mm, inside diameter Capillary discharge tube, 0.96 ± 0.02 mm, inside diameter, 25 ± 0.5 mm, length Steel plunger enclosed in a spring Rubber stopper Public view B.
- CDEFGH.
- Rubber tube

- Rubber ruse Screw clamps Glass capillary Metal hooks for rubber bands Mark etched for placement of lower edge of stopper

In the generally accepted procedure of the American Society for Testing Materials (1) and the British Fabrics Research Com-mittee (7) for determining the fluidity of 0.5% solutions of cotton fabrics and 2% solutions of regenerated rayon fabrics in cuprammonium, the same method of calculating the fluidity values has been used for all the dispersions regardless of the true viscous or anomalous character of the liquids. These organizations and These organizations and several investigators (4, 5, 10) use the following formula:

$$F_e = \frac{C'}{t - \frac{K}{t}} \quad \text{or} \quad F_e = \frac{C}{d\left(t - \frac{K}{t}\right)} \tag{1}$$

 F_{e} is the fluidity in rhes corrected for kinetic energy, C is the instrument constant obtained by calibration (1) with mineral oils of known viscosity, $C' = \frac{c}{d}$, in which d is the density of the cuprammonium solvent in grams per milliliter, t is the time of flow in seconds, and K is the kinetic energy correction constant obtained by calibration (1, 5). It is convenient to consider dconstant since the density of cuprammonium suspensions do not differ essentially from the density of the cuprammonium solvent. Formula 1 is a convenient way of expressing the reciprocal of the well-known Poiseuille equation. C in Equation 1 is equal to $\frac{8LV}{\pi gr!h}$ in the Poiseuille equation, and K equals $\frac{mVC}{8\pi L}$. The Poiseuille equation and Equation 1 are applicable only to the streamline flow of true viscous liquids.

Since many cellulose-cuprammonium dispersions are not true viscous liquids, and the Poiseuille equation is not strictly applicable and gives so-called "apparent fluidities", Downey and Elmquist (13) adapted the following equation to the calculation of the fluidities of dispersions of cellulose fabrics in cuprammonium:

$$F_0 = \frac{q}{C (P - p)} \tag{2}$$

 F_0 in rhes is Bingham's (3) mobility value which is not corrected for kinetic energy, q is the rate of flow in milli-liters per second, C is the instrument constant obtained by calibration with mineral oils of known viscosity, P is the hydrostatic pressure in grams per square centimeter, and p is the yield value. The yield value is the minimum pressure required to establish the flow of a plastic material, and is graphically determined as the intercept of the graph prolonged on the axis of the abscissa when the hydrostatic pressure is plotted as abscissa and the rate of flow, q, as ordinate (Figure 2). When the dispersion is a true viscous liquid the yield value, p, is 0, and Equation 2 becomes

$$F_0 = \frac{1}{CP}$$
, which in terms of the Poi-
seuille equation is $F_0 = \frac{8LV}{\pi gr^4 h dt}$ for $C = \frac{\pi gr^4}{R} = \frac{R}{R} = \frac{R}{R}$ and $a = \frac{V}{R}$

Equation 2 is suitable for calculating the mobility of plastic materials. It would be satisfactory for calculating the fluidity values of cellulose-cuprammonium dispersions if they were plastic liquids having real yield values and flowing at such a slow rate that the kinetic energy correction is not necessary.

The most recent contribution to the calculation of the fluidity of cellulose-cuprammonium dispersions was

made by Conrad (6), who adjusted the fluidity observed at different mean velocity gradients to a standard or reference velocity gradient.

8L '

When a liquid flows through a capillary tube, the central part of the column of liquid flows most rapidly while the liquid in conthat with the capillary wall is nearly stationary, and the layers of the liquid column slip past each other between those two limits. The velocity gradient is the rate of change in the velocity of the adjacent layers of the liquid per unit of distance measured at right angles to the direction of the velocity. In the capillary flow method the viscosity or fluidity of a true liquid is independent of the velocity gradient, but the fluidity of an anomalous liquid depends on the velocity gradient and has an indefinite number of values at different points in the cross section of the capillary tube.

Conrad (6) calculated the mean velocity gradient in capillary tubes by the equation:

$$G = \frac{8V}{3\pi r^3 l}$$
(3)

which was derived by Kroepelin (9) in 1929. G is the mean velocity gradient in centimeters per second per centimeter and V is the volume in milliliters of the solution discharged in t seconds through a capillary of radius r centimeters. Conrad recognized that G, calculated from Equation 3, is an approximation rather than a true value for anomalous dispersions of cellulose in cuprammonium solvent.

The velocity gradient adjustment was shown by Conrad (6) to eliminate the variation of the fluidity values of highly anomalous cellulose-cuprammonium dispersions determined at different average pressures in the buret consistometer. He also pointed out that the velocity gradient adjustment overcomes differences in fluidity values between instruments in the cellulose-cuprammonium fluidity determination. However, he studied dispersions in the very limited fluidity range of approximately 2 to 3 rhes. The scope of the anomalous behavior of cellulose-cuprammonium dispersions has not been determined heretofore.

EXPERIMENTAL PROCEDURE

The buret consistometer with dimensions and parts as illustrated in Figure 1, B, was used in the fluidity determinations. The consistometers were calibrated according to the method of Herschel and Bulkley (8) with mineral oils of known viscosity ob-tained from the National Bureau of Standards. The value of m, the coefficient of kinetic energy correction for which the constant value 1.12 is ordinarily assumed, was calculated for each of thirty consistometers (8) and was found to vary from 1.04 to 1.32.

The inside capillary diameters of thirty instruments were calculated according to Herschel and Bulkley (8) and were found to vary between the limits of 0.0942 to 0.0985 cm. Con-stants C' and K in Equation 1 were calculated according to the directions of the American Society for Testing Materials (1) and Clibbens and Little (5). The hy-drostatic pressure, P, in the flow-pressure graphs, was calcugraphs, was calculated by the equation P = hd. The average head, h, was obtained with Meissner's for-



Figure 2. Flow-Pressure Graphs of Simple, Complex, and Plastic Liquids



The density of the cuprammonium solvent, d, has a value of 0.94

(1, 7). The cuprammonium solution contained 15 ± 0.1 grams of copper, 200 ± 5 grams of ammonia, and less than 0.5 gram of nitrites per liter, which are the specifications of the British Fabrician terms of the committee (7) and the more accurate limits stated rics Research Committee (7) and the more accurate limits stated by the American Society for Testing Materials (1). The solution was prepared, stored, and delivered with equipment similar to that designed by Mease (10).

The concentrations of the cellulose-cuprammonium dispersions were 0.5 and 2.0% by volume for the cotton and regenerated cellulose rayon fabrics, respectively. Forty-two cuprammonium rayon, 165 viscose rayon, and 773 cotton samples at various stages of degradation were used to investigate the flow characteristics of cellulose-cuprammonium dispersions. These samples had been subjected to ordinary household wear and laundering without drastic chemical treatment.

The procedure employed for determining the fluidity of the cellulose-cuprammonium dispersions was essentially the same as that described by the American Society for Testing Materials (1), except the rate of flow of the dispersions from the buret consistometer was obtained with a "split second" stop watch in two ways in the same determination: as a series of observations corresponding to the successive 5-ml. quantities, and as the rate of flow of a single 20-ml. discharge. The 20-ml. volume rather than the 25-ml. quantity was used because it more nearly corresponds to the volume between calibration marks 1 and 2 of the viscometer (Figure 1, A). The temperature during conditioning and timing was controlled at 20° = 0.1° C.

One fluidity determination with a buret consistometer furnishes sufficient data for a flow-pressure graph. The single-volume viscometer does not provide data for such a graph unless determinations are repeated at different pressures, which would require additional apparatus.

STUDY OF FLUIDITY DATA

FLOW-PRESSURE RELATIONSHIPS OF REGENERATED CELLULOSE RAYON FABRICS IN CUPRAMMONIUM. Flow-pressure graphs, in



Figure 3. Flow-Pressure Graphs of Simple Liquids A (left), observed flow valves. B (right), flow valves corrected for kinetic energy.





which the average hydrostatic pressure, P, is plotted as abscissa and the rate of flow, q, as ordinate, indicate the flow properties of a liquid. It is well known that the flow-pressure graph of a simple liquid, also called a Newtonian or true viscous liquid, is a straight line passing through the origin-for example, I in Figure 2. The American Society for Testing Materials (2) defines a simple liquid as one in which the rate of shear is proportional to the rate of stress, and a complex liquid as one in which the rate of shear is not proportional to the shearing stress. The flow-pressure graph of a complex liquid, II in Figure 2, passes through the origin but is not linear. Complex liquids have also been called pseudoplastic (14). A complex liquid does not have a real yield value; the apparent yield value, f in Figure 2, is obtained by disregarding the lower curved part of the graph. III in Figure 2 is the flow-pressure graph of a plastic material, a straight line which does not pass through the origin. A plastic material has a real yield value, p in Figure 2, which is the minimum pressure required to establish flow.

In Figure 3 the flow-pressure graphs of cuprammonium dispersions of cuprammonium and viscose rayon are compared with those of known simple liquids—that is, mineral oils J, H, and D, and cuprammonium solvent. Each fluidity value given for a cellulose dispersion is the average of the 4 values obtained in a single discharge with the buret consistometer. The rates of flow in Figure 3, A, are uncorrected; those in Figure 3, B, are corrected for kinetic energy.

In the uncorrected flow-pressure graphs, the liquids with a slow rate of flow—for example, mineral oil J and cuprammonium rayon samples 11, 14, and 17—are represented by linear graphs. For these liquids the kinetic energy correction is relatively unimportant. As the rate of flow increases and the kinetic energy correction becomes more important, the uncorrected curves become increasingly concave to the pressure axis. When the data were corrected for kinetic energy, the curvature of the flowpressure graphs was removed, and all the graphs in Figure 3, B, became linear, passing through the origin.

Forty-two cuprammonium rayon samples ranging in corrected fluidity value, F_o , from 4.52 to 8.26 rhes were found to form the typical flow-pressure graphs of simple liquids. The characteristic flow-pressure graphs of three representative cuprammonium rayon dispersions are included in Figure 3. The flow-pressure graphs of 165 viscose rayon dispersions rang-

The flow-pressure graphs of 165 viscose rayon dispersions ranging in F_e values from 7.51 to 32.9 rhes were those of simple liquids. As the fluidity of the six representative viscose dispersions in Figure 3 increases, the curvature of the uncorrected graphs becomes more evident,

KINETIC ENERGY CORRECTION. The importance of the kinetic energy correction is apparent in the comparison of the graphs in Figure 3. In a fluidity determination the kinetic energy correction varies continuously as the dispersion flows from the tube, and decreases as the flow becomes slower. The effect of the kinetic energy correction on the fluidity calculations when the buret consistometer is used is shown in Table I with representative data for the simple rayon dispersions. The uncorrected fluidity values, F_{0} , of the dispersions of higher fluidity, viscose 64, 156, and 164, increases in value as the rate of flow decreases in the discharge from the consistometer. When corrected for kinetic energy, the corresponding values, F_{e} , in Table I become constant within experimental error.

The magnitude of the kinetic energy correction was calculated over the entire range of fluidities of cellulose fabric dispersions using capillary discharge tubes with inside diameters varying from 0.094 to 0.098 cm., a specification nearly the same as 0.088 ± 0.002

from 0.094 to 0.098 cm., a specification nearly the same as 0.088 ± 0.002 cm. inside diameter recommended by the American Society for Testing Materials (1). In Figure 4 the average of the uncorrected fluidity values of representative cuprammonium rayon, viscose rayon, and cotton samples obtained with the consistometer is plotted as ordinate and the average kinetic energy correction as abscissa. This graph shows that the uncorrected fluidity values below 7 rhes have a kinetic energy correction of not more than 0.1 rhe, a negligible error of approximately $1\frac{9}{20}$ or less. Thus,

than 0.1 rhe, a negligible error of approximately 1% or less. Thus, for fluidities less than 7 rhes the equation, $F_0 = \frac{C'}{t}$ (Equation 4),

in which F_0 is not corrected for kinetic energy, may be used.

In the range of uncorrected fluidities from 8 to 13 rhes, the magnitude of the kinetic energy correction varies from approximately 2 to 5%, and whether Equation 1 or 4 is used for the calculation depends on the accuracy required. For uncorrected fluidity values of more than 13 rhes, the kinetic energy correction becomes greater than 5%, increasing markedly as the fluidity increases, and Equation 1 is suitable. Clibbens and Geake (4) recognized that the kinetic energy correction is important in cellulose-cuprammonium fluidity calculations and stated that it may amount to 20 to 30% in the case of highly modified cellulose samples.

FLOW-PRESSURE RELATIONSHIP OF COTTON FABRICS DIS-PERSED IN CUPRAMMONIUM. The series of flow-pressure graphs of the dispersions of cotton fabrics in cuprammonium which are plotted in Figure 5 are representative of the graphs of the 773

Table I. Observed Fluidity Values, Fluidity Values Corrected for Kinetic Energy, and Kinetic Energy Correction for Four Rayon Fabrics

(from of the second)			Fluidity	an interior
Sample	Consistometer Ring Interval Ml.	Observed Fluidity ^a Rhes	Corrected for Kinetic Energy ^b Rhes	Kinetic Energy Correction Rhes
Cuprammonium rayon 6	0- 5 5-10 10-15 15-20	4.93 4.90 4.94 4.98	4.97 4.94 4.97 5.00	$\begin{array}{c} 0.04 \\ 0.04 \\ 0.03 \\ 0.02 \end{array}$
Viscose rayon 64	0- 5 5-10 10-15 15-20	12.02 12.16 12.26 12.38	12.6912.7412.7112.7112.71	$\begin{array}{c} 0.67 \\ 0.58 \\ 0.45 \\ 0.33 \end{array}$
Viscose rayon 156	0- 5 5-10 10-15 15-20	$16.05 \\ 16.39 \\ 16.71 \\ 16.82$	17.6917.9217.9417.71	$1.64 \\ 1.53 \\ 1.23 \\ 0.89$
Viscose rayon 164	0- 5 5-10 10-15 15-20	$\begin{array}{r} 22.96 \\ 24.72 \\ 25.60 \\ 26.47 \end{array}$	$30.14 \\ 31.64 \\ 31.35 \\ 31.05$	7.186.925.754.58

• Observed fluidity values calculated by equation, $F_0 = \frac{C'}{T}$.

^b Fluidity values corrected for kinetic energy calculated by equation, $F_e = \frac{C'}{t - \frac{K}{c}}$.



Figure 5. Flow-Pressure Graphs of Cotton Fabrics Dispersed in Cuprammonium A (left), uncorrected flow values. B (center), flow values corrected for kinetic energy. C (right), flow values adjusted for kinetic energy and velocity gradient

cotton dispersions studied. Each fluidity value is the average of the 4 values obtained in a single discharge with the buret consistometer.

The curvature of the uncorrected flow-pressure graphs of the more rapidly flowing dispersions of cottons 161, 167, and 177 is concave to the pressure axis (Figure 5, A). When the rate of flow is corrected for kinetic energy, the graphs for these cottons become linear and pass through the origin (Figure 5, B). Thus, the cuprammonium dispersions of cottons 161, 167, and 177 are those of simple liquids, the Poiseuille equation is applicable, and the fluidity values should not be described as "apparent"

The uncorrected curves in Figure 5, A, of the cotton dispersions of lower fluidity, cottons 54 to 158, are convex to the pressure axis, the curvature decreasing with increase in fluidity. This convex curvature is not removed by applying the kinetic energy correction (Figure 5, B). The graphs of these dispersions of cottons varying in F_e values from 2.72 to

15.5 rhes are those of complex or pseudoplastic liquids (Figure 2). They do not form the curves of plastic materials; and the terms "plastic-ity" or "plastic behavior" should not be used to describe the flow properties of these 0.5%

176

cuprammonium dispersions of cotton fabrics. When the kinetic energy and the velocity gradient adjustments are both applied to the rate of flow of the complex cotton-cuprammonium dispersion 54 to 158, the convex curvature is removed and the flow-pressure graphs all become linear and pass through the origin (Figure 5, C). The velocity gradient adjustment does not influence the flow-pressure graphs of the dispersions of cotton 161, 167, and 177 (Figure 5, C) since they are simple liquids.

VELOCITY GRADIENT ADJUSTMENT. The effect of the velocity gradient adjustment on the fluidity values of dispersions of cellulose fabrics is shown with some representative examples in Table II. The F_e values were calculated with Equation 1, and the G values, mean velocity gradients, with Equation 3. The F values are the fluidities adjusted both for kinetic energy and velocity gradient.

The average \overline{F} value may be read directly from a fluidityvelocity gradient graph (explained below, see Figure 8) by interpolation or extrapolation where the sloping line crosses the vertical standard velocity gradient line. However, if the \overline{F} values corresponding to the successive 5-ml. volumes delivered by the buret consistometer are required, as in Table II, they are calculated from Equation 5:

$$\log F - \log F_o = \text{regression coefficient} \times (\log G - \log G)$$
 (5)

This is the well-known equation of a straight line, $y - y_1 = m(x - x_1)$, where m is the slope of the line which passes through



Figure 6. Comparison of Magnitude of Velocity Gradient Adjustment

point x_1 , y_1 . The regression coefficient, the slope of the line, is obtained graphically. G is the mean velocity gradient calculated with Equation 3 and \overline{G} is the standard velocity gradient.

Table II, A and B, shows that F_c values obtained with a buret consistometer for the complex cotton dispersions 54, 111, 138, and 158 decrease with a decrease in mean velocity gradient as the liquid flows out of the consistometer and the pressure head becomes smaller. If the F_c values are calculated to a standard or reference velocity gradient, the values are corrected for the variation caused by the change in the velocity gradient. When the fluidity of the complex cotton-cuprammonium dispersions are calculated to the standard velocity gradient of 1500, corrected fluidity values, \overline{F}_{1500} , become constant within experimental error (Table II, C).

The standard velocity gradient is entirely arbitrary and it would appear from Figure 8 that almost any intermediate velocity gradient could be selected. Conrad (6) recommended the use of a standard velocity gradient of 500 cm. per second per cm., "since a large part of the data recorded in the literature has been obtained probably at velocity gradients between 100 and 1000 cm. per second per cm., a convenient value might be intermediate, say at 500 cm. per second per cm.". Under the conditions of this study, which are recommended by the American Society for Testing Materials (1), the maximum average velocity gradient is approximately 3000 cm. per second per cm. for complex 0.5% cottoncuprammonium dispersions with F_e values less than 17 rhes (Figure 8). Thus a common velocity gradient of 1500 is suggested, since it is intermediate for these complex dispersions.

When the average F_o values of Figure 8 are plotted against the velocity gradient adjustment, Figure 6, a standard velocity gradient of 1500 gives an adjustment curve which nearly approaches zero tangentially as the F_o values increase to those charac-

which nearly approaches zero tangentially as the F_c values increase to those characteristic of simple liquids. At some velocity gradient slightly above 1500, a curve corresponding to that in Figure 6 would more nearly approach zero. If a standard velocity gradient of 500 had been used, an anomalous dispersion with a F_c value of approximately 4 rhes would have a zero velocity gradient adjustment



Figure 7. Fluidity-Velocity Gradient of Viscose and Cuprammonium Rayon Fabrics Dispersed in Cuprammonium

Table II. Comparison of Fluidity Values Corrected for Kinetic Energy (Fc) with Fluidity Values Adjusted for Both Kinetic Energy and Velocity Gradient Using the Standard Velocity Gradient of 1500 (F 1800)

		Buret Co Consis	onsistomete cutive 5-M A	r Value 1. Volu	es from mes	Sin Value	gle-Volume es, Varying Lower D	Viscon Placer Mark	neter nent of
Type of Dispersion	Sample	tometer ring interval	Mean velocity gradient	B Fc	$\stackrel{ ext{C}}{ ilde{F}_{1400}}$	Vol- ume	Mean velocity gradient	E Fe	F 71500
		Ml.	sec./cm.	Rhes	Rhes	Ml.	sec./cm.	Rhes	Rhes
	Cotton 54	0-5 5-10 10-15 15-20	566 427 288 179 Av	3.20 2.94 2.55 2.20 .2.72	$\begin{array}{r} 4.40 \\ 4.51 \\ 4.47 \\ 4.53 \\ 4.49 \end{array}$	0-5 0-10 0-15 0-20	566 487 396 304 Ay	3.20 3.05 2.82 2.56 2.91	4.50 4.52 4.49 4.47 4.50
Complex cot-	Cotton 111	0-5 5-10 10-15 15-20	1015 800 575 384 Av	5.84 5.48 5.05 4.61 5.24	$ \begin{array}{r} 6.44 \\ 6.41 \\ 6.42 \\ 6.48 \\ 6.44 \end{array} $	0-5 0-10 0-15 0-20	1015 895 755 608 Av	5.84 5.63 5.38 5.07 5.48	6.49 6.47 6.47 6.47 6.47
ton-cupram- monium dispersions	Cotton 138	0-5 5-10 10-15 15-20	1435 1169 876 601 Av	8.41 8.20 7.91 7.48 8.00	8.46 8.47 8.48 8.42 8.42	0-5 0-10 0-15 0-20	1435 1288 1114 918 Av	8.41 8.29 8.12 7.88 8.18	8.46 8.48 8.49 8.48 8.48
in when the	Cotton 158	0-5 5-10 10-15 15-20	2548 2139 1655 1203 Av.	15.89 15.61 15.45 15.12 15.52	$15.36 \\ 15.26 \\ 15.35 \\ 15.33 \\ 15.32 $	0-5 0-10 0-15 0-20	2548 2326 2049 1742 Av.	15.89 15.74 15.62 15.43 15.66	15.27 15.23 15.26 15.26 15.26
ien en wittind octoren genote	Cuprain- monium rayon 6	0-5 5-10 10-15 15-20	859 711 553 396 Av	4.97 4.94 4.97 5.00 4.97	4.97 4.94 4.97 5.00 4.97	0-5 0-10 0-15 0-20	859 778 685 579 Av.	4.97 4.95 4.96 4.98 4.98	4.97 4.95 4.96 4.98 4.96
Simple cellu- lose-cupram- monium dispersions	Viscose rayon 25	0-5 5-10 10-15 15-20	1907 1615 1271 917 Av.	11.34 11.27 11.28 11.13 11.26	11.34 11.27 11.28 11.13 11.26	0-5 0-10 0-15 0-20	1907 1749 1554 1324 Av.	$11.34 \\ 11.28 \\ 11.31 \\ 11.23 \\ 11.29$	11.84 11.28 11.31 11.23 11.29
	Cotton 177	0-5 5-10 10-15 15-20	3680 3123 2545 1840 Av.	25.38 25.30 26.08 25.02 25.44	25.38 25.30 26.08 25.02 25.44	0-5 0-10 0-15 0-20	3680 3379 3046 2617 Av.	25.43 25.31 25.63 25.41 25.44	25.43 25.31 25.63 25.41 25.44

(Figure 6) which is characteristic only of simple dispersions. Thus, in this study, the standard velocity gradient of 1500 was preferred.

According to Figure 6 the velocity gradient correction to a common velocity gradient of 1500 is not necessary if F_{ϵ} is greater than 10 rhes.

The fluidity values of the complex cotton fabric dispersions obtained from the two types of capillary instruments are not the same unless the velocity gradient adjustment is applied (Table II, B and E). Using the consistometer as a single-volume viscometer, the F_o values of the complex cotton dispersions 54, 111, 138, and 158 vary with the position of the lower mark, decreasing as the viscometer volume increases (Table II, E). However, when the velocity gradient adjustment is applied, the fluidity values become constant, regardless of where the mark is placed in the single-volume viscometer (Table II, F).

allow of the single-volume viscometer (Table II, F). Also, until the velocity gradient adjustment is applied, the average of the four values obtained with the buret consistometer from the discharge of 20 ml. of liquid is not equal to the fluidity value calculated from the rate of flow of a single 20-ml. quantity discharged from the same instrument when used as a viscometer (Table II).

Since the velocity gradient adjustment is readily obtained with the buret consistometer in one discharge, the buret type of capillary instrument has an advantage over the single-volume viscometer type for the determination of the fluidity of complex cotton-cuprammonium dispersions with F_o values less than 10 rhes.

In the fluidity calculations of the cellulose-cuprammonium dispersions which are simple liquids—for example, cuprammonium rayon 6, viscose 25, and cotton 177 in Table II—the fluidity values are constant with the application of the kinetic energy correction; and the fluidity is not influenced by the velocity gradient.

The fluidity values for the simple cellulose-cuprammonium dispersions obtained with the two kinds of instruments are the same for any viscometer volume or part of the buret consistometer. Thus either the buret consistometer or the viscometer may be used for these simple dispersions.

FLUIDITY-VELOCITY GRADIENT RELATIONSHIPS. Fluidity-velocity gradient graphs as well as flow-pressure graphs indicate the simple or complex character of a liquid. The former are plotted on log-log paper with the mean velocity gradient, computed with Equation 3, as abscissa and the corresponding F_c value obtained with the buret consistometer as ordinate.

The fluidity-velocity gradient graph of a simple liquid, such as mineral oils J and H in Figure 7, is a horizontal straight line because the fluidity of a simple liquid is independent of the velocity gradient. The fluidity-velocity gradient graphs of Figure 7 show that 2% cuprammonium rayon dispersions ranging from F_e values of 4.52 to 7.98 rhes are simple liquids. Likewise, 2% viscos dispersions with F_e values from 7.51 to 31.0 are all simple liquids. Thus the same information concerning the flow properties of the regenerated rayon-cuprammonium dispersions is obtained from both the flow-pressure (Figure 3) and the fluidity-velocity gradient graphs.



Figure 8. Fluidity-Velocity Gradient of Cotton Fabrics Dispersed in Cuprammonium

The fluidity-velocity gradient graphs of the complex cupram-monium dispersions of cottons 54 to 160 in Figure 8 are linear and sloping. The velocity gradient values of complex cotton-cuprammonium dispersions increase as their fluidities increase. In proceeding from the graphs of cotton 54 to 160, the slopes decrease and approach zero, and the dispersions become less complex. The fluidity-velocity gradient graphs of cottons 161, 167, and 177 are linear and horizontal, those of simple liquids, which is in agree-ment with the information obtained from the flow-pressure graphs of Figure 5.

It is apparent from Figure 8 that under the experimental conditions the cotton-cupranumonium dispersions with fluidities of approximately 17 rhes are borderline between simple and com-plex liquids. The fluidity-velocity gradient graphs of 61 cotton dispersions varying in F_c from 16 to 21 rhes were examined in order to determine the limits of the borderline values. The graphs of 12 dispersions varying in $F_{\rm e}$ values from 16.0 to 17.1 rhes were definitely sloping. Twenty-nine graphs of dispersions with $F_{\rm e}$ values between 17.2 and 18.7 rhes were variable; of these, nine graphs sloped, five were horizontal, and 15 could have been considered either horizontal or slightly sloping. Twenty been considered either horizontal of slightly stoping. Twenty graphs with F_e values from 18.9 to 21.0 rhes were unquestionably horizontal. Thus 0.5% cotton-cuprammonium dispersions with F_e values less than 17 rhes are complex liquids, and those with F_e values greater than 19 rhes are simple liquids. The cases where the E robust or between 17.0 er the constraint of the E robust of the formula of the constraint of the formula of the formu the F_e values are between 17.0 and 18.9 rhes are borderline.

These observations on the range of complex flow of 0.5% cotton-cuprammonium dispersions agree with tests by Clibbens and Little (6) of the deviations of cotton cupranmonium dispersions from the Poiseuille law by means of a time ratio, t_1/t_2 . In this ratio t_1 is the time in seconds for the first volume of liquid to flow from a two-volume viscometer, and t_2 the time for the second

quantity. The t_1/t_2 ratio for a true viscous liquid was equal to unity, provided the kinetic energy correction was small; the time ratio for an anomalous liquid was less than unity. For an F_c value of 15.0 rhes, they reported t_1/t_2 equal to 0.98 and for an F_c value of 21.3, t_1/t_2 was 1.00. They gave no values between 15 and 21.3 rhes.

SUMMARY AND CONCLUSIONS

The flow characteristics of cotton and regenerated cellulose fabrics dispersed in cuprammonium were determined by means of flow-pressure and fluidity-velocity gradient graphs. Under the experimental conditions recommended by the American Society for Testing Materials, 0.5% cotton-cuprammonium dispersions with fluidity values (F_{σ} corrected for kinetic energy) greater than 19 rhes and 2% regenerated cellulose dispersions are simple liquids; 0.5% cotton-cuprammonium dispersions with F_c values less than 17 rhes are complex liquids rather than plastic materials, since they do not exhibit a real yield value.

The formula, $F_0 = \frac{C'}{t}$, may be used for the calculation of fluidity

values less than 7 rhes, since the kinetic energy correction for Equation 1, $F_e = \frac{C'}{t - \frac{K}{t}}$, more frequently used in calculating the

fluidity of cellulose dispersions, is suitable for calculating fluidity values greater than 7 rhes. The velocity gradient adjustment is applicable to the complex cotton-cuprammonium dispersions with F_e values less than 10 rhes. Equation 2, intended for plastic materials, should not be used for calculating the fluidities of cellulose fabrics since they form either simple or complex rather than plastic dispersions, and they often require the kinetic energy correction.

Either the buret consistometer or the viscometer may be used for the regenerated cellulose dispersions or the cotton dispersions with F_c values greater than 10 rhes. The buret type of capillary instrument has an advantage over the single-volume viscometer type for the determination of the fluidity of complex cottoncuprammonium dispersions with F_c values less than 10 rhes, since the velocity gradient adjustment is readily obtained with the buret consistometer in one discharge.

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Antimony Trichloride Reaction of Vitamin D

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N RECENT years, many investigators have reported on methods for the physicochemical estimation of vitamin D in fish liver oil. Many of these methods (1-4, 7, 8) depend upon the measurement of the yellow color developed when antimony trichloride or some modification (5, 6, 9) of this reagent is added to the vitamin D-containing fraction which is usually freed from vitamin A, sterols, and other color-producing substances by a chromatographic procedure.

Some years ago when these laboratories were actively investigating this problem, a reference calibration curve of the antimony trichloride yellow color was made up using crystalline calciferol (British Drug House) as a standard. It was found that variations in the conditions of concentration, time, light, and temperature all had a marked effect in the development of the yellow color at 500 m μ . Some of these effects have been overlooked by other investigators. These observations are published here in the hope that they may enable others to obtain closer agreement in their results.

EXPERIMENTAL PROCEDURE

One milliliter of a chloroform solution of calciferol was meas-ured into a colorimeter tube, and 10 ml. of a chloroform solution of antimony trichloride (saturated at 20° C.) were added rapidly from an automatic pipet. The intensity of the orange color was determined in an Evelyn photoelectric colorimeter, using a 500 mµ filter. (The filter was made up by E. E. Richardson of the Eastman Kodak Research Laboratories by adding some components to the 500 m μ filter supplied by the Rubicon Company to give a sharper band.) From the galvanometer reading function L, approximately proportional to the optical density, was determined. Using this basic procedure, the conditions of concen-tration of calciferol, time, light, and temperature were varied.

EFFECT OF VARYING CONDITIONS

CONCENTRATION. The intensity of the yellow color of the antimony trichloride-calciferol reaction product was not proportional to the amount of calciferol in the aliquot tested, except at very low concentration (5 micrograms or less per ml.). With larger amounts the color development was much less than would be expected from the intensity of color at lower concentrations (Figure 1, upper). These observations were confirmed by measurements made at 500 mµ on a recording spectrophotometer. Thus a calibration curve is recommended. If a conversion factor is used, it must be limited to a small range of optical density.

TIME. Calciferol-antimony trichloride colors must be measured after an exact interval of time. At 30° C. the color intensity reached a maximum after 4 minutes, then slowly and steadily faded (Figure 1, center).

LIGHT. The maximum color development was reached when the reaction was allowed to take place in the dark. When the color was developed in a shaded corner of the room on a bright day, the results were about 10% low, and when allowed to stand near the window, the results were about 15% low.

TEMPERATURE. Changes in temperature had a profound effect on the color development (Figure 1, lower). The intensity increased with temperature to a maximum at 42° C., beyond which it decreased. Between normal ranges of room temperature (19° to 33° C.) there was a difference of 40% in the color intensity of the same solution.

DISCUSSION

The author is not attempting to set up strict conditions under which vitamin D determinations with antimony trichloride should be run. This is left to the individual investigator, but attention is called to the variables which must be controlled







closely if reproducible results are to be obtained. In this laboratory satisfactory checks were obtained $(\pm 2\%)$ on samples of calciferol by the following procedure:

One cubic centimeter of chloroform solution, calculated to contain about 0.07 to 0.25 mg. of calciferol, was measured into a colorimeter tube which had been allowed to come to constant temperature by inserting in a rack of steel tubes immersed in a controlled temperature bath at 30° C. Ten cubic centimeters of antimony trichloride solution (saturated in chloroform at 20° C.) were then added. The reagent had also been previously brought to 30° C. by immersing the container in the constant-temperature bath. The steel tubes were covered to exclude light and the color was allowed to develop for exactly 4 minutes. The colorimeter tubes were removed and immediately read on an Evelyn photoelectric colorimeter, using a 500 m μ filter. The amount of vitamin D was calculated from a calibration curve prepared from crystalline calciferol.

In the estimation of vitamin D by the antimony trichloride procedure, the conditions of concentration, time, light, and temperature must be rigidly controlled to obtain reproducible results.

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A Versatile Liquid-Liquid Extractor

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ANY liquid-liquid extractors have been described. A large number of these are patterned after the device described by Marshall (1) which, although labor-saving, is slow and therefore expensive to operate. In addition certain materials are heat-labile to the extent that they are destroyed in the boiling flask.

The apparatus herein described utilizes the well-known gas lift principle to overcome these objections and presents many additional possibilities for extraction procedures, catalytic reactions, adsorptions, etc. It is compact, simple to build, and very economical to operate. Low vacuum (0.5 inch) or a slight air or gas pressure serves equally well to operate the unit

whether it be used as a small laboratory unit or for large-scale extractions. The extractant may be either the heavier or the lighter liquid.

The basic apparatus, which may be used as a batch extractor and which has been used to advantage in procedures normally carried out with separatory funnels. is shown in Figure 1. In operation, vacuum at 1 or pressure at 2 causes the lighter liquid in 3 to drop to 4, where a plug of air enters tube 5 and pushes the liquid in 5 into reservoir 6. Increased height of the liquid at this point causes a downflow through tube 7, where at this point causes a download entogen due 1, indee it bubbles out through a fritted-glass bubbler and rises to the liquid interface, 8, thence to point 4, momen-tarily sealing opening to tube 5. Gas entering through tube 3 again forces liquid into reservoir 6. A low vacuum or gas pressure causes a continuous, rapid bubbling action. When the heavier liquid is to be bubbling action.



Figure 1

the extractant, an outlet should be provided at the bottom of the flask, 9.

Figure 2 illustrates the extractors used in conjunction with a boiling flask and condenser for continuous operation. Extraction time is much reduced by this arrangement.

Figure 3 is a design of an apparatus utilizing this principle for extracting or percolating solid materials or for conducting adsorptions or catalytic reactions. The cylinder, 1, may be packed, or a thimble containing the material to be extracted may be inserted into the chamber. The unit is operated in the same manner as the liquid-liquid extractor.

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Elimination of Nitrate Impurities from 30 Per Cent Hydrogen Peroxide

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HE phenol-disulfonic acid method for the determination of nitrates in plant tissue is being used in this laboratory. Many modifications have been reported.

Roller and McKaig (2) developed a modified method involving the use of 30% hydrogen peroxide as an oxidizing agent for or-ganic matter. Because of the appreciable nitrate impurity in hydrogen peroxide, it was found necessary to purify this reagent, and distillation under reduced pressures was suggested by Roller and McKaig. [At the present time, 30% hydrogen peroxide low in nitrates is sometimes difficult to obtain in large quantities upon immediate request, and the commercial product-e.g., Superoxol c.p. grade—obtainable in somewhat larger quantities, generally contains approximately 200 p.p.m. of nitrate.]

This method of purification is time-consuming, and further-more 30% hydrogen peroxide when distilled under reduced pressures (15 to 60 mm. of mercury) has seldom been found by the author to yield a distillate of more than 20% hydrogen peroxide. Consequently, attempts were made to purify the reagent by other means. Experiments indicated that this could be done by per-colating the reagent through layers of activated carbon suitably separated as shown in Figure 1.

APPARATUS AND PROCEDURE

water-cooled ad-A sorption column with dimensions as indicated was used. A sinteredglass filter plate sealed into the lower end of the tube was found necessary to prevent small carbon particles from passing into the purified reagent. The column is loosely packed with 5to 10-gram portions of activated carbon (Columbia brand activated carbon, type F, with glass beads, glass wool plugs, and perforated porcelain plates. The separatory funnel at the top of the column is filled with hydrogen peroxide, suction ap-plied at the receiving flask, and the rate of percolation regulated by the stopcock on the separatory funnel to produce a desirable flow.

DISCUSSION

It was necessary to design a column and to find a suitable adsorbent which could be used to remove nitrate from hydrogen peroxide without subsequent decomposition of this reagent. The effectiveness of various forms of active carbon was determined experimentally.



Glass wool

Very fine active carbon, such as powdered Nuchar or Norit A. was unsatisfactory in the author's column because of the slow rate of percolation of reagent, and the rapid rate of decomposition due to the particle size. A coarse product such as Nuchar 4/10-mesh was somewhat more suitable than a fine carbon, but did not compare favorably with the Columbia Carbon product. Commercial organic anion-exchange materials could not be used because of the rapidity with which they are oxidized and broken down by hydrogen peroxide. Under the author's working conditions, Columbia brand activated carbon appeared to be best adapted to requirements.

In order to obtain maximum efficiency, the carbon is pre-treated as follows: A slow stream of sulfur dioxide is passed for several hours into a large Erlenmeyer flask containing 500 grams of carbon. The carbon is then oven-dried at 110° C. for 24 hours, and is ready for use. Active carbon not treated in this manner may be used, but the nitrate content of the purified peroxide is generally somewhat higher and varies from 15 to 30 p.p.m.

The percentage concentration of the final product appeared to be related to the rate of percolation of fluid (Table I). At a low rate of flow, appreciable decomposition occurred because of catalytic activity of the carbon. As the rate was increased, the percentage composition tended to approach that of the original reagent. Consequently, it may be necessary to determine by trial and error at what rate the reagent should be percolated through the column in order to yield best results. The author has found that for his apparatus a rate of percolation of approximately 200 cc. per minute is most effective.

A water-cooled system was considered necessary since heat is liberated at the carbon-fluid interface. The rate of decomposition is increased appreciably with increase in temperature, and an explosive rate may be approached if an air-cooled unit is used (1).

The purification of the reagent is obviously dependent upon the nature of the adsorbing agent; however, the manner in which the column is packed and the thickness of the carbon layers. as well as the distance between them, are important in maintaining proper temperatures, a rapid rate of percolation, and, subsequently, a concentrated purified product.

RESULTS

By passing successive portions of hydrogen peroxide through the column, it was found that approximately 35 grams of active carbon were sufficient to purify over 500 cc. of the reagent. The

UNIT Transfer	Table I. N	itrate in Hy	drogen Pero	xide
(Column pack	ed as indicate	d in Figure 1 mately 200 p.	l. Original N .p.m.)	O: content, approxi
Rate of	H2O2 in	H2O1 in	NO: in	Temp. of
Percolation	Original	Purified	Purified	Purified
of H ₂ O ₂	Product	Product	Product	Reagent
Cc./min.	%	%	P.p.m.	° C.
Thickness of C	Carbon Layers,	2 Cm. Dist of Carbon La	tance between ayers, 4	Layers, 9 Cm. No.
200	31	28	6	Approximately 23
100	31	24	5	Approximately 23
60	31	21	5	Approximately 23
Thickness of C	Carbon Layers,	4 Cm. Dist of Carbon 1	tance between Layers, 4	Layers, 5 Cm. No.
200	31	23	4	Approximately 23
100	30	19	4	Approximately 23
60	30	16	5	Approximately 23
Column Packe	ed with Glass	Beads Thore Active Car	oughly Mixed	with 35 Grams of
100ª	29	5	6	60
50	31	2	6	60-70
^a A rate of position of H ₂	percolation of	200 cc. per n	ninute was not	attained. Decom-
	02 interfered w	ith rapid per	colation of flu	id.

purified product contained less than 10 p.p.m. of nitrate and its average percentage concentration was approximately 27 to 29% hydrogen peroxide. [The nitrate content of both untreated and purified hydrogen peroxide was determined according to Scott (3). An aliquot of hydrogen peroxide containing 0.1 mg. or less of nitrate was used.]

No investigations were made as to a method of "recharging" the carbon by replacement of adsorbed nitrate with other anions, so that carbon might subsequently be utilized again. Once the column has become saturated with nitrate, its contents are replaced with fresh material.

The nitrate content of the purified reagent offers no difficulty in the determination of nitrates (the small amount present can be accounted for in the blank determination), the peroxide concentration remains sufficiently high to produce the desired results, and the time necessary for the purification of the peroxide has been reduced appreciably.

ACKNOWLEDGMENT

The author desires to express appreciation to T. C. Broyer for suggestions on this paper.

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Operating Procedure for Determining the Heat of Combustion of Gasoline

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The paper describes details of operating procedure for determining the heat of combustion of gasoline. The degree of precision and the economy of conducting the tests compare favorably with those possible for petroleum products of low volatility.

ANY of the specifications for aviation gasoline now in M effect in the United States include a minimum limit for lower or net heat of combustion. The prescribed procedure is to determine the gross calorific value in an approved oxygenbomb calorimeter and obtain the net value by making a suitable correction for the latent heat of vaporization of water formed during combustion of the fuel.

Practically all published directions for determining the gross calorific value of aviation gasoline are exemplified by Method 250.2 of the Federal Specification for Lubricants and Liquid Fuels (2). This prescribes the use of the standard A.S.T.M. method of test for thermal value of fuel oil (1) modified as follows for volatile fuel:

Fill a dry, weighed, gelatin capsule of suitable size with dry cotton fiber, weigh the capsule again, and record the weight of gelatin and cotton. Fill the capsule by immersing it in the fuel and closing it under the surface. Dry the outside of the capsule, weigh the capsule immediately, and record the weight of the fuel. Wrap the ignition wire around the capsule three or four times and place the capsule is both or four times and place the capsule immediately in the bomb. Fill the bomb with oxygen at 30 atmospheres pressure, and proceed with the test as outlined in Method 250.1.

Repeat the test if traces of sooty deposit or odor of unburned fuel are noticed when the bomb is opened after combustion.

Corrections. Make all corrections outlined in Method 250.1 and in addition correct for the heat of combustion of the gelatin and the cotton by subtracting from the total heat developed.

These directions, obviously, leave a great deal to the imagination of the operator. The authors' laboratory has had occasion to acquire a large amount of experience with this particular determination, and the present paper discusses the details which are missing in the published directions quoted above, and gives specific instructions followed by their operators.

CONDITION AND SIZE OF GELATIN CAPSULES

The use of a dry gelatin capsule of suitable size is prescribed. As purchased, capsules contain a large and indeterminate amount As purchased, capsules contain a large and indeterminate amount of water. One batch dried in a desiccator over calcium chloride showed a loss of weight of about 10% for the first day, and an additional 4.5% in the 20 days following. Complete drying could be effected by heating in an oven at 221° F., but the cap-sules then became brittle and unusable. It was found that cap-sules "as received" did not change appreciably during the nor-mal time of the weighing operation, regardless of whether the humidity was high or low, and it appeared that the important feature was to ensure uniform water content in a batch, and to avoid extraneous surface moisture.

Capsules having a suitable capacity of about 0.1 ml. are designated as "No. 00 size" by at least one commercial supplier.

FILLING OF CAPSULES

The published directions call for filling a weighed capsule containing a determined quantity of dry cotton, by immersing it in the fuel and closing it under the surface of the liquid. The cotton serves to minimize splashing when the capsule is ignited



in the bomb. Ignited asbestos serves the same purpose and has the obvious advantage of contributing nothing to the heat generated during the combustion period. However, by observing certain simple precautions it is possible to dispense with cotton or asbestos. Splashing does not occur if the capsules are completely filled with liquid and free from even the smallest bubble of air or other permanent gas.

The prescribed operation of filling by pushing together the two halves of the capsule below the surface of the liquid fuel can, if necessary, be performed with the fingers. The use of a special brass holder, such as is shown in Figure 1, has obvious advantages, particularly as regards the size of the container and the quantity of fuel required. It is not considered good practice to fill more than one capsule from the portion of gasoline which has been poured into the dish.

EVAPORATION LOSSES

The fact that capsules are not perfectly tight is recognized in the published directions, by the provision for weighing "immediately" after filling, and placing the capsule in the bomb "immediately" after adjusting the ignition wire. This is to minimize evaporation losses which change the composition of the fuel and introduce an uncertainty as to the weight of the charge actually burned in the bomb. The error due to change in composition of the gasoline seems to be unavoidable but is of negligible magnitude when dealing with the present types of aviation fuel and is perhaps 0.02 or 0.03% for each full per cent evaporation loss. The error due to loss of material is in direct proportion to the amount of gasoline that is vaporized.

A simple practical scheme, devised for determining the evaporation loss between the time of completing the final weighing of the filled capsule and the time of closing the bomb, involves determining the rate of evaporation loss (rejecting the capsule if this is excessive) and measuring the time interval between the completion of the weighing and the closing of the bomb. When the initial evaporation loss is not in excess of 0.0010 gram per minute, the rate remains practically constant for at least 2 additional minutes. An experienced operator can usually transfer a capsule from the pan of the balance to the bomb in one minute or less.

DETAILED WORKING DIRECTIONS

PREPARATION OF SUPPLY OF CAPSULES. Place approximately 1000 gelatin capsules in a bottle with a tight screw top. Allow to stand for at least 30 days to ensure equalization of the moisture content of all individual capsules. In case of emergency, this "soaking" period may be reduced to one week by using an oversize bottle and shaking its contents vigorously at least twice

a day. At the time the soaking period is started, prepare test por-tions for determination of the calorific value of the gelatin. Each portion consists of about ten capsules, cut into small pieces and placed inside a capsule. Put these test portions, with the halves of the containing capsules separated, in a small shallow dish or a perforated gill can, which is placed in the bottle with the main supply. At the end of the soaking period, remove the can, as-semble the capsules, and place them in a small bottle which is tightly closed. Remove the gelatin-filled capsules from this bottle one at a time for determination of their calorific value. Make at least three determinations, and if the average deviation from the mean of these results exceeds 45 B.t.u. per pound, make additional determinations until the average deviation is less than this amount.

Transfer at least 100 capsules from the large bottle to a set of small screw-top bottles of similar type, putting 10 to 15 capsules (approximately 2 days' supply) in each bottle. Avoid making the transfer under conditions which might cause the capsules to pick up surface moisture. The relative humidity should not be too high and the capsules should not be far enough

below room temperature to bring about condensation. FILLING OF CAPSULES. Withdraw a capsule from the current working supply, restoppering the bottle immediately. Weigh with an accuracy of 0.1 mg. and record as W_1 . Pour some of the sample to be tested into a small beaker or crucible. Place each half of the capsule in a suitable brass holder such as is shown in Figure 1. Immerse the halves of the capsule in the gasoline, with the open ends obliquely upward, and agitate very gently for 20 to 30 seconds, to get rid of bubbles of occluded air or other permanent gas which would interfere with complete filling. Then put the two halves together, still keeping them immersed. Withdraw from the liquid, wipe dry with a clean cloth, and place on the pan of the balance.

Weigh to 0.1 mg. and record as W_2 . When balance is attained, start a stop watch and obtain another weight exactly 60 seconds later. Record as W_3 . Insert the filled capsule in a coil of ignition wire, already attached to the terminals of the bomb and push it down into the cup or crucible. The coil is

made by wrapping three or four turns of ignition wire around a rod of the same diameter as the capsules. Care should be taken not to warm the capsule appreciably while transferring from the balance to the coil of ignition wire. If the operator uses bare fingers, they must be dry and his touch must be light. Other precautions, such as the use of special tongs, are obviously permissible. Stop the watch when the lid of the bomb is in place. Do not include the operations of screwing on the lock ring, etc., in the time period thus measured.

Compute the weight of gasoline burned, W_b , from the following formula:

$$W_b = (W_2 - W_1) - (W_2 - W_3) \frac{t}{60}$$

t is the time in seconds elapsed between completion of the t is the time in seconds elapsed between completion of the first weighing of the filled capsule and the closing of the bomb, specifically, it is the stop-watch reading. $(W_2 - W_1)$ is the weight of gasoline originally in the capsule and $(W_2 - W_1)$ the amount lost by evaporation during the 60-second period the filled capsule was kept on the balance pan. A normal figure for this loss is from 0.0001 to 0.0010 gram. If it is as much as 0.0015 gram, or if any bubble of air or vapor is observed in the capsule before the bomb is closed, the capsule is rejected.

Obtaining a weight at some predetermined instant is easy with various types of automatic-reading balances now available. If the simple conventional type of balance is used it is recommended that its sensitivity be determined and that $(W_2 - W_3)$ be measured in terms of change in the swing rather than by trying to shift the rider. It is, however, possible to measure the time for, say, 0.0010-gram loss rather than the loss during 60 seconds. If this is done, the formula above should be suitably modified.

OTHER METHODS FOR BOMB-CALORIMETER DETERMINATIONS WITH VOLATILE FUELS

A somewhat different procedure, using gelatin capsules, has been described by Jones and Starr (4). It has not been tried in the authors' laboratory but they believe it is slightly less convenient and no more accurate than that described It has not been above.

The method of Richter and Jaeschke (7) involves weighing the charge of gasoline in a special platinum crucible covered with a thin skin of collodion. It has not been tried, but the accuracy claimed is no better than that normally attained with the procedure described above.

The most precise method known to the authors is that originally described by Richards and Barry (β) , and later improved by Jessup (β) and Prosen and Rossini (β) . The charge is weighed in a hermetically sealed special glass bulb with flattened sides. This bulb, if properly made and completely filled, opens in the bomb without splashing, when exposed to the heat generated by the combustion of the iron fuse wire. The procedure is more time-consuming than that described above and the technique of fabricating, filling, and sealing the bubs requires a higher de-gree of manipulative skill than is necessary when using gelatin capsules.

The authors take this opportunity to suggest that the ideal solution of the problem is to weigh the charge in a special closed container which opens mechanically in the bomb when the ignition wire is burned. With adequate ingenuity and experimentation a practical device of this type might be developed.

Table I. Benzene Blank Determination for a Typical Period of 29 Consecutive Working Days

(Values in British thermal units per pound)

18,032	18,020	18,005	18.071
18,030	18,031	18,057	18,057
18,011	18,069	18,043	18,039
18,032	18,065	18,048	18.045
18.048	18.034	18,067	18.030
18.041	18.057	18.045	18.033
18,042	18.005	18,060	18,058
18 010	A PARTIE AND	The state of the state of the state of the	

Mean, 18,041 Av. deviation from mean, 15.5 B.t.u., or 0.086% Max. deviation from mean, 36 B.t.u., or 0.200%

Vol. 16, No. 3

PRECISION ATTAINABLE

It is customary in the authors' laboratory to make a blank determination once a day on a sample of "chemically pure" benzene. Table I shows the results obtained in a period, selected at random, of 29 consecutive working days.

The exact calorific value of the benzene used is not known, hence these "blank" determinations are an index of the reproducibility rather than the absolute accuracy of the determinations. The basic standard is benzoic acid, obtained from and certified by the National Bureau of Standards.

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Chromatographic Determination of Carotene in Alfalfa

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A chromatographic method is presented, with supporting experimental data, which avoids the oxidative losses of carotene generally encountered in freshly harvested plant tissues, as well as errors due to incomplete extraction and incomplete separation of carotenes from other pigments present. The method includes an enzyme in-

N THE assay of plant tissues for carotene three important factors are capable of causing large errors in determined values. (1) The carotenes are unstable, undergoing oxidation under ordinary conditions and isomerization or other changes (1) under certain conditions. This necessitates the use of proper precautionary measures throughout the analysis. (2) Difficulty is encountered in many instances in extracting all the carotene. Each different plant tissue must be handled as a separate extraction problem and checks must be carried out to prove that extraction has been complete. (3) Separation of carotenes from other substances in the extract prior to measurement is difficult. The carotenes occur in intimate association with other carotenoids whose close chemical and physical relationship to the carotenes makes their elimination a serious problem. Several investigators (4, 7, 11, 12) have concluded that in methods based on phasic separations, noncarotene pigments are measured as carotene. The chromatographic technique appears to be the only one extant which is capable of completely removing these interfering substances.

A method for routine use has been evolved which overcomes for practical purposes all the difficulties referred to and requires only very simple equipment. Using this method one operator can analyze eighteen prepared alfalfa samples per 8-hour day. While modifications have been applied to a variety of plant tissues, the discussion from this point on deals principally with the determination as applied to freshly cut alfalfa.

PROCEDURE

FIELD SAMPLING. From each field plot to be sampled a representative sample of about 1000 grams is collected by cutting off within an inch of the ground small handfuls of alfalfa at a number of random positions throughout the plot. Immediately after collection the sample is wrapped in paper with enough cracked dry ice (as shown by experience) to freeze it quickly and maintain a frozen condition until subsampling and enzyme destruction can be carried out. The resulting bundles of alfalfa rolled in paper are tagged and placed in an insulated double plywood box for transportation to the laboratory.

SUBSAMPLING AND ENZYME DESTRUCTION. Each field sample is taken from the box the same day as cut and while still frozen is unwrapped and run twice through a Russwin food chopper (not a meat grinder) with any remaining dry ice, then mixed thor-oughly by hand to render it as homogeneous as possible. At this

activation and sample storage procedure, making possible the collection and preparation of large numbers of samples on fixed dates. The chromatographic technique has been modified for the purpose at hand, by converting the adsorption column to an adsorption filter which avoids losses of adsorbed carotene.

point all desired subsamples, about 5 grams each, are weighed im-mediately and directly into 125-ml. Erlenmeyer flasks containing about 25 to 30 ml, of the slightly alkaline ethanol preparation described below. The flasks are shaken briefly and placed on a hot plate, where they are allowed to simmer under a reflux condenser for 10 minutes. After partial cooling the flasks are com-pletely filled with Skellysolve B, stoppered tightly with rubber stoppers, and placed in a refrigerator at -1° C, until taken for analysis

EXTRACTION. At any convenient time, as long as 30 days thereafter, the entire contents of each flask are transferred quan-titatively to the container of a Waring Blendor with the aid of a stream of Skellysolve B from a wash bottle. A convenient type of wash bottle for this purpose has been described (2). The Blendor is run for about 2 minutes, after which the contents are filtered directly into a 500-ml, separatory funnel. A convenient filter for this purpose is a funnel large enough to accommodate the entire contents of the Waring Blendor container, fitted with a piece of sheeting or other closely woven white cotton cloth. The solids retained by the filter are washed with Skellysolve and squeezed out repeatedly therein.

PREPARATION OF SOLUTION FOR CHROMATOGRAPHING. After the lower layer is discarded, the resulting solution must be freed of most of the chlorophyll present and of other polar solutes, since these would interfere with the subsequent chromatographic separation if allowed to remain. This is accomplished by washing the solution repeatedly according to the following directions:

1. Add 25 to 30 ml. of 10% (weight per volume) solution of po-tassium hydroxide in 80% ethanol and shake the separatory funnel vigorously for 4 or 5 seconds. Discard the lower layer.

Repeat (1) once.

3. Add about 100 ml. of water and shake gently for a few seconds. Discard the lower layer.

4. Add about 100 ml. of approximately 4% sulfuric acid solution and shake gently for a few seconds. Discard the lower layer.

5. Add about 200 ml. of water and invert the funnel three or four times quickly but without undue force. Discard the lower layer.

 Repeat (5) once.
 Finally, immediately before chromatographing, draw off and discard the last water which settles.

These operations may be performed rapidly. Only one separatory funnel is required for each sample, since it is always the lower layer which is discarded. The carotene solution remains in All the separations of layers referred to take place rapidly unless preceded by too vigorous shaking, which is unlikely to occur ex-cept in the two final rinsings with water. In practice six carotene determinations are carried out simultaneously. With a battery of six separatory funnels, no waiting for separation of layers is necessary. All the discarded layers have been analyzed repeatedly and have never been found to contain measurable amounts of carotene.

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CHROMATOGRAPHIC SEPARATION OF CAROTENE. After the last bit of water which separates is discarded, the contents of the separatory funnel are passed through a drying tube charged with anhydrous sodium sulfate placed above an adsorption tube packed with an adsorp-tive mixture (1 part of magnesia to 8 parts of soda ash by weight) into a 250-ml. graduated cylinder connected for removal of air by suction (see Figure 1). The percolation cannot be speedily ac-complished by gravity alone. The drying complished by gravity alone. The drying and adsorption tubes should be wetted previously with Skellysolve B. As soon as all the solution from the separatory funnel has passed into the drying tube, the funnel is rinsed with 25 to 30 ml. of Skellysolve B which is also passed into the percolation system. The system is now washed further with Skellysolve con-taining 1% ethanol by volume until the upper pigment bands begin to move down. This guarantees that no carotene, adsorbed or unadsorbed, remains in the column.

The adsorption tubes are prepared by packing the adsorbent mixture into filter tubes of about 20- to 25-mm. inside di-ameter, plugged at the constriction by a wad of cotton or glass wool. A depth of 5 cm. in a 20-mm. tube is adequate for carotene determinations in 5-gram fresh alfalfa samples. The tubes are packed by pressing small portions of the adsorbent firmly into place in the tube supported vertically. This packing is done with a plunger consisting of a long stout rod and properly fitting rubber stopper. When the tube is held in a horizontal position, if the surface layer retains its position it has been packed tightly enough.

PHOTOMETRIC MEASUREMENT OF CARO-TENE. After percolation is complete the

volume of the percolate is noted and its carotene content is measured in a photometer previously standardized against pure β -carotene or a suitable secondary standard solution. In this laboratory an Amineo type F photoelectric photometer was used routinely with the No. 42 filter in place. From the data thus obtained and the weight of the sample, the carotene content of the material analyzed is calculated.

EXPERIMENTAL

SAMPLING AND EXTRACTION. Since the samples for experimental work at this station had to be collected in large numbers on given days during the growing season, some method of storing them without loss of carotene prior to analysis was necessary. Preliminary work showed (1) that cold storage of samples in an atmosphere low in oxygen cannot be relied on to preserve carotene in alfalfa samples; and (2) that chopping alfalfa for representative sampling initiates very rapid destruction of carotene. Twenty-one samples which had been run through a food chopper showed in 16 hours an average loss of 37.2% of their carotene.

Rapid losses of this kind probably take place only in the presence of oxidases which occur in the plant. If so, alfalfa samples for carotene assay must be treated immediately after they are weighed out by some solvent or reagent capable of destroying the enzymes. Since Zimmerman et al. (13) recommended boiling diacetone as an enzyme-destroying agent and solvent, it was tried on alfalfa samples. Other agents tried were ethanol, and hot and cold ethanolic potassium hydroxide (5, 9). In all cases the volume used was 25 ml. on a sample weighing 5 ± 0.5 grams. The results are shown in Figure 2.

The destruction of carotene is evident in samples heated with either diacetone or alcohol. Noteworthy is the fact that a strongly alkaline reagent, 10% ethanolic potassium hydroxide, gave higher values than either of the other solvents. This fact and the report of Beadle and Zscheile (1) that acids cause destruction of carotene, as well as the further fact that the ethanol

used in the preceding experiment carried slight acidity, led to a trial of ethanol containing in solution a small excess of potassium hydroxide. Such a solution was prepared by adding to commercial ethanol enough powdered potassium hydroxide to neutralize its acidity, then 0.5 gram per liter excess.

Several 5-gram subsamples taken under the same conditions from a single well-mixed sample of ground alfalfa were weighed into 125-ml. Erlenmeyer flasks containing 25 ml. of the alkaline ethanol described above. The flasks were placed on a hot plate and left there for the contents to boil for 10 minutes. Since it was also desired to determine the effect of excluding air, the sub-samples thus treated were divided into two lots. The flasks in samples thus treated were divided into two lots. The flasks in one lot were completely filled with Skellysolve B in order to exclude air and were tightly stoppered; those in the other lot were stoppered tightly with the air unreplaced. All were stored in a refrigerator at -1° C. to await analysis. All convenient intervals thereafter sets of four subsamples comprised of one pair from each of the two lots were analyzed. As controls, two other subsamples were taken and analyzed immediately without treatment. Figure 3 presents an average of results obtained in several repetitions of this experiment, in which carotene values have been reduced to percentages of the original content.

No great loss of carotene occurred, either during or after treatment with alkaline ethanol, if the samples were protected from air. If they were not so protected, a slow loss of carotene took place, presumably through spontaneous oxidation, since oxidative losses of carotene in the presence of enzymes appear to be much more rapid than observed here. It may be concluded that the treatment described prevents enzymatic and spontaneous oxidation of carotene in alfalfa samples without serious loss of carotene during treatment.

The foregoing comprises a part of the extraction procedure, since after samples are so treated and stored for a few days under the stated conditions they appear to have undergone a softening or disintegration and to have lost their green color to the supernatant solvents. Subsequent maceration of samples in this con-

Figure 2. Effect of Treatments on Carotene in Alfalfa

- A. No treatment, analyzed at once (taken as 100%)
 B. Refluxed 20 minutes with 10% alcoholic KOH
 C. Digested 20 hours at room temperature with 10% alcoholic KOH
 D. Heated to boiling, boiled 10 minutes with alcohol
 E. Heated to boiling, boiled dry with alcohol
 F. Heated to boiling, boiled 5 minutes with diacetone
 G. Heated to boiling, boiled dry with diacetone

the adsorbent mixture that the carotenes are not adsorbed, but pass through the column while the other pigments are retained. The mixture which just fails to retain carotene was found to be one containing 8 parts of soda ash to 1 part of magnesia by weight. In chromatographing with this adsorbent the mixed carotene band is seen only fleetingly if at all. Thus the adsorption column





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dition is accomplished with great ease in about one minute by means of a Waring Blendor, which is also recommended by other workers (3, 8).

CHROMATOGRAPHY. In the search for a suitable adsorbent for chromatographic separation of carotene from other extracted pigments, it was found that mixtures of soda ash (6, Merck technical) with magnesia (10, Micron brand) showed desirable properties; and that the adsorptive strength can be varied through a considerable useful range of mixture proportions. Inasmuch as the carotenes are subject to destruction while adsorbed (10) and are the least strongly adsorbed of all the pigments present, it was considered desirable so to adjust the composition of becomes in actuality an adsorption filter, and the possibility of loss of adsorbed carotene is eliminated.

The adsorbent mixture is easily reclaimed for further use by placing it in 9-cm. porcelain crucibles in a cold muffle furnace and bringing it gradually to a "low red heat". After 1 or 2 hours at this temperature the furnace is turned off and the contents are allowed to cool in place. This slowly burns out the adsorbed organic substances without destroying the adsorbent, which can be reclaimed in this way at least six times without noteworthy change in activity.

RESULTS AND DISCUSSION

ACCURACY OF THE METHOD. As a measure of accuracy of the method standard deviations were calculated from duplicate values which were available for each of the three cuttings of alfalfa (Table I). The standard deviations are roughly proportional to the mean values found for the three cuttings. This indicates that the inherent precision of the method is at least as great as the accuracy with which the samples were taken.



RECOVERY OF ADDED CAROTENE. A number of recovery tests were run by assaying fresh alfalfa samples along with duplicates to which were added known quantities of pure β -carotene (Smaco) in the form of a concentrated solution in Skellysolve B. The amount of carotene added was determined by measuring photometrically a diluted aliquot of the same concentrate. The results are shown in Table II, where all values for carotene found are averages of two or three separately determined values. A small loss of carotene occurs during analysis by this method. This is not surprising in view of the labile nature of carotene, particularly its great susceptibility to oxidation.

				-				-
Table	1.	Standard	Deviations	of Duplica	te Card	otene V	alues	in
			P	Ifalfa				
		No. of	Sum	of Mea	an of	Stand	lard	

Cutting	Pairs of Values, n	Squares of Deviations, Σx^2	All Values Obtained, γ/g .	Deviation of a Single Value, σ
lst 2nd 3rd	17 27 13	$\begin{array}{r} 65.15 \\ 146.94 \\ 136.40 \end{array}$	$34.5 \\ 48.7 \\ 68.4$	2.02 2.375 3.37

Since in the foregoing recovery tests all samples, with and without added carotene, were subjected to the enzyme-inactivating heat treatment with alkaline ethanol, compensating losses of carotene may have occurred during the heating. Table III shows a comparison of duplicate average values found on subsamples of the same lots of fresh alfalfa analyzed with and without this heat treatment. Unheated subsamples were extracted immediately

ecov- t ered A	dded Rec	overy
erea A	aaea Rec	overy
7	~	0%
		10
14.25	47.0 9	4.1
76.55 28	83.5 9	07.5
24.3 22	20.3 10	01.8
	3 3 2 3	
2	6.55 2 4.3 2	6.55 283.5 9 44.3 220.3 10

Table III. Effect of Enzyme-Inactivation Treatment on Carotene

Sample	Heated γ/g .	Not Heated	Loss on	Destruction
No.		7/0.	Heating γ/g .	%
1	$ \begin{array}{r} 62.9 \\ 54.1 \\ 66.0 \\ 61.4 \end{array} $	64.0	1.1	1.7
2		56.6	2.5	4.4
3		67.35	1.35	2.0
4		63.5	2.1	3.3

to avoid enzyme action. These results indicate a small loss of carotene during treatment, which is not serious for practical purposes and which could be eliminated only by elaborate precautions. According to the results presented, the method described here measures carotene in fresh alfalfa with an accuracy of more than 90% and does not give erroneously high values.

APPLICATIONS TO PRODUCTS OTHER THAN ALFALFA

Since the method was first applied to fresh alfalfa and most of the experimental data were collected using samples of this material, this report has been written accordingly. However, modifications have been applied to a large number of other plant varieties, usually with greater reproducibility of results than reported here. This follows from the apparent greater oxidase activity of alfalfa juice, its more complex pigment system, and its physical form which makes accurate sampling difficult. The modifications referred to are usually in the size of the sample or method of extraction, with concomitant adjustments of adsorbent volume used or of adsorbent mixture proportions. Any adjustment of mixture proportions is governed by the nature of the separation involved-for instance, in the determination of carotene in tomatoes the carotenes must be separated from lycopene. The properties of lycopene, another hydrocarbon, resemble those of the carotenes more closely than do those of the carotenols, etc., found in alfalfa. This separation is therefore usually regarded as a more difficult one; however, it is accomplished easily by use of an adsorbent mixture containing 1 part of magnesia to 6 parts of soda ash by weight. The use of a mixture of this strength permits actual observation of the carotene, which is adsorbed temporarily but can be readily removed by further washing with Skellysolve B.

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Determination of Manganese after Oxidation to Tri-Dihydrogen Pyrophosphatomanganiate

Use of Pyridine to Separate Iron, Chromium, Vanadium, and Cerium from Manganese

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Vanadyl, vanadate, ceric, cerous, and chromic ions are quantitatively coprecipitated with an excess of ferric iron when hydrous ferric oxide is precipitated by pyridine. Chromate divides between the precipitate and filtrate. Manganous and ferrous ions remain quantitatively in the filtrate. Use of pyridine is advantageous in separating the interfering metals, vanadium, chromium, cerium, and a large excess of iron from manganese prior to the polarographic determination of manganese as tri-dihydrogen pyrophosphatomanganiate.

N APPLYING the authors' (1) polarographic procedure for the determination of manganese, after its oxidation to tridihydrogen pyrophosphatomanganiate, to the analysis of ores and steels it was found that large amounts of iron and even small amounts of chromium, vanadium, and cerium interfered with the determination. These elements must be separated from manganese before the polarographic procedure can be applied. It will be shown in a subsequent paper that as little as 1 or 2 mg. of manganese can be determined in the presence of 0.2 gram of iron without a separation; if more iron is present, a separation is necessary. The interference of chromate can be eliminated by reduction with arsenious acid. Otherwise the pyridine separation was found to be the most effective and simple method for eliminating the interference. In this procedure chromium, vanadium, and cerium are removed from solution by coprecipitation with hydrous ferric oxide.

Pyridine, a very weak base having an ionization constant of 1.4×10^{-9} , has been recommended for the quantitative precipitation of certain trivalent metals as the hydrous oxide without appreciable coprecipitation of cobalt, nickel, manganese, and copper (2, 3). A mixture of approximately equal concentrations of the pyridinium salt and pyridine is well buffered and is slightly acidic, having a pH of approximately 5.2 at 25° C. The solid hydrous oxide thus acquires a positive charge due to its primary adsorption of hydrogen ions. Consequently anions such as the sulfate ion, and not cations such as cobalt and nickel, are adsorbed as counter ions and are carried down with the precipitate.

A second property of pyridine undoubtedly contributes to the excellent separations of the hydrous oxides from cobalt, copper, nickel, and manganese. The pyridine molecule, owing to the lone pair of electrons on the nitrogen atom, is able to occupy a place in the coordination sphere in complex-forming metal ions. A great many complexes of the above metals with pyridine are known. The authors found that the formation of a complex of chromic chromium with pyridine actually is a factor in prevent-

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ing the precipitation of chromic ion in the absence of ferric iron or aluminum.

In order that the pH shall not exceed 5.2 when 5 ml. of pyridine are added to approximately 25 ml. of aqueous solution, it is necessary to have 31 milliequivalents of strong acid or its equivalent of metallic ion such as ferric iron present. Each millimole of ferric iron liberates 3 milliequivalents of acid upon precipitating as the hydrous oxide. If 0.6 gram of ferric iron were present, no excess of mineral acid would be necessary. For each 0.1 gram of ferric iron present, the amount of strong mineral acid present should be decreased by 5 milliequivalents. However, 5 ml. of pyridine will precipitate quantitatively as much as 1.0 gram of ferric iron from 100 ml. of solution containing no appreciable excess of acid.

APPLICATIONS

The use of pyridine to separate quantitatively trivalent chromium, iron, or aluminum from manganese, cobalt, and nickel; or uranium from calcium, barium, and strontium, has been recommended by Ostroumov (3). According to him, a sum of 0.1264gram of the oxides of trivalent iron, chromium, and aluminum may be quantitatively separated from a solution containing about 0.02 gram of divalent manganese, cobalt, or nickel with less than 0.2% coprecipitation of these ions with the mixed hydrous oxides. Zinc, if present, divides between the precipitate and solution. Lingane and Kerlinger (2) more recently used a similar procedure to separate ferric iron and chromic chromium from copper, cobalt, and nickel before determining the last three elements polarographically.

One interesting difference was observed in the results of Ostroumov and those of Lingane and Kerlinger. According to Lingane and Kerlinger, trivalent chromium is separated only through coprecipitation with the hydrous ferric oxide, while Ostroumov found that trivalent chromium can be quantitatively precipitated in the absence of iron.

The following factors undoubtedly account for this difference. In Ostroumov's experiments the precipitation was carried out in a hot solution containing no appreciable amount of mineral - acid, while Lingane and Kerlinger added 24 milliequivalents of hydrochloric acid before adding the pyridine to the cool solution. In Ostroumov's procedure the higher temperature is favorable for the decomposition of the complex of chromic ion with pyridine and the higher pH decreases the solubility of hydrous chromic oxide.

EXPERIMENTAL

REAGENTS. Pyridine solution (1 to 2). Dissolve 50 ml. of pyridine in 100 ml. of water. Sodium bisulfite, 20 per cent. Dissolve 2 grams of sodium bi-sulfite in 8 grams of water. Prepare a fresh solution daily.

Table I.	Coprecipitation of	Chromium	with	Hydrous	Ferric	Oxid
	in Pyr	idine Separ	ation	I CONTRACTOR		

Experiment No.	Chromium in Sample	Ferric Iron in Sample	Chromium Remaining in Filtrate
	M_{H} .	My.	%
1	260 CrIII	500	0
2	390 CrIII	500	1.76
3	1.00 CrVI	279.2	<4
4	1.3 CrVI	279.2	10
5	2.6 CrVI	279.2	16
6	5.2 CrVI	279.2	19
7	15.6 CrVI	279.2	31
8	26.0 CrVI	279.2	36
9	52.0 CrVI	279.2	41
10	20.8 CrVI	0	100

PTRIDINE SEPARATION, PROCEDURE I. Transfer the solution containing no excess mineral acid to a 100-ml. volumetric flask, add 1 ml. of sulfuric acid (1 to 1) and dilute to about 80 ml. Add 15 ml. of pyridine (1 to 2) slowly while swirling, dilute to exactly 100 ml., and mix well. Filter through a dry rapid filter paper, such as Whatman No. 41, into a dry beaker. Transfer a 50-ml. aliquot to a clean 100-ml. volumetric flask and continue according to Polarographic Procedure I (1) to determine manganese as tri-dihydrogen pyrophosphatomanganiate.

PRECIPITATION OF CHROMICM BY PYRIDINE. In a series of experiments on the precipitation of chromic chromium in the absence of ferric iron it was found that if no appreciable amount of mineral acid was present when the pyridine was added, the pH of the solution became large enough so that hydrous chromic oxide was precipitated. However, the precipitate redissolved during 16 hours of contact with the pyridine solution, forming a rich green-colored complex with pyridine. When the final concentration of chromic ion exceeded approximately 0.01 M, the precipitation was incomplete. This probably was due to the increasing amount of free mineral acid liberated during the precipitation of hydrous chromic oxide. The pyridine separation, thus, does not seem to be satisfactory for the separation of chromic chromium in the absence of ferric iron or aluminum.

Table I shows the extent of coprecipitation of chromic chromium with ferric iron. The chromium content of the filtrate was determined polarographically. It is evident that as much as 260 mg. of chromic ion is quantitatively coprecipitated with 0.5 gram of ferric iron. This corresponds to a steel containing 34% chromium, a much larger percentage than is generally encountered.

That chromate is only partially coprecipitated with hydrous ferric oxide during the pyridine separation is shown by experiments 3 to 9, Table I. Chromium must be reduced to the trivalent state in order to be quantitatively coprecipitated. This is easily accomplished by adding a little sodium acid sulfite to the solution. The excess sulfur dioxide is removed by boiling.

COPRECIPITATION OF VANADIUM WITH HYDROUS FERRIC OXIDE. Using a sample containing 10 ml. of 0.1 M ammonium metavanadate alone, no precipitate formed at all when the Pyridine Separation Procedure I was carried out. The solution remained yellow in color.

Samples containing 0.279 gram of iron as ferric nitrate and from 0 to 76.4 mg. of vanadium as vanadate were prepared and the pyridine separation was then carried out. The filtrate was analyzed polarographically. No diffusion current due to vanadate was observed in any of the solutions containing up to 61.1 mg. of vanadium corresponding to an atomic ratio for vanadium to iron of 1.2 to 5. The qualitative hydrogen peroxide test also showed the absence of the vanadate ion. When the amount of vanadate was increased to 76.4 and 127.4 mg., the filtrate was yellow-colored. The percentage of vanadate in the filtrate was estimated colorimetrically to be 5 and 6%, respectively. It may be concluded that as much as 18% vanadium (as vanadate) in iron can be separated with hydrous ferric oxide during the pyridine separation. Ferric vanadate is insoluble in neutral solutions but dissolves readily if a small amount of mineral acid is added to the solution. The above separation of vanadate is not, then, necessarily one of coprecipitation. However, if a simple precipitation of ferric vanadate occurred, one would expect a larger percentage of vanadate to be precipitated. The fact that this is not the case indicates that the vanadate is actually coprecipitated with the hydrous ferric oxide. The extent of coprecipitation is limited by the low pH at which the hydrous ferric oxide is formed in the pyridine buffer.

When the pyridine separation was carried out using a sample containing only 25.8 mg. of vanadium, as sodium vanadyl sulfate, a finely divided gray-green precipitate formed which was difficult to separate by filtration. By a polarographic determination, it was established that 92% of the vanadyl ion was precipitated.

Since vanadyl ion is partially precipitated even in the absence of iron, it should be largely coprecipitated with ferric iron. The pyridine separation was employed using samples containing 0.1 gram of iron as ferric nitrate and 5.1 to 127.4 mg. of vanadium as sodium vanadyl sulfate. No vanadyl ion was detected in the filtrate polarographically or colorimetrically. It is evident that the amount of vanadyl ion coprecipitated with ferric iron may even be greater than the amount of ferric iron precipitated.

COPRECIPITATION OF GERIUM WITH HYDROUS FERRIC OXIDE. The pyridine separation was employed using samples containing 14 to 140 mg. of cerium as ceric sulfate and 279 mg. of iron as ferric nitrate. No cerium was detected in the filtrate, showing that as much as 33% of cerium in steel can be coprecipitated during the pyridine separation, provided it is present as ceric ion.

However, if a reducing agent were added to reduce chromium and vanadium, any cerium would finally be present as cerous ion. Accordingly, the extent of the coprecipitation of cerous ion with hydrous ferric oxide was determined.

Samples containing 14 to 140 mg. of cerium as cerous sulfate and 279.2 mg. of iron as ferric nitrate were treated according to Pyridine Separation Procedure I and then analyzed polarographically. No cerium was found in the filtrate from samples containing 70 mg. or less of cerium. However, when the amount of cerium was increased to 140 mg., the cerium was no longer quantitatively coprecipitated. As much as 70 mg. of cerous cerium can be separated with 279.2 mg. of ferric iron during the pyridine separation. This corresponds to 20% of cerium and is a much larger percentage than is generally employed even in special cerium steels.

COPRECIPITATION OF MANGANESE WITH HYDROUS FERRIC OXIDE. If a 50-ml aliquot of the pyridine filtrate is taken for the determination of manganese by Polarographic Procedure I (1), 2.5 ml of pyridine remain in the sample to be determined. It was found that the pyridine introduced did not interfere with the formation of the violet tri-dihydrogen pyrophosphatomanganiate ion. However, the average current per millimolar concentration of tri-dihydrogen pyrophosphatomanganiate was 2.0% lower than the value obtained in the absence of pyridine.

To determine whether manganese was appreciably coprecipitated, a series of experiments (Table II) was performed using samples containing 0.8 gram of iron as ferric nitrate with various amounts of manganese as manganous sulfate. In experiments 7 through 12, 0.8 gram of pure iron was dissolved in 20 ml. of nitric acid (1 to 3) and the excess acid was neutralized with ammonium hydroxide. Pyridine Separation Procedure I and Polarographic Procedure I were then employed (1). To determine if manganese was lost by coprecipitation, a scries of control experiments was carried out in the same manner, except that the manganese was not added until after the precipitation and separation of hydrous ferric oxide. Comparing the true diffusion currents obtained with the manganese added before and after the pyridine separation it may be observed that the current was, within experimental error, the same. These results substantiate Ostroumov's (3) observation that the loss of manganese due to coprecipitation with hydrous ferric oxide by the pyridine method is extremely small.

BEHAVIOR OF FERROUS IRON IN PYRIDINE SEPARATION. Some ferric iron may be partially reduced if sodium bisulfite is added to reduce chromate. The behavior of ferrous iron during the pyridine separation is not important in the polarographic procedure for the determination of tri-dihydrogen pyrophosphatomanganiate but may be of importance if a quantitative separation of iron is desired. A sample containing 55.8 mg. of iron as ferrous sulfate yielded no precipitate at all when the pyridine separation was used in an atmosphere of carbon dioxide. To determine if ferrous iron is coprecipitated with ferric iron, the pyridine separation was employed using 10 ml. of 0.1 N ferrous sulfate solution and 5 ml. of 1 M ferric nitrate solution. Titration of an aliquot of the filtrate with 0.1 N potassium dichromate showed that ferrous ion, like manganous ion, is not coprecipitated with hydrous ferric oxide during the pyridine separation. Any ferrous ion formed during the reduction with sodium hisulfite can be oxidized by boiling the solution which contains a little nitric acid.

SIMULTANEOUS SEPARATION OF IRON, CHROMIUM, VANADIUM, AND CERIUM FROM MANGANESE. It has been shown that the vanadyl, vanadate, ceric, cerous, and chromic ions are quantitatively precipitated with an excess of ferric iron during the pyridine separation of hydrous ferric oxide. Chromate, however, divides. In order to ensure the quantitative separation of these ions, the dichromate ion in particular, some reducing agent must he added. Addition of a little 20% sodium bisulfite solution instantly reduced the dichromate in a slightly acid solution. The vanadate was reduced upon warming the solution. The addition of sodium bisulfite, furthermore, is desirable to effect the solution of any manganese dioxide which may have precipitated during the solution of the sample and aids in the removal of any excess of oxidizing agent added during the solution of the sample.

That the separation of chronium as well as vanadium and cerium with hydrous ferric oxide was quantitative if sodium bisulfite was used as a reducing agent was shown in the following experiment. A sample containing 5 ml. of 1 *M* ferric nitrate, 5 ml. of 0.05 *M* potassium bichromate, 5 ml. of 0.1 *M* ammonium vanadate, and 2 ml. of 0.1 *M* ceric sulfate was transferred to a 100-ml. volumetric flask. One milliliter of 20% sodium bisulfite was added and the solution was boiled for a few minutes. The pyridine separation was employed and the solution was then analyzed according to Polarographic Procedure I (1). Since only the residual current of -0.07 microampere was obtained at +0.1 volt vs. the saturated calomel electrode using capillary I (1) the separation of chromium, vanadium, and cerium with hydrous ferric oxide was quantitative.

That the simultaneous separation of chromium, vanadium, and lerric iron does not result in loss of manganese was shown in a series of experiments using solutions corresponding to a chromvanadium cobalt steel. The following comprised the sample:

5 ml. of M Fe(NO₃)₃ containing 279.2 mg, or 60 to 77% of Fe 5 ml. of 0.05 M K₂Cr₂O₇ containing 26.0 mg, or 5 to 7% of Cr 5 ml. of 0.1 M NH₄VO₃ containing 25.5 mg, or 5 to 7% of V 5 ml. of 0.1 M Co(NO₃)₂ containing 29.5 mg, or 6 to 8% of Co Various volumes of 0.1 M MnSO₄ containing 2.2 to 110 mg, or 0.6 to 23% of Mn

Pyridine Separation Procedure I and Tri-dihydrogen Pyrophosphatomanganiate Polarographic Procedure I (1). Capillary I, m^{1/4}(1^{/6} = 1.314 mg.^{2/3}ecc.^{-1/2}, av. *id* per millimolar concentrated MnIII = 1.51 microamperes at +0.1 volt (S.C.E.)] Experiment Final MnIII Time of Addition

	of Mu	Mn Taken	Mn Found
Millimolar		Mg.	Mg.
0.5	Before ppt.	2.75	2.73
0.5	After ppt.	2.75	2.77
2.0	Before ppt.	10.98	10.91
2.0	After ppt.	10.98	11.01
5.0	Before ppt.	27.46	27.73
5.0	After ppt.	27.46	27.76
0.5	Before ppt.	2.75	2.73
0.5	After ppt.	2.75	2.80
4.0	Before ppt.	21,97	21.82
4.0	After ppt.	21,97	21,80
5.0	Before ppt.	27.46	27,35
5.0	After ppt.	27.46	27.43
	At illimolar 0.5 2.0 2.0 5.0 0.5 0.5 0.5 4.0 4.0 4.0 5.0	of Mn Millimolar 0.5 Before ppt. 0.5 After ppt. 2.0 Before ppt. 2.0 After ppt. 5.0 After ppt. 0.5 Before ppt. 0.5 Before ppt. 4.0 Before ppt. 5.0 After ppt. 5.0 After ppt. 4.0 After ppt. 5.0 After ppt. 5.0 After ppt.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

The sample was transferred to a 100-ml. volumetric flask and 5 ml. of nitric acid (1 to 3) were added. One milliliter of 20% sodium bisulfite was added and the solution was boiled several minutes to expel the sulfur dioxide and reoxidize any ferrous iron. After neutralizing the excess acid with ammonium hydroxide, Pyridine Separation Procedure I and Polarographic Procedure I were employed. The results in Table III show that no manganese within experimental error was lost due to coprecipitation.

Table III. Separation of Manganese from Hydrous Ferric Oxide and Interfering Elements

(Using samples corresponding to a chromium vanadium cobalt steel. Sodium acid sulfite reduction of chromium followed by Pyridine Separation Precedure I and Tri-dihydrogen Pyrophosphatomanganiate Polarographic Procedure I, I)

	riocedure 1, 1)	
Final MnIII	Mn Taken	Mn Found
Millimolar	Mg.	Mg.
0	2.20	2.18
0.2	2.20	2.18
0.5	5.49	5.47
1.0	10.1	10.0
2.0	20.2	20.4
5.0	54.9	55.2
10.0	109.8	109.4

SUMMARY

Vanadyl, vanadate, ceric, cerous, and chromic ions are quantitatively coprecipitated with an excess of ferric iron when hydrous ferric oxide is precipitated by the use of the weak organic base, pyridine. Chromate, however, divides between the precipitate and filtrate. Manganous ion, as well as ferrous ion, remains quantitatively in the filtrate. Pyridine is well suited for separation of the interfering metals, vanadium, chromium, cerium, and a large excess of iron from manganese prior to the polarographic determination of mauganese as tri-dihydrogen pyrophosphatomanganiate.

The separation of hydrous chromic oxide in the absence of ferric iron is quantitative only under special conditions, because chromic ion forms a soluble green-colored complex ion with pyridine. However, in the presence of at least a twofold excess of ferric iron by weight, the coprecipitation of chromic ion with hydrous ferric oxide is quantitative. During the precipitation of hydrous ferric oxide, chromate ion in all proportions divides between the filtrate and precipitate. The loss of chromium in this way was prevented by the addition of a little sodium bisulfite solution followed by boiling with a little nitric acid to remove the excess sulfur dioxide and reoxidize any ferrous iron.

In the absence of ferric ion, vanadyl ion is incompletely separated as a finely divided gray-green precipitate. In the presence of even a smaller amount of ferric iron by weight the coprecipitation of vanadyl ion is quantitative. Vanadate ion is quantitatively coprecipitated with hydrous ferric oxide if the weight of ferric iron is over four times greater than that of vanadium.

Ceric ion is quantitatively coprecipitated with hydrous ferric oxide. Cerous ion likewise is quantitatively coprecipitated with hydrous ferric oxide, provided the weight of ferric iron is four times greater than that of the cerous ion.

The excellent separation of the hydrous oxides from manganous and ferrous ions is explained by the fact that the solution is weakly acidic during the precipitation and by the ability of pyridine to form complex ions with manganous ions as well as ferrous (cobaltous, and nickelous) ions.

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FROM a Ph.D. thesis submitted by J. I. Watters to the Graduate School of the University of Minnesota, 1943.

Determination of Vitamin A and Carotenoids in Butterfat Spectroscopic Characteristics of Butterfat Fractions and Problems Involved in Biological Interpretations

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Results of tests made with modifications of the saponification and ether-extraction procedure (8) for determination of vitamin A in butterfat are reported, with a discussion and partial interpretation of the spectroscopic characteristics of such ether extracts.

N^O SINGLE method for the direct spectroscopic determination of vitamin A in butterfat has been generally employed. A related application of spectroscopic methods (1) to the study of the vitamin A content of milk has been made by Dornbusch, Peterson, and Olson (3). However, little has been done in the study of errors involved with different butterfat samples or the correlation of spectroscopic data with biological assays.

In experiments in cooperation with the Technical Committee on Vitamin A Researches (3), a procedure of saponification and extraction with ether was developed. Details for spectrophotometric application have been reported (15). This paper reports the results of tests made with modifications of this procedure and presents a discussion and partial interpretation of the spectroscopic characteristics of such ether extracts. Attempts were made to correlate results calculated from direct spectroscopic data with those of the biological method in the case of samples (6, 7) which had been assayed by the rat-growth method.

EXPERIMENTAL

Since β -carotene and vitamin A per se are responsible for practically the entire vitamin A potency of normal butter, the analytical problem is primarily the determination of these two compounds in the presence of related carotenes and carotenols. The carotene content is no indication of the vitamin A alcohol content; hence, for direct determination of vitamin A, ultraviolet spectrophotometry of an extract is necessary.

Clarification of butter samples consisted of filtration of the melted fat through filter paper at 55° C. during 2 to 3 hours, to remove water and salt.

Carotenoids were estimated from absorption values at 4370 and 4360 Å., which are the coincident points for the absorption curves of β - and neo- β -carotenes in ether (15) and hexane (2), respectively. Wave lengths 4525 and 4675 Å. are of possible utility in the estimation of individual carotenoids (see Figures 1 and 2). They may be used with most spectrophotometers with a minimum possibility of error due to inexact wave-length calibration or to wide spectral regions isolated because the maximum of β carotene occurs at 4525 Å. and the minimum of β -carotene at 4675 Å. [also near the flat region of the neo- β -carotene curve (2)].

The nature of the carotenoids found in butter is dependent largely upon the feed of the cows, as pointed out by Strain (13) and others. In Figure 1 are representative characteristic curves of the total carotenoids found in the butters studied. Sample 106 was specially churned at the Purdue creamery. The standard curves of β -carotene and its isomer neo- β -carotene (2) are included for reference. [This neo- β -carotene fraction probably consists largely of the isomer designated by Polgár and Zechmeister (10) as neo- β -carotene B.] All curves were placed to coincide at 4370 Å. It is noted that curve 8 is characterized by higher relative absorption than curve 7 in regions near 4000 and 4250 Å., which is in agreement with similar observations of Strain (13).

To obtain a characteristic absorption curve of the total carotenoids with a minimum amount of induced isomerization, a butter sample from a cow fed a carrot-root carotene supplement was simply dissolved in ether, washed with water, dried with sodium sulfate, and filtered. The characteristic curve showed evidence of the presence of α -carotene and was very close to absorption curves of the ether extract after saponification, in spite of solvent differences due to the large amount of fat present. In this experiment a 7-cm. thickness was studied spectroscopically by comparing an 8-cm. cell with a 1-cm. cell, both filled with the butterfat solution to avoid differences in apparent absorption due to refractivity differences.

Another butterfat, 106, was dissolved in hexane, and washed free of carotenols with 94% diacetone alcohol (2). The characteristic curve (Figure 2) of the resultant carotene fraction corresponded well between 4360 and 4950 Å. with that of a mixture of β -carotene and neo- β -carotene. Upon analysis for these two components (2) the percentage of β -carotene was 77.1 at 4780 Å. and 79.1 at 4850 Å. Adsorption of this solution on columns of magnesia and alumina indicated the presence of two or more pigments. Figure 2 includes curves of the carotene fraction from each type of silage butter and from referee sample No. 3 (15), all of which were prepared by evaporating the ether extract almost to dryness, dissolving in hexane, and finally washing with 92% aqueous methanol. All curves were placed to coincide at 4360 Å.

Vitamin A was estimated from the absorption value at 3240 Å. which is the absorption maximum of vitamin A alcohol in ether solution (15). The characteristic curves of Figure 3 were arbitrarily placed to coincide with the standard curve of vitamin A alcohol at 3400 Å. The carotenoid content of butterfats is subject to wide variation and carotenoids other than β -carotene are



Figure 1. Absorption Spectra of Total Carotenoids in Ether Solution

106.	Winter crea	mery bu	tter, no artificial color added
7.	Butter from	cow fed	alfalfa hay
8.	Butter from	cow led	carrot-root carotene supplement
B-3,	Butter from	cow fed	alfalfa-brome silage
S-3.	Butter from	cow fed	com silage



106. AB-3. CS-3. Winter creamery butter, no artificial color added Butter from cow fed alfalfa-brome silage Butter from cow fed com silage

usually present. The ultraviolet absorption characteristics of such miscellaneous carotenoids have not been established. Colorless materials which absorb in the ultraviolet region probably also accompany vitamin A in the ether extract. Accurate corrections at 3240 Å. for absorption by carotenoids and other substances in such extracts are impossible at present. The necessity for some correction, even though it be somewhat arbitrary, is indicated by the curves of Figure 3, some of which agree fairly well with that of vitamin A below 3400 Å. They are invariably higher than the vitamin A curve at longer wave lengths, in part because of different carotenoid contents. Sample B3 was almost colorless and was obtained from a cow fed on a ration lacking carotenoids but supplemented with vitamin A in the form of a fish liver oil concentrate.

RELIABILITY OF EXPERIMENTAL PROCEDURE (8, 15). Saponification Time. A sample of commercial butter was clarified and saponified with aqueous methanolic potassium hydroxide in duplicate for 5, 10, 15, and 30 minutes. The eight absorption values of the ether extracts were constant to $\pm 2.5\%$ at 3240 Å. and to = 1% at 4500 Å. A 15-minute saponification with ethan-olic instead of methanolic potassium hydroxide gave essentially the same result. Methanol is preferred because it is more stable with potassium hydroxide.

Number of Ether Extractions. Successive ether extracts were examined spectroscopically to determine their relative effectiveness in the removal of carotenoids and vitamin A. A rendered creamery butter with no artificial coloring matter was used. The first extract (100 ml.) removed 70% of the substance absorbing at 3240 Å. and about 91% of the carotenoids. The second extract (50 ml.) accounted for 20% additional absorption in the ultraviolet and removed all the remaining carotenoids. The third extract (50 ml.) accounted for 6.3% ultraviolet absorption and the fourth extract of 50 ml. left in the hypophase no appre-

ciable quantity of material absorbing at 3240 Å. Effect of Ordinary Laboratory Illumination. Commercial butter was clarified and analyzed in duplicate in two kinds of glassware. In one case, all manipulations were done in amber glassware (Kimble amber laboratory glassware), as recommended by Embree (4); in the other, ordinary Pyrcx ware was used. Results on the two samples agreed within 1% in both the visible and ultraviolet regions, indicating that ordinary diffuse laboratory light does not affect the spectroscopic values obtained under these conditions. Absorption values of pure vitamin A in ethanol solution were not changed by fairly intense irradiation from an incandescent source (14).

Sampling Error. Many duplicate determinations made dur-ing this study indicate that butter is easily sampled after removal of water and salts. The surface butterfat exposed to air was

of water and salts. The surface butteriat exposed to air was avoided when possible. Spectroscopic results were easily dupli-cated with differences of 1% or less. *Recovery of Added Vitamin A.* Two samples of pure vitamin A alcohol (0.325 mg.) were carried through the entire analytical procedure in the absence of butterfat. The resultant extract had a characteristic curve identical with that of vitamin A and a spectroscopic recovery of $93 \pm 1\%$ was obtained. In another ex-periment, 3 mg. of crystalline vitamin A alcohol were dissolved in 30 grams of melted butterfat that was very low in carotenoids. One gram of this butterfat-vitamin mixture was then diluted tenone gram of this butterfat-vitamin mixture was then diluted ten-fold with more melted butterfat. After analysis the absorption values of the butterfat sample alone were subtracted from those of the enriched sample (in duplicate). Characteristic absorption of the enriched sample (in duplicate). Characteristic absorption curves that agree well with those of pure vitamin A alcohol were thus obtained. Recoveries of 97.0 to 95.5% were calculated. A similar experiment was performed on duplicate samples of a but-terfat (sample 7) rich in carotenoids. Exact duplication of the characteristic vitamin A curve was obtained in this case. Re-coveries of 99.4 and 94.2% were calculated. Stability of Extracts. The ether solutions from sample 7 were examined spectrosconically after 2 weeks in cold storage at 4° C

examined spectroscopically after 2 weeks in cold storage at 4° C. While no change, qualitative or quantitative, was detected in the region above 4000 Å., a general decrease in absorption was found below this wave length. This decrease amounted to 9% at 3240 Å. A decrease of similar magnitude in 30 hours was noted in the extract from a relatively "colorless" sample. These results are typical and indicate the necessity for prompt spectroscopic readings in the ultraviolet, whereas observations in the visible region may be considerably delayed if extracts are stored under the proper conditions.

Attempts to Improve Ultraviolet Characteristic Curves. Attempts were made to reduce the general absorption in the ultraviolet by purification of the vitamin A extract through removal of interfering substances.

Clarification. The authors' observations indicate that spectroscopic data on butters in the visible region may be converted to the butterfat basis by multiplying by the factor 1.20, as calcu-lated from carotenoid absorption in the visible region. This is presumably due only to the removal of water and salt as colorless material by clarification. Clarification also removes certain materials which absorb in the ultraviolet, and the corresponding correction factor at 3240 Å. was ca. 1.35 for the three samples examined. It is advisable to clarify samples of butter before analysis because such materials may not be uniform in all butters and because the analytical data are thus placed on the fat basis, making variations in water or salt content unimportant.

Adsorption. When the ether extract was passed through a 10-cm. (4-inch) column of magnesia-Supercel (50-50) and the 10-cm. (4-inch) column of magnesia-supercel (50-50) and the ether percolate made to volume, no change was noted in the ab-sorption spectrum of the carotenoids in the visible region, or in the quantity of total carotenoids present. The ultraviolet ab-sorption, however, increased about 10% at 3240 Å. Treatment of a "colorless" butterfat with Lloyd's reagent, which has been used to decolorize butters and remove vitamin A (12) foiled to reveal to be a surver which caude the intervented as

(12), failed to provide a base curve which could be interpreted as representative of the general absorption—i.e., other than that represented by vitamin A. The difference between the butterfat curve and that of decolorized fat did not approach the curve of vitamin A.

Acid Extraction. When the final ether solution from sample 106 was extracted with 0.5 N hydrochloric acid, followed by 0.5 Nsodium hydroxide and water, a small decrease in ultraviolet absorption occurred and small changes (perhaps isomeric) were found in the visible absorption. Freezing. The ether extract was chilled in a dry ice-acetone

bath and rapidly filtered on a cold filter in an effort to freeze out impurities. A 14% decrease occurred in the absorption value at 3240 Å. but the decrease was general in the ultraviolet and, therefore, no improvement in the characteristic curve resulted.

STABILITY OF CAROTENOIDS IN STORED SAMPLES. Ten months after the first spectroscopic observations, referee samples 6 (15) and 7 (both kept at -20° C.) were re-examined. For the former sample, the 4370 Å. absorption remained constant but the value at 4780 Å. decreased 5%. In the case of sample 7, however, the absorption at 4370 Å. decreased 5% but that at 4780 Å. decreased 28% and the resultant characteristic curves of the total carotenoids and the carotene fraction from this sample now resembled those from CS-3, a silage butter. The cause of these changes was not investigated, but it is evident that the carotenoids in butterfat may undergo considerable change with time, even at low storage temperatures. Isomerization may be involved.

CORRELATION BETWEEN SPECTROSCOPIC AND BIOLOGICAL RE-SULTS. Twenty-four samples were assayed biologically by the rat-growth method. Fourteen relatively "colorless" samples were produced from two cows fed rations lacking in carotenoids but supplemented by various amounts of vitamin A in the form of a fish liver oil concentrate. Ten samples of yellow butter were from cows fed alfalfa hay or a diet supplemented by various amounts of carrot-root carotene (7). All samples were stored at -20° C. Unfortunately, the time intervals (1 to 21 months) were rather great between the dates of churning and the spectroscopic observations.

The vitamin A activity of the relatively "colorless" samples is attributed almost exclusively to vitamin A per se, derived from cod liver oil of the ration supplement. Corresponding values of $E_{1 \text{ cm.}}^{1 \text{ \%}}$ (observed on unclarified butters) were corrected for water and salt content by multiplication of the observed value by 1.35 and for general absorption by 0.78, a factor discussed previously (1δ) . The vitamin A contents corresponding to such absorption values were calculated on the assumption that the corrected absorption in the ultraviolet was due to vitamin A alcohol ($E_{1 \text{ cm.}}^{1 \text{ \%}} = 1825$ at 3240 Å.).

Most of the samples high in carotenoids were clarified before analysis; for such samples the ultraviolet absorption values were simply multiplied by the factor 0.78 before calculation of vitamin A content, and total carotenoids were determined from absorption measurements at 4370 Å. (15). The total carotenoid content was divided by 2 (9) and added to the vitamin A content.

With neither set of butters were spectroscopic calculations sufficiently well correlated with biological results to establish a clear cut relationship. When a line was drawn through the ori-



^{106.} Winter creamery butter, no artificial color added 7. Butter from cow fed alfalfa hay 8. Butter from cow fed carrot-root carotene supplement AB-3. Butter from cow fed carot-root silage CS-3. Butter from cow fed con silage B-3. "Colorless" butter from cow fed on ration lacking carotenoids

gin to approximate the median line, individual samples of "colorless" butters deviated from this line a maximum of 20%, with a mean absolute deviation of 10%. With the yellow series, it was apparent that the two very different types of rations make a separate treatment desirable with regard to correction factors. Deviations from median lines similar to those from the "colorless" series could be obtained.

DISCUSSION

The varied nature of the curves for total carotenoids from different types of butter (Figure 1) and the changes which carotenoids may undergo during storage make difficult the optical estimation of the particular carotenoids that have vitamin A potency. The wave length 4370 Å, appears to be the best choice for total carotenoid estimation, at least until more detailed spectroscopic data are available on the various individual carotenoids present and on such of their isomers as may occur in butter.

It is reasonable that a measure of total carotenoids, such as obtained by the use of wave length 4370 Å, should be inadequate in itself and should require a correction factor, the magnitude of which is dependent on the dietary source of the carotenoids.

Carrot-root carotene contains large amounts of α -carotene, and some γ -carotene in addition to β -carotene, as well as appreciable quantities of other carotenoids, while alfalfa hay contains β carotene, various carotenols, and decomposition products of carotenoids. Recent developments in the application of isomerization methods to the study of carotenoids (2, 10) show the complexity of this problem.

The rather high content of carotenols found in the referee butters (1δ) causes the carotene fraction to be considerably more significant than the total carotenoids from the standpoint of measurement of vitamin A potency. It is possible that measurements on the carotene fraction would have required smaller correction factors than were applied to the total carotenoid absorption.

It is noted in Figure 2 that the curves for sample 106 and referee sample 3, creamery butters of January and July, respectively, are very close together and approximate the curve of a mixture of β -carotene and neo- β -carotene. Indeed, the characteristic curves for all six referee samples, taken at intervals throughout the year, were remarkably similar in both the ultraviolet and visible regions. Clarification and hot saponification may promote isomerization of β -carotene but it is not unlikely that neo- β -carotenes occur naturally in butterfat. Strain reported no spectroscopic change in the carotenoid spectrum after heating 3 hours at 50° C. during clarification (13). It is evident that the carotene fraction of butters from silage-fed cows is qualitatively different from those of butters from other sources, in agreement with previous work on this subject (11).

Ultraviolet characteristic curves of ether extracts from some butterfats show a decreasing (or at least not greatly increasing) absorption below 3240 Å. Most of the interfering absorption in this region may be due to carotenoids. Removal of the carotenol fraction from referee sample 3 by 90% methanol decreased the ultraviolet absorption very much. However, the ultraviolet characteristic curve of the carotenol fraction (after transference to ether) did not resemble that of vitamin A any more closely than did the curve of the original ether extract.

Numerous other methods of handling the data were tried in an attempt to obtain a straight-line relationship which would result in smaller deviations, but no better results were obtained. In the case of the butters of the yellow series, the carotenoids were treated as a mixture of β -carotene and neo- β -carotene. Addition of the calculated β -carotene content (after division by 2) to the vitamin A content gave no better correlation. The maximum deviations for these samples are smaller than those reported by Fraps, Kemmerer, and Meinke (5), who applied corrections of a somewhat similar nature to butters.

Efforts to obtain agreement between spectroscopic and biological results with six silage butters failed completely. The pigment system in such butters is too complex to permit a similar interpretation at the present time. This is recognized as a serious objection to the use of this method at present. Considerable improvement is needed before this method can be successfully employed on butterfats from cows on different diets, even for comparative purposes.

The calculation method presented above was based on numerous assumptions which are not necessarily better than others that might well be made. The necessity for such assumptions arises from the great complexity of the problem and the multitude of factors which interfere with a direct and simple spectrophotometric determination of vitamin A-potent substances in butterfat. Errors inherent in the biological method must also be considered in such correlations as were attempted here. An exact statistical treatment of the data was not considered profitable because of the many sources of error involved. It is hoped that these observations may be of assistance in the final development of a more direct treatment and more general application of absorption data to obtain contents of vitamin A-potent substances in butterfats. The extraction procedure employed is considered adequate and reliable. Further fractionation appears desirable, especially the separation of vitamin A from other carotenoids.

SUMMARY

Samples of butterfat produced under different dietary conditions were studied by the direct spectroscopic method. Total carotenoids were estimated and ultraviolet measurements were made on the unsaponifiable fraction. Characteristic curves of the total carotenoids and of the carotene fraction from very light "colorless" butters, yellow butters, and butters from cows fed alfalfa-brome grass and corn silages, were compared with that of β -carotene. Corresponding curves of the unsaponifiable fraction in the ultraviolet region were compared with that of vitamin A.

Effects of clarification, adsorption, acid extraction, and freezing upon the characteristic curves were studied, as well as various factors affecting the reliability of the experimental procedures.

Twenty-four samples were assayed biologically and attempts made to correlate spectroscopic with biological values. No clear-cut relationship could be established. The feed of the cows has a great influence on the nature of the carotenoids present in the butterfat. More extensive purification of the vitamin A fraction is desirable for the successful application of direct spectrophotometry to the determination of vitamin A in butterfats.

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Adaptor for Angle Centrifuge Tests

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COMMONLY used laboratory centrifuge is the International, usually fitted with tubes or cups swinging on trunnions. Other types hold the tubes in some fixed inclination relative to the axis of rotation. The patented angle centrifuge as



supplied by Ivan Sorvall employs angles up to 50° and for certain classes of work-offers advantages of speed and efficiency as compared with the trunnion cup type. The International Equipment Co. offers interchangeable angle heads.

Any laboratory already equipped with an ordinary centrifuge may readily improvise the means for testing the efficacy of the angle centrifuge in some particular application and thereby justify the investment in the second machine. Under present conditions the improvised equipment may well suffice for regular operation where a two-tube angle centrifuge is adequate. In some work it is advantageous after angle centrifuging to transfer the tubes to the ordinary pivoted trunnions, thus to compact a precipitate at the bottom of the centrifuge tube. Routine simultaneous treatment by pairs in this manner is conveniently accomplished with the present device.

The sketch shows the construction of a simple adaptor which was made for conducting tests with a size 2 International centrifuge, No. 241 centrifuge head, No. 310 trunnion rings, and No. 302 bronze tubes. When the adaptor is rested upon the two opposite trunnion rings and the No. 302 bronze tubes are inserted in the collars and trunnion rings, the system becomes rigidly positioned and is ready for operation as an angle centrifuge.

Titrimetric Determination of Zinc Application to Alloy Analysis

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The purpose of the work described was to develop a rapid control method for the determination of zinc in alloys and ores. The procedure consists of precipitation of zinc as the oxalate in aqueous acetic acid solution, centrifugal separation of the precipitate, solution of the precipitate in sulfuric acid, and titrimetric determination with standard permanganate solution of the oxalic acid formed. The application of the method to alloys and concentrates is described.

THE principal purpose of the work described in this paper was to develop a rapid control method for the determination of zinc in alloys, which might be used in place of the phosphate method. It was believed advisable to determine zinc in its customary position in the procedures usually used for alloy analysis. There has been no attempt to change the methods of determination of the other elements; only an attempt to simplify and shorten the zinc determination.

Since oxalate precipitates have two very desirable properties namely, ease of ignition and applicability to permanganate titrations—the possibility of obtaining a zinc oxalate precipitate was investigated. The simplicity and speed of the titration of oxalic acid by permanganate solution were the factors which led to the choice of such a titration as a rapid method for the final determination of the zinc. A study was also made of the use of the centrifuge as an aid in the separation and washing of the zinc oxalate precipitate. The technique of the method as finally developed was largely based on that used by Elving and Caley (θ) for the determination of magnesium.

The most important methods used for the separation of zinc are probably the precipitation of the zinc as the ammonium phosphate or as the sulfide.

The precipitation of zinc as the ammonium phosphate, Zn-NH₄PO₄, is accomplished by adding a large excess of diammonium hydrogen phosphate to a neutral solution containing a high concentration of ammonium salts. The zinc ammonium phosphate precipitate can be weighed as such by drying at 105° to 110° C, or it may be changed to zinc pyrophosphate, $Zn_2P_2O_7$, by ignition at 900° C. This method is used for the determination of zinc in brasses and bronzes. The procedure for analysis requires that the tin, lead, and copper be first removed as stannic oxide, lead oxide or sulfate, and copper. If iron is present, it is precipitated as the hydroxide and filtered off. Zinc is then determined in the filtrate.

The precipitation of zinc sulfide is very often used in the analysis of ores. Zinc can be separated from aluminum, iron, cobat, nickel, manganese, and chromium by saturating a buffered solution of the ions with hydrogen sulfide. The solution must have a pH ranging from 2 to 3; several buffering systems have been proposed for obtaining this hydrogen ion concentration (5, 7, 9-12). The sulfide precipitate may be converted to the oxide by ignition at 800° to 900° C., to the sulfate by dissolving in hydrochloric acid and evaporating with sulfuric acid, or to the pyrophosphate by solution and precipitation. It may be weighed as zinc sulfide after special treatment or its zinc content may be determined titrimetrically as subsequently described.

The electrolytic separation of zinc is best accomplished in a solution which has been made slightly acid with acetic acid and contains a considerable amount of sodium acetate. Alkaline solutions tend to give high results, due to the presence of zinc oxide or hydroxide deposit. The electrolytic methods, because of the special equipment needed, the experience and care necessary to get reliable results, and the unavoidable errors involved,

¹ Present address, Publicker Commercial Alcohol Co., Philadelphia, Pa. ³ Present address, Monsanto Chemical Co., St. Louis, Mo. are often less desirable than the sulfide or the ferrocyanide method.

The most commonly used titrimetric method for the determination of zinc is the one in which a standard solution of potassium ferrocyanide is used as the titrant.

The zinc is first separated from the other interfering ions in solution by precipitation with hydrogen sulfide. The sulfide precipitate is dissolved in dilute hydrochloric acid, and the hydrogen sulfide is expelled by boiling. The solution is made neutral with ammonium hydroxide and then acid again with dilute hydrochloric acid. After addition of ferrous sulfate the solution is titrated with a standard potassium ferrocyanide solution. Zinc is precipitated according to the following reaction:

 $3Zn^{++} + 2K^{+} + 2Fe(CN)_{5}^{----} = K_{2}Zn_{3}[Fe(CN)_{5}]_{2}$

Several indicators have been employed for this titration. Uranyl nitrate, ammonium molybdate, or ferric chloride is often employed as external indicator. The preferable internal indicators are diphenylamine, diphenyl benzidine, or sodium diphenylamine sulfonate.

In connection with their determination, several elements have been precipitated as the oxalate. Calcium is almost universally determined in limestones and cements by the precipitation of calcium oxalate in an ammoniacal or acetic acid-buffered solution. In an aqueous medium a great many metallic oxalates appear to form complex oxalate ions which can be broken up with the resulting precipitation of the metallic oxalate by the addition of a relatively large volume of acetic acid (3, 4, 6, 13, 14, 15).

Zinc oxalate was precipitated by Classen (4) in the following manner:

A large excess of potassium oxalate and an equal volume of acetic acid were added to the solution containing zinc, iron, and aluminum nitrates. After standing at about 50 ° C. for 6 hours, the precipitate was filtered and washed with a solution containing equal volumes of acetic acid, ethyl alcohol, and water. The zinc oxalate was converted to zinc oxide by heating for several minutes at red heat. The oxide was weighed. Nass (13) repeated Classen's work.

Ward $(1\bar{o})$ precipitated zinc oxalate from an acetate solution by adding 2 grams of oxalic acid and a volume of acetic acid equivalent to the volume of zinc acetate solution present. The solution was allowed to stand overnight and was then filtered through a mat of asbestos on a Gooch crucible. The zinc oxalate was dissolved in dilute (1 to 4) sulfuric acid and the resulting solution was then titrated with potassium permanganate solution.

In these studies the necessary conditions for successful precipitation were not sufficiently studied and the practical application of the method was not described.

REAGENTS AND APPARATUS

REAGENTS. Baker's c.p. acetic acid was used; its purity was found by evaporating 50 ml. of the acid in a platinum dish. Onetenth of a milligram of residue was found after ignition in a muffle furnace at 550° C. Standard zinc solutions containing 0.2008 and 0.999 mg. of zinc

Standard zinc solutions containing 0.2008 and 0.999 mg. of zinc per ml. were prepared by dissolving the proper amount of Mallinckrodt's analytical reagent grade zinc in dilute sulfuric acid. Each solution was checked by evaporating a definite volume in a platinum dish. The residue was ignited at 550° C. and after cooling was weighed as zinc sulfate. A saturated solution of ammonium oxalate was prepared by dissolving ammonium oxalate in hot water and allowing the excess oxalate to crystallize by cooling.

APPARATUS. The steam bath used for digestion of the oxalate precipitate consisted of a large steam cone which was covered with a metal sheet with holes cut in it of such size as to allow as much of the pear-shaped centrifuge tube as possible to be ex-

Table I.	Effect of One Oxalate in a	Gram of Sa 70% Acetic	It on Precipita Acid Solution	ation of Zinc
Salt	Zine F	Present	Zine Found Ma	Difference Ma.

	Mg.	Mg.	141 g.
NH4NO1	10.0	10.0	0.0
NH4NO3	10.0	9.9	-0.1
(NH4)2SO4	10.0	10.0	0.0
(NH ₄) ₂ SO ₄	10.0	9.9	-0.1
NH4Cl	10.0	0.0	a
^a No precipitate for	med after 1.5 hours	s of digestion.	After 12 hours some

" No precipitate formed after 1.5 hours of digestion. After 12 hours some precipitate appeared.

Table II. Determina Po (Zinc oxalate prec	tion of Zinc by Titratic otassium Permanganate ipitated from a 70% aceti	on of Oxalate with ic acid medium)
Zinc Taken Mg.	Zinc Found Mg.	Difference Mg.
1.0	0.8 0.6 0.8 0.8	$ \begin{array}{r} -0.2 \\ -0.4 \\ -0.2 \\ -0.2 \end{array} $
10.0	9.9 9.9 10.0 10.0	$-0.1 \\ -0.1 \\ 0.0 \\ 0.0$
25.0	24.9 24.9 25.0 25.0	$ \begin{array}{c} -0.1 \\ -0.1 \\ 0.0 \\ 0.0 \end{array} $

posed to the steam. An ordinary metal can or box would serve as well if steam could be passed into it.

The centrifuge used was a Precision Scientific Company model of the type commonly used for the determination of water and sediment in petroleum products (2). The tubes, which were those usually employed for the same determination, had a pearshaped bulb with a narrow stem and were of 100-ml. capacity. Any type of centrifuge tube, large enough and of construction to allow the precipitate to be slung to the bottom without being disturbed, might have been used. A straight-walled centrifuge tube of 100-ml. capacity with a tapering stem of the type also used for the determination of water and sediment in petroleum products (2) might avoid the difficulty occasionally encountered when the precipitate. The removal of the centrifugate was accomplished by immersing a tube, which was connected to an aspirator through a series of two traps, in the supernatant liquid. This tube was drawn to a long tapering point, so that it could be immersed in the centrifuge tube without touching the sides.

PRECIPITATION OF ZINC OXALATE

EFFECT OF ACETIC ACID CONCENTRATION. The precipitation of zinc oxalate was studied in the following manner:

A known amount of standard zinc solution, containing 1, 10, or 25 mg. of zinc, was transferred to a 250-ml. beaker. Enough water was added to make the final volume, after the addition of acetic acid and oxalate solution, the desired concentration. For example, 10 ml. of standard solution which contained 1 mg. of zinc per ml. were pipetted into a 250-ml. beaker; then 15 ml. of water were added; next 70 ml. of glacial acetic acid; and finally 5 ml. of saturated ammonium oxalate solution were added dropwise with constant stirring. This gave an acetic acid concentration of 70%.

The precipitate was allowed to digest on a steam bath for 1 to 2 hours. The time required for digestion decreased with increasing acetic acid concentration. After digestion was completed, the solution was filtered through Whatman No. 42 filter paper and the precipitate was washed with an acetic acid solution of the same concentration as the medium in which the precipitation was carried out. A rubber policeman which had been soaked in glacial acetic acid for 3 days was used as an aid in transferring the precipitate to the filter paper. The paper and precipitate were placed in a weighed porcelain crucible and ignited at 650° C. The zinc was then weighed as the oxide. The results obtained indicated that the optimum concentration of acetic acid is 70%. At this concentration precipitation was complete, the precipitate coagulated rapidly, and the solution was easily filtered.

EFFECT OF AMMONIUM SALTS. After the optimum acetic acid concentration had been determined, a study was made of the effect of certain ammonium salts on the precipitation of zinc oxalate (Table I).

One gram of ammonium chloride, ammonium nitrate, or ammonium sulfate was added to 95 ml. of a solution containing 70 ml. of acetic acid and 10 mg. of zinc, and 5 ml. of saturated ammonium oxalate were then added with constant stirring. The precipitate was digested, filtered, washed, and ignited in the same manner as in determining the optimum concentration of acetic acid.

Apparently, ammonium sulfate and ammonium nitrate have no effect upon the precipitation of zinc oxalate. Ammonium chloride evidently inhibited precipitation, for no precipitate was obtained after 3 hours of digestion. However, some precipitate was obtained when the solution was allowed to digest overnight.

INDIRECT TITRIMETRIC DETERMINATION OF ZINC. Since most oxalates can be changed upon acidification to oxalic acid which can be titrated with standard permanganate solution, it was deemed advisable to titrate the oxalic aid formed by treating the zinc oxalate with sulfuric acid. The procedure finally evolved for the titrimetric determination of zinc was as follows:

The zinc solution is transferred to a 100-ml. centrifuge tube of the type described, 70 ml. of glacial acetic acid are added with enough water to make the final volume 95 ml., and 5 ml. of saturated ammonium oxalate solution are then added with stirring. The precipitate is allowed to digest on a steam bath for 1.0 to 1.5 hours. When digestion is complete, the tubes are placed in a centrifuge and rotated rapidly for 3 or 4 minutes. When the precipitate has been completely slung to the bottom of the tube, the centrifugate is removed by suction. Care is necessary, since some of the precipitate might be removed with the liquid. Any precipitate remaining on the sides of the tube can be removed by rubbing the side with a rubber policeman. The loosened precipitate is slung to the bottom as before.

The precipitate is slow to the bottom as before. The precipitate is loosened from the bottom of the tube and washed by spraying a stream of 70% acetic acid on it. This is best done by tipping the tube in such a way that the supernatant liquid drains from the precipitate. The washing is done in such a manner that all the precipitate. The washing medium. Between washings the tube is centrifuged and the supernatant liquid is removed by suction. Occasionally it may be advisable to digest the precipitate for 10 minutes on the steam bath before centrifuging. When washing is completed (two washings are usually enough), the precipitate is dissolved in 25 ml. of dilute sulfuric acid (5 + 95). The solution is transferred to a beaker and the tube is rinsed three times with portions of the dilute sulfuric acid. The final volume is made up to 65 ml. The solution is titrated with 0.025 N potassium permanganate solution according to the procedure recommended by Fowler and Bright (3).

The results obtained by using this procedure with varying amounts of zinc present appear in Table II. This method is both rapid and accurate if the necessary precautions are observed.

An alternative method of separating the zinc oxalate would be to carry out the precipitation and digestion in a beaker, to filter and wash the precipitate on paper or a filtering crucible, and to dissolve the washed precipitate in warm or hot sulfuric acid (5 +95), the solution obtained being used for the titrimetric determination of oxalate. Such a procedure would in many cases be preferable to the centrifugal separation as regards speed and convenience.

INTERFERENCES IN PRECIPITATION OF ZINC OXALATE

In order to determine the ions whose oxalates might precipitate in a 70% acetic acid solution, several qualitative tests were made with varying concentrations of several ions.

Standard solutions containing approximately 1 and 10 mg. per ml. were used. A definite amount, 0.1, 0.5, 1, or 10 mg., was added to a test tube. Enough water was added to make the volume 2.5 ml. Then 7 ml. of acetic acid and 0.5 ml. of saturated ammonium oxalate solution were added. If no precipitate appeared, the solution was heated in a hot water bath to determine whether precipitation would occur upon digestion. In case a precipitate appeared, the test was made again in the same man-

Table III.	Qualitative F A	Precipitation of cetic Acid	Oxalates in 70%
Ion Tes	ted Mg.ª	NH ₄ OH Addition	Result
Sn++++	1.0	No	No ppt.
Cu++	$0.5 \\ 1.0 \\ 1.0$	No No Yes	Light blue ppt. Light blue ppt. No ppt.
Pb**.	0.1 0.5 0.5	No No Yes	No ppt. White ppt. White ppt.
Fe++ +	10.0	No	No ppt.
A1+++	25.0	No	No ppt.
Mn++	0.1 0.1 0.5	No Yes Yes	Light white ppt. No ppt. Light white ppt.
Ni++	$0.1 \\ 0.5 \\ 0.5 \\ 1.0 \\ 1.0$	No No Yes No Yes	No ppt. Light green ppt. No ppt. Light green ppt. Light green ppt.
· Final volume,	10 ml.		

142	Table IV.	Comp	osition	of Na	tional	Burea	u of St	andards Samples"
No.	Alloy	Cu %	Zn %	Sn %	Pb %	Fe %	Ni %	Others
37b 52 ,62	Sheet brass Cast bronze Manganese	$70.36 \\ 88.33 \\ 59.07$	$27.09 \\ 1.89 \\ 35.06$	0.99 7.90 0.82	$\begin{array}{c} 0.90 \\ 1.52 \\ 0.56 \end{array}$	${}^{0.21}_{0.12}_{0.13}$	${0.45 \\ 0.13 \\ 0.64}$	Sb 0.18 Mn 1.59, Al 1.13
,63	Phosphor bronze	78.05	0.48	9.91	9.74	0.27		Sb 0.55, As 0.19, P 0.62

ner, except that the solution was made basic with ammonium hydroxide before adding acetic acid. The purpose of adding ammonium hydroxide was to attempt to tie up the ions in the form of ammonium complexes and to determine whether the oxalate would precipitate in the presence of the ammonium salt. The results appear in Table III.

Nickel, lead, and copper interfere when present in concentrations of 0.5 mg. or more in 10 ml. of the 70% acetic acid solution. Lead and copper are usually removed previous to the determination of zinc in a copper-base alloy and should cause no particular trouble. Nickel, however, is not removed by the usual procedure. Ammonium hydroxide added to the solution before the addition of acetic acid tended to prevent precipitation of the nickel oxalate. In order to determine if the nickel interference could be avoided, quantitative measurements were made by precipitating 10 mg. of zinc as the oxalate in the presence of 1 mg. of nickel ion and 1 mg. of ferric ion. The ferric ion was added because it is not usually removed from the solution before the determination of zinc. Iron, however, could be removed from solution by the addition of ammonium hydroxide and filtration of the ferric hydroxide. If the iron was to be determined this step would seem advisable. The results of these experiments were high by several tenths of a milligram, although results presented below show that the determination of zinc by the oxalate method in alloys containing up to 0.65% of nickel is satisfactory. If enough nickel is present to disturb the zinc determination, the nickel should be first precipitated and determined as the dimethylglyoxime derivative. When dealing with a sample containing an unknown amount of nickel this procedure is to be recommended. Manganese, if present in appreciable amounts, should be removed. In the complete analysis of an alloy it can be removed with the R2O3 group after oxidation with bromine or persulfate to ensure its complete precipitation. If manganese is not removed, it will be precipitated along with the zinc and the value obtained for zinc will have to be corrected on the basis of the manganese present as determined by a colorimetric method applied to the original sample. If the zinc oxalate precipitate is determined by conversion upon ignition to the oxide, the manganese in the residue can be determined colorimetrically.

Interference is to be expected from the presence of any elements such as calcium and magnesium, whose oxalates are insoluble in 70% acetic acid solution.

DETERMINATION OF ZINC IN BRASSES AND BRONZES

Zinc was determined by the oxalate method in four alloys issued as standard samples by the National Bureau of Standards. Two samples, sheet brass 37b and manganese bronze 62, contained a high percentage of zinc; whereas two other samples, cast bronze 52 and phosphor bronze 63, contained less than 2.00% zinc. The certified analysis of the samples used appears in Table IV.

Tin, antimony, lead, and copper were taken out of solution according to the methods adopted by the American Society for Testing Materials (1). Platinum electrodes of the gauze type were used for the electrodeposition of the copper. The anode rotated and the cathode remained stationary. Electrolysis was done on a Waco electrolytic apparatus, manufactured by the Wilkens-Anderson Company.

Several variations of the following procedure were tried, but the procedure given seems to be best.

SHEET BRASS AND MANGANESE BRONZE. Samples of approximately 0.5 gram are used. The alloy is dissolved in 10 ml. of concentrated nitric acid in a 200-ml. porcelain casserole and the solution is carefully evaporated to dryness. The residue is baked for a few minutes and then dissolved in 10 ml. of concentrated nitric acid. The volume of the solution is brought to 50 ml. by adding boiling water. The precipitate is digested near the boiling point for one hour, filtered, and thoroughly washed with hot water. The filtrate, in a 200-ml. electrolytic beaker, is electrolyzed with an initial current of 0.2 ampere and a

The filtrate, in a 200-ml. electrolytic beaker, is electrolyzed with an initial current of 0.2 ampere and a potential between 1.8 and 2.0 volts. After electrolysis has been carried on for about 10 minutes one drop of 0.1 N hydrochloric acid is added to the solution. After 30 minutes, electrolysis completed and most of the lead deposited on the anode, 3 ml. of concentrated sulfuric acid are added and the current is increased to 0.4 to 0.5 ampere. Voltage should not exceed 2.1 volts.

After allowing ample time for the copper to be completely separated, usually 2 hours, and while the current is still on, the electrodes are removed and immediately washed with water. The washings are caught in the electrolytic beaker. The solution is neutralized with ammonium hydroxide, evaporated to a volume of 25 to 50 ml., and then transferred to a 100-ml. volumetric flask. Enough nitric acid is added to dissolve any R₂O₄ precipitate which may have appeared after the addition of the ammonium hydroxide. An excess of the acid should be avoided. Manganese can be removed before or after evaporation by precipitation as the hydrous oxide in the solution obtained from the electrolysis.

After dilution to 100 ml., a 25-ml. aliquot is placed in a 100-ml. pear-shaped centrifuge tube. The solution is again brought back to the neutral point with ammonium hydroxide. Only a few drops of the hydroxide should be required. Seventy ml. of acetic acid are added, followed by 5 ml. of saturated ammonium oxalate solution. The procedure outlined for the titrimetric determination of zinc is then followed. The precipitates containing tin, lead, and copper are treated in the customary manner.

CAST AND PHOSPHOR BRONZES. Cast and phosphor bronzes are run in the same manner as the high-zinc alloys, except that the whole sample is used for the zinc determination instead of an aliquot. After electrodeposition of the copper the solution is evaporated in the electrolytic beaker to dense fumes of sulfur trioxide, diluted to 10 ml. with water, allowed to cool, neutralized with ammonium hydroxide, and transferred to a centrifuge tube. The beaker is rinsed with water until the volume of solution plus washings is 25 ml.; water rinsings are abandoned and glacial acetic acid is used for the final rinsings. Glacial acetic acid is added to the solution in the centrifuge tube until a volume of 95 ml. is reached. The regular titrimetric procedure is then followed.

The results obtained from following such a procedure appear in Table V. This procedure is fairly simple and can be carried out with fairly inexpensive equipment. Two or more samples can be centrifuged while other samples are being digested or titrated.

ATTEMPT TO DETERMINE ZINC IN AN ALUMINUM ALLOY

Because of the favorable results obtained in the analysis of copper-base alloys, an attempt was made to determine zinc by a

		Sam	ples	,	Zinc Four	nd
Sample	Pres- ent %	-Zine- Found %	Differ- ence %	Mean %	Av. devia- tion %	Av. devia- tion of mean %
Manganese bronze, N.B.S. No. 62	35.00	$\begin{array}{r} 35.16\\ 35.20\\ 35.25\\ 35.47\\ 35.25\\ 35.12\\ \end{array}$	$\begin{array}{c} 0.10 \\ 0.14 \\ 0.19 \\ 0.41 \\ 0.19 \\ 0.06 \end{array}$	35.24 35.20ª	0.08 0.04	0.03 0.02
Sheet brass, N.B.S. No. 37b	27.09	27.27 27.09 26.91 27.03 27.09 27.04 27.05	$\begin{array}{r} 0.18 \\ 0.00 \\ -0.18 \\ -0.06 \\ 0.00 \\ -0.05 \\ -0.04 \end{array}$	27.07 27.06ª	0.07 0.03	0.03 0.01
Cast bronze, N.B.S. No. 52	1.89	1.982.002.022.022.02	0.09 0.11 0.13 0.13	2.01	0.02	0.01
Phosphor bronze, N.B.S. No. 63	0.48	$\begin{array}{c} 0.51 \\ 0.52 \\ 0.52 \\ 0.50 \end{array}$	$\begin{array}{c} 0.03 \\ 0.04 \\ 0.04 \\ 0.02 \end{array}$	0.51	0.01	0.00
Zine concentrate, N.B.S. No. 113	61.1	$\begin{array}{c} 60.8\\ 60.9\\ 61.2\\ 61.2\\ 60.9\\ 60.5\\ \end{array}$	$ \begin{array}{r} -0.3 \\ -0.2 \\ 0.1 \\ 0.1 \\ -0.2 \\ -0.6 \end{array} $	60.9	0.2	0.1
^a Calculated on bas	tia of on	nission (one or	two resu	lts whose	deviation

^a Calculated on basis of omission of one or two results whose deviation exceeds four times the average deviation.

similar procedure in an aluminum base alloy, National Bureau of Standards Sample 86, containing 1.50% of zinc. The zine oxalate could not be precipitated from the solution obtained by the dissolution of the alloy because the high concentration of salts greatly interfered when the solution was adjusted for the precipitation of zinc oxalate. The addition of ammonia caused the precipitation of aluminum hydroxide which could be filtered from the solution only if a very large volume were used. If this were done, a very large volume of filtrate was obtained. So much time was consumed in the evaporation of such a large volume that the method was abandoned. A preliminary separation of zinc by hydrogen sulfide did not seem to present any advantages over this method, because it would be much easier to weigh the oxide which could be obtained by ignition of the sulfide precipitate.

DETERMINATION OF ZINC IN ZINC CONCENTRATES AND ORES

Two National Bureau of Standards samples, Nos. 113 and 2a, were analyzed for zinc content. Sample 113 was a zinc concentrate containing 61.1% of zinc. This sample has not been completely analyzed by the National Bureau of Standards; however, the following analysis in per cent has been reported for this concentrate: moisture, 0.05; acid-insoluble material, 4.97; cadmium, 0.42; copper, 0.03; iron, 0.88; aluminum, not determined separately; lead, 0.33; calcium carbonate, 0.77; magnesium carbonate, 0.32; sulfur, 31.25; zinc (by difference), 60.99. Sample 2a was a synthetic one prepared from ores from all over the United States, containing a pure zinc blende from Joplin, Mo.; a mixture of franklinite, willemite, calcite, etc., from Franklin, N. J.; an impure blende from Colorado containing a good deal of iron, copper, and lead; and enough cadmium sulfide to give about 0.6% cadmium. The zinc content of this sample was 30.53% on the as-received basis.

DETERMINATION OF ZINC IN ZINC CONCENTRATE. A 0.20gram sample is weighed into a porcelain casserole, 5 ml. of concentrated nitric acid are added, and the casserole is covered with a watch glass and placed on a steam bath. When only 3 ml. of solution remain, 7 ml. of concentrated hydrochloric acid are added and digestion is continued until only 2 or 3 ml. remain. Three to 4 ml. of concentrated sulfuric acid are added and the solution is evaporated well beyond the point of the appearance of the first sulfur trioxide fumes. The solution is cooled and diluted to 20 to 25 ml. The silica is then removed by filtering the solution through No. 42 Whatman filter paper. The residue is washed several times with hot water. The filtrate which was collected in a 100-ml. volumetric flask is made just basic to modified methyl red and then made slightly acid with dilute sulfuric acid. The solution is finally cooled and diluted to 100 ml. Aliquot volumes of 25 ml, are analyzed for zinc by the titrimetric procedure described.

The results of analyzing the zinc concentrate appear in Table V. This method seems very applicable to rapid assay analysis of zinc concentrates of this type because the zinc can be determined immediately after the dissolution of the sample. The results obtained by this method agree within a few tenths of a per cent with that reported by the Bureau of Standards.

The attempts to analyze sample 2a failed to give very satisfactory results. This sample was of such a peculiar composition that it was believed that any procedure evolved would be useless for samples obtained from natural ores. A procedure for the analysis of this sample could probably be worked out, and would resemble that commonly used for limestone analysis with the added step of copper separation by electrolysis.

The procedure tried was as follows:

Dissolution was obtained by aqua regia. Silicon, iron, and calcium were removed according to methods recommended by the American Society for Testing Materials. The resulting solution was evaporated to dryness after the addition of 10 ml. of concentrated nitric acid and 20 ml. of concentrated hydrochloric acid. The residue was taken up with 10 ml. of dilute sulfuric acid (5 \pm 95) solution and the resulting solution evaporated to sulfur trioxide fumes. The residue was washed into a 100-ml. centrifuge tube with hot water. If 25 ml. of water were insufficient to obtain complete washing, glacial acetic acid was used to complete the washing. Enough acetic acid was added to make a 70% solution, and precipitation and titration of the oxalate were carried out as described.

The results varied from 29.2 to 31.2%, compared to 30.53% zinc reported by the National Bureau of Standards. Better results could probably have been obtained if copper had been separated before the precipitation of the zinc oxalate. A method such as this would be of value only if a complete analysis were carried out.

DISCUSSION

The method which has been developed seems to have several definite advantages in certain cases as compared to the phosphate and sulfide methods. When the diammonium phosphate method is applied in alloy analysis, it is often necessary to destroy the excessive amounts of ammonium salts prior to precipitation. Zinc oxalate can be precipitated in the presence of a fairly large amount of ammonium salts, which therefore need not be destroyed. The zinc ammonium phosphate is usually kept hot for 30 minutes and digested in the cold for at least 2 hours. The digestion of zinc oxalate rarely takes more than 1.5 hours. The end point of the permanganate titration is sharp even when very dilute standard solutions of potassium permanganate are used. The oxalate method appears to be more accurate for samples containing small percentages of zinc and probably would be more accurate for the larger percentages, if the entire sample were used instead of an aliquot. The use of the entire sample containing high percentages of zinc would, however, decrease the speed of analysis because of the time which would be consumed in evaporating the solution to 25 ml.

The separation of zinc sulfide is not an easy operation; therefore, when no interferences would occur, the oxalate separation would be preferred. In the analysis of ores and in certain types of alloys the sulfide precipitation appears to be preferable. In the complete analysis of a zinc ore, it might be advisable to determine zinc by the method proposed here. When only zinc is determined, the sulfide method of separation is more desirable. The application of the oxalate method to the determination of zinc in zinc concentrates seems to be very rapid for assay analysis. The accuracy of the determination will depend upon the interfering elements present. Procedures for analyzing concentrates

Table V. Determination of Zinc in National Bureau of Standards

and ores should always be tested by a sample representative of the type to be analyzed.

The apparatus required for the oxalate method can be found in almost every analytical laboratory. Any type of centrifuge tube which allows the use of a large enough volume can be used. The centrifugal method of separation of precipitates is as rapid or more rapid than filtration, but washing by the centrifugal method is much easier and more complete. In many cases two washings are sufficient to remove all excess ammonium oxalate.

SUMMARY

Zinc can be completely precipitated as the oxalate in a 70% acetic acid medium. The zinc oxalate can be separated by use of a centrifuge or by filtration and dissolved in sulfuric acid. The oxalic acid formed can be titrated with a standard potassium permanganate solution. Ammonium nitrate and ammonium sulfate do not interfere with the precipitation, but ammonium chloride does. Elements which form oxalate precipitates in 70% acetic acid solution interfere.

A procedure was developed for the determination of zinc in brasses and bronzes. Four Bureau of Standards alloys were analyzed for zinc and favorable results were obtained. A procedure was attempted for aluminum-base alloys, but the high concentration of aluminum salts made the method unfeasible. An attempt was made to determine zinc in an ore but the sample which was available was of such an unusual composition that further work was inadvisable. A procedure for the determination of zinc in a zinc concentrate was developed and favorable results were obtained on a National Bureau of Standards sample.

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Determination of Total Phthalic Anhydride in Oil-Modified Alkyd Resins

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Several modifications of the Kappelmeier procedure for the determination of phthalic anhydride in oil-modified alkyd resins are proposed. Anhydrous potassium phthalate is recommended as the weighing form instead of the alcoholate. A simplified saponification procedure is suggested. The adverse effect of water and its elimination are described. A volumetric procedure is offered in place of the gravimetric one.

HIS determination of total phthalic anhydride, free and combined, in oil-modified alkyd resins has been the subject of a number of papers (3, 5, 8-11, 14, 15). In the case of the alkyd hypothetically represented below, dipotassium phthalate, potassium linoleate, and glycerol are obtained upon alkaline hydrolysis:



The monomer within the bracket is useful in representing the molecule for analytical purposes but should not be taken as an indication of the actual molecular structure.

The analytical problem involved is twofold: (1) to isolate the dibasic acid quantitatively and (2) to determine its quantity. Its determination as phthalic acid (3, 10), lead phthalate (5), potassium carbonate (14), potassium phthalate alcoholate (8), and potassium sulfate (9) has been reported. Most of these methods are laborious, time-consuming, or subject to various errors (9, 15). The Kappelmeier method (8), which generally is accepted today, involves hydrolysis of the alkyd resin with alcoholic potassium hydroxide, precipitating potassium phthalate containing one mole of alcohol of crystallization.

WEIGHING FORM

The necessity for drying the alcoholate to constant weight over concentrated sulfuric acid in a vacuum desiccator makes this weighing form inconvenient for routine work. Kappelmeier reported (8) that the alcohol is lost with difficulty at 100° C., that heating in air results in a brownish discoloration, and that drying the alcoholate in a vacuum between 100° and 120° C. results in a slow loss of weight until 16% has been lost, which corresponds to exactly one molecule of alcohol.

The tenacity with which the alcohol is held was verified. However, the alcoholate was decomposed in air quantitatively without discoloration by heating at 150° C. for 3 to 4 hours. The theoretical loss is 15.97%; 15.97 ± 0.07 was found (Table I). This treatment yields the anhydrous salt which is therefore recommended as the weighing form.

METHOD OF SAPONIFICATION

The standard method of saponification requires a preliminary heating below the boiling temperature, followed by a prolonged Table I. Formation of Anhydrous Dipotassium Phthalate from the Alcoholat

		Acone	Jiate		
Weight of CeHi- (COOK)2 C2HiOH Grams	Weight of CoH4- (COOK): Grams	C2H8OH Lost %	Weight of CoH4- (COOK)2 C2H3OH Grams	Weight of C&H4- (COOK)2 Grams	C ₂ H ₅ OH Lost %
1.676 1.824 1.462 1.162	$1.409 \\ 1.532 \\ 1.226 \\ 0.977$	15.90 16.01 16.14 15.92	$1.634 \\ 1.879 \\ 2.110 \\ 1.512$	$1.374 \\ 1.579 \\ 1.772 \\ 1.272$	$15.92 \\ 15.97 \\ 16.02 \\ 15.87$

Table II. Rate of Hydrolysis of Alkyd Resins

Temp. ° C.	IIr.	-Resin 1—- Phthalic anhy- dride %	Hydrol- ysis %	Temp. ° C.	R	esin 2 Phthalic anhy- dride %	Hydrol- ysis %
50	1 2 4 8	28.0 36.0 36.2 36.0	77.4 100.0 100.0 100.0	60	1 2 4 8	$\begin{array}{r} 41.5 \\ 42.0 \\ 42.0 \\ 42.0 \\ 42.0 \end{array}$	100 100 100 100
40	1 2 4 8	19.3 29.3 35.3 36.5	53.4 80.9 97.5 100.0	50	1 2 4 8	$\begin{array}{r} 42.0 \\ 42.0 \\ 42.0 \\ 42.0 \\ 42.0 \end{array}$	100 100 100 100
30	1 2 4 8	13.6 22.0 30.0 35.3	37.6 60.9 82.8 97.5	40	1 2 4 8	28.0 42.0 42.0 42.0 42.0	66.7 100 100 100

gentle refluxing. This involves the use of water baths, air-cooled condensers, and the likelihood of violent bumping. A simplified method was investigated in view of the exceptionally rapid rate of hydrolysis of alkyd resins (16).

Similar-sized samples of a given resin were weighed into a series of corked Erlenmeyers. A solution of 0.5 N potassium hydroxide in absolute alcohol was prepared and equal volumes were added to each flask. They were then set in ovens maintained at the given temperature $\pm 2^{\circ}$ C. for varying periods of At the end of this time they were placed in a water bath time. and cooled rapidly to room temperature, ether was added, and they were filtered into Gooch crucibles within 10 minutes after removal from the oven. The weight of phthalic anhydride was calculated on the resin solids basis, using the dipotassium phthal-ate alcoholate as the weighing form (15).

The extent of hydrolysis as a function of time may be calculated by considering the reaction complete at the point where maximum and constant value is obtained. The data in Table II indicated that refluxing is unnecessary. Indeed, saponification has been found to be complete in flasks which have been allowed to stand 18 hours at 25° C. It is recommended that saponification be carried out at 55° C. for 4 to 6 hours. It may be necessary to heat difficultly saponifiable resins overnight. Higher temperatures may result in building up excessive pressures within the flask and it is advisable to stopper the flask loosely.

This modification was tested upon two commercially prepared alkyd resins, using the customary reflux procedure as a control. Both the above weighing forms were used to secure the data in Table III. The modified saponification procedure gave results agreeing to $\pm 0.35\%$. This less drastic saponification procedure has been used successfully on hundreds of samples of oil-modified alkyd resins of the type of Rezyl 7818-1 (American Cyanamid & Chemical Corp.), Beckosol 1334 (Reichhold Chemicals, Inc.), Falkyd A-4-D (Falk and Co.), Glyptal ZV-1125 (General Electric Company), etc.

EFFECT OF WATER

The necessity of precipitating the dipotassium phthalate under anhydrous conditions has been noted (9). The quantitative effect of known quantities of water on the precipitation of dipotassium phthalate was observed.

The alcoholic potassium hydroxide was prepared by drying commercial absolute alcohol over lime for 48 hours, followed by

distillation over sodium. The fraction distilling over at $78-79^{\circ}$ C was used to prepare the 0.5 N alcoholic potassium hydroxide. The c.r. potassium hydroxide contained 13% water and thus introduced 0.5% of water into the alcoholic potassium hydroxide solution. Solutions containing up to 8% more water were prepared by adding calculated quantities of water to this stock solution.

Table IV shows a maximum of 37.4% phthalic anhydride obtained where no water was added. An error of 1% is introduced in the presence of 2% added water. A further increase in water content leads to large errors. In another series of determinations where the same alkyd resin was analyzed using commercial absolute alcohol and c.p. potassium hydroxide the average of six determinations was $37.05 \pm 0.05\%$.

PREPARATION OF LIMED ALCOHOLIC POTASSIUM HYDROXIDE. For each determination 4.5 grams of c.P. potassium hydroxide are added to 125 ml. of absolute alcohol, 10 grams of calcium oxide, to remove a maximum of 2.5% of water, are added, and the solution is refluxed for 20 minutes. The warm solution is filtered rapidly with suction, a minimum of air being sucked through to avoid absorption of carbon dioxide.

To observe the effect of lime in the preparation of the alcoholic potassium hydroxide, two commercial resins were analyzed. Table V shows that the use of lime results in an increase of about 1% in the determination of phthalic anhydride. A comparison of columns A and C shows that the effect of the addition of ether is negligible. Apparently, only in the presence of an appreciable quantity of water does the ether decrease the solubility of the salt sufficiently to warrant its use (8).

VOLUMETRIC PROCEDURE

The advantages of the Kappelmeier procedure in isolating the phthalic anhydride as the dipotassium salt would be best realized if a convenient and accurate volumetric procedure could be developed. A volumetric procedure which partially fulfills these

Table III. Phi	ihalic Anhyc	lride by Ka	ppelmeier Reflu	ux and
Modi	ified Kappeln	neier (55°	C.) Methods	
	Res A %	in 3 B	Res A	in 4 B
Reflux 55° C.	35.67 35.53 35.57	35.69 35.56 35.56	36.43 36.42 36.60	36.45 36.42 36.33
Weighing form.	$\begin{array}{rcl} 35.63\\ A &= C_{\delta}H_{4}(C)\\ ed. \end{array}$	35.69	· 36.31	36.31
Duplicate results list		OOK):.C:H:	OH. B = C ₆ I	I4(COOK):

Table IV.	Effect of Water on Quantitative Precipitation of
Susta include	Dipotassium Phthalate

H ₂ O	Phthalic	T	H ₂ O	Phthalic	(interio)
Added	Annyariae	LOSS	Added	Annydride	Lossa
%	%	%	%	%	%
0.0	37.4	0.0	2.0	37 0	1.0
0.5	37.3	0.2	4.0	35.1	6 2
1.0	37.3	0.2	8.0	29.6	20.7
a Assum	ning 100% prec	ipitation wh	ere no water	was added.	

Table V. Effect of Lime in Preparation of Alcoholic Potash in Modified Kappelmeier Procedure

Phth	Resin 3, nalio Anhyd	lride _	Phth	Resin 4, alic Anhydr	ide
A	В	C	A	B	C
%	%	%	%	%	%
35.4 35.3 35.4 35.3	$ \begin{array}{r} 35.6 \\ 35.5 \\ 35.6 \\ 35.5 \end{array} $	35.3 35.4 35.3 35.3	36.3 36.3 36.4 36.4	36.9 37.1 36.9 37.5°	36.5 36.5 36.5 36.5

Results listed in quadruplicate

A

Modified Kappelmeier, using normally prepared alcoholic potassium hydroxide. Modified Kappelmeier, using "limed" alcoholic potassium hydroxide. Same as A except for omission of ether before filtration of potassium phthalate.

^a This sample contained only half the concentration of resin used in all the other samples.

Table VI. litration of Dipotassium Phthalate with	Perchloric Acid
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	in Glacial Ac	etic Acid	
Weight of CtH4(COOK)2 Taken A	Caled. Weight of CoH4(COOK): from Titration B	Weight of KClO₄ Found C	Calcd. Weight of Call4(COOK) from KClO4 D
Grams	Grams	Grams	Grams
0.928 0.986 1.154	$\begin{array}{c} 0.935 \\ 0.995 \\ 1.162 \end{array}$	$1.061 \\ 1.131 \\ 1.329$	0.929 0.990 1.160

requirements is based on the use of a feebly basic solvent to increase the basicity of the phthalate ion. Hall and Werner (?) have shown that perchloric acid is the most suitable of the common acids for titrimetric purposes in a glacial acetic acid solvent. The use of indicators in titrating amines with perchloric acid in glacial acetic has been reported (2).

The titration of dipotassium phthalate or its alcoholate can be followed with several indicators-for example, bromophenol blue, bromocresol purple, and methyl violet-the latter was very satisfactory (1, 4). It is necessary to remove the water present in the solutions to secure quantitative results (6). The addition of acetic anhydride converts the water to acetic acid; excess acetic anhydride has no effect on the titration (12). The anhydrous perchloric acid solution was standardized by the use of sodium carbonate as a primary standard (2), the end point being taken at the green-yellow stage. The perchloric acid presents a little danger in handling. The 0.1 N solution should be prepared carefully as indicated below. Once the perchloric acid is present in the dilute solution it is relatively harmless. The glacial acetic solutions are most conveniently used in a wellventilated hood.

The standard solution of approximately 0.1 N perchloric acid In glacial acetic acid was prepared by adding 9 ml. of 60% per-chloric acid dropwise to 36 ml. of acetic anhydride kept in a chilled glass-stoppered liter Erlenmeyer (7). The resultant solu-tion was then diluted with 720 ml. of glacial acetic acid and 24 ml. of acetic anhydride and allowed to stand 2 weeks until the reac-tion with water was completed (13). To standardize the solu-tion a definite quantity of sodium carbonate was dissolved with gentle warming in a solution of 20 ml. of glacial acetic acid and 2 ml. of acetic anhydride and brought to boiling (hood) in order to react with any water. Upon cooling, this solution was titrated with the above perchloric acid solution using methyl violet indicator, 2 drops per 10 cc. of 0.2% methyl violet in glacial acetic acid.

The results obtained by titrating dipotassium phthalate isolated by the modified Kappelmeier procedure are given in Table VI. A comparison of columns A and B shows that the volumetric procedure gives results that are 0.8% high. A white precipitate, formed upon addition of the perchloric acid, contained potassium and was soluble in hot water and insoluble in cold water. The precipitation of potassium perchlorate under these conditions has been noted (7). The precipitate was filtered off, dried to constant weight, and used as a basis for calculating the weight of dipotassium phthalate. A comparison of columns A and D indicates that precipitation is quantitative.

Sodium perchlorate is soluble in glacial acetic acid while the potassium salt is insoluble. A procedure for determining both potassium and sodium simultaneously under certain limited conditions is indicated. Semiquantitative results were secured on mixtures of potassium acetate and sodium carbonate.

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Determination of Total Phthalic Anhydride in Modified Alkyd Resins

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HIS paper presents confirmatory evidence of the modified Kappelmeier method (3) described in the preceding paper (2), independently obtained during the spring of 1942 by a similar modification which is used in this laboratory. This modification, which also eliminates the tedious drying of the residual crystals over sulfuric acid, consists in removing the alcohol of crystallization by heating at 210° C. for one hour. The work done here indicates that the modification is applicable also to alkyd resins complicated by maleic anhydride or fumaric acid.

	Table I. Alkyd R	lesin Analy	sis	
	and all frequencies and an and the second and the second s	Ph Stan met A	thalio Anb dard hod B	ydride Modified method C
Resin	Other Acids Present	%	%	%
1 2 3 4 5 6 7 8 9 10 11	Maleic anhydride Maleic anhydride Maleic anhydride Maleic anhydride Rosin Fumaric acid Fumaric acid	$\begin{array}{r} 34.10\\ 35.09\\ 34.80\\ 42.05\\ 35.42\\ 34.78\\ 25.95\\ 17.94\\ 28.78\\ 34.32\\ 36.08 \end{array}$	$\begin{array}{r} 34.06\\ 35.17\\ 34.78\\ 42.01\\ 35.43\\ 34.84\\ 25.87\\ 17.87\\ 28.80\\ 34.30\\ 36.06 \end{array}$	$\begin{array}{r} 34.06\\ 35.05\\ 34.80\\ 42.55\\ 35.45\\ 34.65\\ 25.63\\ 17.87\\ 28.88\\ 34.68\\ 35.72\\ \end{array}$

PROCEDURE. The standard Kappelmeier procedure (1) is followed up to the point of drying the filtration residues over concentrated sulfuric acid in vacuum. The crucibles containing the residues are transferred from the low-temperature oven to a 210° C. oven for one hour. They are then cooled over Dehydrite, weighed, and converted to phthalic anhydride, assuming dipotassium phthalate as the weighing form.

Table I lists representative results on the basis of which the two methods may be compared.

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Constant-Level Float Valve

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THE constant-level valve illustrated in Figure 1 makes it possible to fill a glass bottle with distilled water from the still reservoir without running it over and without giving it constant attention during the last stages of filling. It can be made from material available in any laboratory, and is efficient when gravity supplies the pressure. Its applications are numerous and varied. With the slit turned downward, the valve will



Figure 1. Float Valve

Upper.	Valve closed.	Center.	Valve open.	Low	er.	For use Ir	hot water
	A. Glass	bulb	The War an	1.	Liqui	d flow	
	B. Rubb	er tubing	Hard. mill	2.	End e	open	
	E. Liqui	dlevel		4.	Fire-t	allshed	
	F. Capil	lary					
	G. Slit						

VALVE. A piece of 7-mm. soft-glass tubing is heated in a hot flame and turned to thicken it at one end. When the glass is sufficiently thick, it is blown into a bulb 5 to 7.5 cm. (2 to 3 inches) in diameter. If it is to be used inside a bottle, the bulb should be as large as can easily pass through the mouth.

should be as large as can easily pass through the mouth. The length of the stem may be varied; the longer the stem the greater the closing pressure, but 2.5 to 3.75 cm. (1 to 1.5 inches) is a convenient length. The end is scaled off in the flame.

A piece of heavy-walled rubber tubing 3.75 cm. (1.5 inch) long is slit half through and the stem of the bulb is forced into the end nearly up to the slit. A piece of 7-mm. glass tubing, bent at an angle, is forced nearly up to the slit from the other end. This glass tubing is held in position by running it through a cork stopper and holding the cork in a clamp. If the angle of the glass tubing is about 120° instead of 90° as shown, the closing effect is better and the rubber is kept above the liquid level.

The glass float must have a small hole in it, if it is to be used in hot water. This can best be made by heating the float on one side, touching the heated portion with the molten end of a glass rod, and pulling out a fine capillary. When the end of the capillary is broken and fire-polished, a small hole is left, which will not fill with liquid. If sufficient heat is available, a small round Pyrex flask may be fused to a piece of Pyrex tubing. This will usually withstand the pressure developed inside the bulb.

If the pressure is very great, the valve will squirt a small stream of water high into the air during the last stages of closing. This may be prevented by a guard:

A section of flat rubber (tube patching is good) is cut in a rectangular piece about as long as the rubber tubing of the valve and as wide as the circumference. Two strips of the same material are wrapped, one on the other, around the upper section of the rubber tube, and the rectangular piece is placed on top of them, extending well over the slit and down over the sides. These pieces should be wired in place, or fastened with a rubber band.

Hot Distilled Water Reservoir

WILBURN A. BOGGS, 2218-B. Cabrillo Ave., Torrance, Calif.

THE arrangement shown in Figure 1, using the float valve described in the preceding article will provide a constant supply of about 6 liters (1.5 gallons) of hot distilled water per hour, if only a small amount (500 ml. or less) is drained off at a time. Fresh water is added continuously, but the volume is large enough to prevent variation of pH or temperature. The quality of the water is equal to that which has been boiled for 2 hours or longer, and is delivered from the buret at a temperature of above 98° C.

Tubes G, M, and N are placed in the positions shown and held in place by clamps above the bottle's mouth. The top of the bottle is left open to allow the steam to escape.

The steam coil is conveniently made by running 0.6-cm. (0.25inch) copper tubing through a piece of pipe and then winding it around the outside of the pipe. The buret shown may be made from a Pyrex test tube $(3.75 \times 50 \text{ cm.}, 1.5 \times 8 \text{ inches})$, to which a 7-mm. tube is attached. It is filled by opening pinchcock R_1 and emptied

100

R-SPCs

C

by R_2 . The hole in the bottom of the Pyrex bottle is made by drilling with a piece of 1.9-cm. (0.75-inch) copper tubing rotated by hand or by a small motor. A small constant supply of wet Carborundum or valve-grinding compound must be supplied to the drill.

If steam is not available, the bottle is placed on a hot plate and supplemental heat furnished by a standard inside heating element. A more constant rate of heating can be attained by using a hot plate in conjunction with the steam coil.

> Figure 1. Reservoir A. Pyrex bottle, 5 gallons B. Closed steam coll C. Float valve E. Pyrex buret F. Base, 5-gallon can G. Distilled water inlet M. Steam outlet O. Rubber stoppers P. Glass tubing R. Pinchclamps S. Soft rubber tubing T. Stiff wire braces U. Buret exhaust V. Hot water level

Mineral Contamination Resulting from Grinding Plant Samples

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Various grinding methods have been compared to determine the number of elements added during grinding and their relative seriousness as contaminants in preparation of plant samples. This paper reports the effects of type of method, type of plant material, duration of grinding, and size of plant sample upon contamination.

THE program of this laboratory is concerned with the nutritive value of food crops, and thus includes studies dealing with the importance of the micro nutrient elements in plant and animal nutrition. Several of these investigations require extensive mineral analyses of a variety of plant materials. Although a number of methods for grinding plant materials for analysis are available, a survey of the literature revealed few data concerning the mineral contamination resulting from different grinding methods.

Hamilton and Morris (3) considered it inadvisable to use iron mills in the preparation of feeds to be analyzed for iron. Two samples of unground corn were found to contain, respectively, 30 and 39 micrograms of iron per gram of sample, 56 and 67 micrograms after Wiley mill grinding, and 110 and 139 micrograms per gram after burr mill grinding. Nakamura and Mitchell (β) found that grinding corn in a Wiley mill increased the iron content from a value of 35 to 61 micrograms per gram, and that burr mill grinding increased the content to 125 micrograms per gram.

Preliminary investigations using common grinding methods revealed extensive contaminations and indicated the necessity of a more detailed study of both extent of and conditions affecting contamination.

EQUIPMENT AND METHODS

The types of grinding equipment used were: Wiley mill, hammer mill, mortar and pestle, and jar mill, with flint, porcelain, and Mullite balls. (Mention of equipment and concerns by the U. S. Department of Agriculture does not constitute a recommendation or an endorsement. No discrimination is intended and no guarantee is implied.) The Wiley mill used was an A. H. Thomas Co., Size 1 mill, equipped with copper alloy screens. The hammer mill was manufactured by the Christy and Norris Co. of England. A No. 7 (23-cm.) Coors porcelain mortar and pestle was used to grind samples by hand. Two jar mills were used—a single-jar, 2-gallon, interior glaze, Abbe Engineering Co. porcelain mill, and an H. K. Porter Co., 12-place mill with 2-gallon, glazed porcelain jars manufactured by the Stevenson Co., Wellsville, Ohio. The porcelain balls were furnished with the 12-jar mill, the flint balls were supplied with the Abbe mill, and the Mullite balls were purchased from the Coors Porcelain Co. Well-mixed samples of seeds were used in this investigation in order to obtain representative unground samples. Chemical analyses were carried out by the procedure of Parks, Hood, Hurwitz, and Ellis (7) for twelve biologically important elements: iron, zinc, copper, cobalt, molybdenum, manganese, phosphorus, sulfur, calcium, magnesium, potassium, and sodium. In addition, boron was determined by the method of Naftel (6). Duplicate analyses of single samples were made in all cases, and the results reported on a dry weight basis. Of the total quantity of element in a given sample after grinding, the proportion which resulted from contamination due to grinding is designated as per cent contamination, using the increase over the unground sample as the measure of contamination. By this method of calculation, a fourfold increase in mineral content is reported as 75% contamination, instead of the more common method of presenting it as a 300% increase. This avoids the cumbersome use of contaminations expressed as hundreds and thousands of per cent.

RESULTS

Various grinding methods were compared to determine both the number of elements added during grinding and their relative seriousness as contaminants in plant sample preparation. In each comparison, the data for the elements which were not added as contaminants during grinding are omitted. In several of the tables, the content of a given element is slightly less in a ground sample than in the average of two unground samples. These differences are all within the limits of sampling and analytical error, as indicated by the analyses of duplicate unground samples (Tables I and II).

Table I shows contaminations introduced by various grinding methods. Iron and copper contaminations were high for all types of grinding except mortar and pestle. In addition, zine, cobalt, and sodium were added in appreciable amounts by the jar mill. No significant contaminations of molybdenum, manganese, phosphorus, boron, sulfur, calcium, magnesium, or potassium were introduced by these grinding methods in this comparison.

Since the jar mill is extensively used in the preparation of samples for microelement analyses, a further comparison was made of contaminations introduced by various types of balls used in jar mill grinding. The comparisons in Table II of seven elements showing contamination by flint, porcelain, or Mullite balls indicate that the latter two materials are even more unsatisfactory than flint, both in the number of elements added and the relative magnitude of the contaminations. The remaining six elements determined were not added as contaminants.

THE RACE CHAO JAL MAN
balls wear appreciably
during grinding is shown
by Table III. In this
comparison, the balls
were washed, dried,
counted, and weighed
before and after grind-
ing. The losses in
weight of the ballsduring
grinding indicate that
appreciable wear took
place. The amounts of
rock flour recovered, as
compared to loss in
weight of the balls, show
that there was no sig-
nificant wear on the mill

			Table I.	Comp	osition of	Oat Gr	ain Sampl	es			
		(C	ontaminat	ion result	ting from v	arious gi	inding met	hods)			
]	Iron	14 14	Zine	C	opper	C	obalt	So	dium
Mill	Grinding	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con tam natio
		γ/g.	%	y/g.	%	×10.	%	y/g.	%	Mo/o.	%
None None Mortar and	Unground Unground By hand	24.9 24.9	0.0	$21.9 \\ 21.3 \\ 18.8$	0.0	$4.0 \\ 3.5 \\ 4.0$	5.0	0.01 0.01 0.01	0.0	$0.25 \\ 0.32 \\ 0.28$	0.6
Wiley mill	10-mesh	38.2	35.0	21.0	0.0	9.0	57.8	0.01	0.0	0.32	9
Hammer mill	10-mesh	43.3	42.5	17.3	0.0	4.4	13.6	0.01	0.0	0.32	9.4
Jar mill, flint	19 hours	35.0	28.9	166.0	86.8	5.5	30,9	0.03	66.7	0.42	30.9

^a Proportion of total quantity of element in a given ground sample, resulting from contamination due to grinding. Calculations based on averages of two unground samples.

of Oat Grain Sa

			100	ole II.	Composit		Jat Olalli	Sample	3				
		(Conta	mination r	esulting	from differ	ent types	s of balls u	sed in jar	mill grind	ling)	1		
I	ron	2	linc	C	opper	C	obalt	So	dium	Са	leium	Sı	lfur
Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a
y/g.	%	7/0.	%	y/0.	%	y/g.	%	Mg/g.	%	Mg/g.	%	Mo/o.	%
24.9	ion, files	21.9	un sa ann	4.0	st in	0.01		0.25	- 839- ··	1.6		1.47	
		21.3		3.5		0.01		0.32		1.0		1.42	(execution of the second secon
35.0 159.5 365.0	28.9 84.4 93.2	166.0 196.0 140.0	86.6 89.0 85.4	5.5 9.3 13.3	$30.9 \\ 59.1 \\ 71.4$	0.03 1.12 0.30	66.7 99.1 96.7	$0.42 \\ 1.07 \\ 2.23$	30.9 72.9 87.0	$1.2 \\ 1.5 \\ 2.4$	0.0 13.3 45.8	$1.40 \\ 1.49 \\ 3.35$	0.0 2.7 56.8
	$ \begin{array}{r} 1 \\ Content \\ v/g. \\ 24.9 \\ 35.0 \\ 159.5 \\ 365.0 \\ \end{array} $	Iron Con- tent Con- tami- nation ^a γ/g. % 24.9 35.0 28.9 159.5 84.4 365.0 93.2	$\begin{array}{c c} & (Conta \\ \hline \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Iron Zine Copper Con- tami- tent Con- tent Con-	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

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Proportion of total quantity of element in a given ground sample, resulting from contamination due to grinding. Calculations based on averages of two unground samples. ^b Grinding time, 19 hours.

Table III. Abrasion on Balls and Mill during Jar Mill Grinding^a

	(Effect	of different typ	es of balls)	
Type of Ball	Initial Weight of Balls	Final Weight of Balls	Loss in Weight of Balls	Rock Flour Recovered ^b
	Grams	Grams	Grams	Grams
Porcelain Mullite Flint	5361 6693 4412	5315 6644 4397	46 49 15	45 72 16
^a 11 days ^b Probabl	grinding, no pla y 95–98% recov	nt sample. ery.		

jar when flint or porcelain balls were used, but a large amount of wear on the walls of the mill jar with Mullite balls. This effect is notable, since the data indicate that the use of silica, tungsten carbide, or other balls which are harder than the material of the jar will cause serious contamination due to wear on the jar wall.

To determine whether contamination is equally severe for different types of plant material, vetch seed and oat grain ground under identical conditions were compared. The striking differences in the amounts of contamination of zinc and copper (Table IV) were also found for iron, cobalt, and sodium.

Table IV. Composition of Oat Grain and Vetch Seed Samples

(Effect of type of plant material on contamination resulting from various grinding methods)

			Zinc							
contractory on the Augustal		()ats	v	Vetch		ats	Vetch		
Mill	Gr	inding	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a
			7/9.	%	y/a.	%	×10.	%	×10.	%
None Mortar a	and By	ground nand	$\begin{array}{c} 21.6\\ 18.8 \end{array}$	0.0	45.5 46.9	3.0	3.8 4.0	5.0	$\begin{array}{c} 11.6\\ 10.6\end{array}$	0.0
Wiley mill	10-	mesh	21.0	0.0	42.0	0.0	9.0	57.8	11.7	0.9
Hammer 1	nill 10-	mesh	17.3	0.0	45.7	0.4	4.4	13.6	11.1	0.0
Jar mill, fl balls	lint 19	hours	166.0	86.8	64.0	28.9	5.5	30.9	10.7	0.0
· Proper	tion of t	otal ana	ntitu of	aloment in	a miwan a	round com	nla rogul	ting from .	antemir	ation due

/ GRAM PLANT TISSUE 2 200 UNGROUND SAMPLE 12 15 18 Gram LOSS IN WEIGHT OF BALLS

Figure 1. Iron Contamination of Oat Grain as a Function of Loss in Weight of Mullite Balls during Jar Mill Grinding

can probably be accounted for by nonuniform chipping, particularly with the flint pebbles, which exhibit a characteristic conchoidal chipping during grinding. The rock chips are never

found as such in the plant samples.

The erratic nature of the contamination during Wiley mill grinding is less easily explained, but is readily verified. In Table VII are presented the iron analyses of six replicate oat grain samples, each ground once through the Wiley mill with uniform feeding from the hopper. The several-fold variation in contamination cannot be related to any of the factors being studied. In some laboratories a magnet is passed over such samples to remove loose particles of iron. The efficiency of this system might also be expected to vary with different types of plant material.

The contaminating elements in flint rock flour are present (Table VIII) in approximately the same proportion as in

contamination of the oat grain sample ground in the jar mill with flint pebbles. Because of the lack of homogeneity of the flint

Table V.	Loss in Weight of	Flint Balls during .	Jar Mill Grinding
	(Effect of different	t types of plant mate	rial)
Plant Sample	Initial Weight of Balls Grams	Final Weight of Balls Grams	Loss in Weight of Balls Grams
None Clover ^b Vetch ^c ^a 11 days ^b 100 gra	4412 4397 4617 of grinding in each cas	4397 4386 4614 Chis sample complete	15 11 3
e 100 gra	ms of vetch seed.	and bumpie complete	

Loss in weight of balls during jar mill grinding with different types of plant material (Table V) substantiates the view that grinding contamination varies with type of plant material.

to grinding.

Studies of the effect of duration of grinding on contamination of three elements are reported in Table VI. Although there is some evidence of an increase in contamination with increased time of grinding, the results are erratic for all types of mills. For the jar mill samples ground with Mullite balls, loss in weight of the balls during grinding was determined. When the contamination of the samples with iron is plotted against loss in weight of the Mullite balls during grinding (Figure 1), a direct correlation is found. A similar trend occurred for calcium, sodium, sulfur, zine, cobalt, and copper. The unequal rates of wear of the balls Table VI. Composition of Oat Grain Samples

Ellect of t	anic of grine	ing on	method	s)	iting irom	various	grinding
	Iron Zinc Copper						
Mill	Grinding	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a	Con- tent	Con- tami- nation ^a
		r/a.	%	r/0.	%	y/g.	%
None Wiley mill, 10-mesh screen Jar mill, flint balls Jar mill,	Unground Once Twice Four times 19 hours 33 hours 66 hours 19 hours	$\begin{array}{r} 24.9\\ 38.3\\ 61.6\\ 49.2\\ 35.0\\ 48.3\\ 45.0\\ 365.0\\ 365.0\end{array}$	$\begin{array}{r} 35.0\\ 59.5\\ 49.4\\ 28.9\\ 48.5\\ 44.6\\ 93.2\end{array}$	$\begin{array}{c} 21.9\\ 21.0\\ 20.0\\ 21.6\\ 166.0\\ 159.0\\ 236.0\\ 148.0\\ 148.0\\ \end{array}$	0.0 0.0 86.8 86.5 90.6 85.4	3.8 9.0 9.9 12.0 5.5 4.8 6.5 13.3	57.8 61.6 08.3 30.9 20.8 41.5 71.4
Mullite balls	33 hours 66 hours	677.0 464.0	96.3 94.5	643.0 533.0	96.8 96.0	18.5 13.7	79.5 72.2

^aProportion of total quantity of element in a given ground sample, resulting from contamination due to grinding.

Table VII. Composition of Oat Grain Samples

colicate			Iron
amples	Grinding	Content	Contamination
		2/0.	%
12	None Mortar and pestle	$24.9 \\ 24.9$	0.0
3 4	Wiley mill ^b Wiley mill ^b	65.0 194.0	61.7 87.1
5 6	Wiley mill ^b Wiley mill ^b	72.5 219.0	65.7 88.7
7	Wiley millb	136.0	81.7

^a Proportion of total quantity of element in a given ground sample, resulting from contamination due to grinding.

10-mesh screen, each sample ground once.

balls with respect to mineral content, successive grindings might be expected to introduce variable contamination of a given element.

Table IX illustrates the lack of homogeneity in the flint balls, by comparison of the analysis of a single pebble picked at random from the mill charge, with the analysis of the rock flour.

The effect of varying the size of plant sample used during jar mill grinding was also studied. The results for five of the elements showing contamination are illustrated in Figure 2. The increase in contamination with reduction in size of sample ground is very marked for these five elements. Calcium and phosphorus were also added in appreciable amounts during the grinding of the 30-gram sample.

DISCUSSION

All the grinding methods studied except mortar and pestle gave serious contamination of one or more of the micro elements. As a result, the only satisfactory methods of plant sample preparation apparent at this time are use of mortar and pestle or not grinding the tissue. With care, it is possible to grind a plant sample by hand in a large mortar and pestle without losses and without contamination of any of the elements studied. Sampling becomes much more difficult when the tissue is unground. One partially satisfactory method of meeting this difficulty would be to take samples small enough to be ashed or digested in their entirety.

Other solutions of this grinding problem may be possible. Purr (8) found it possible to grind fresh animal tissue by freezing with liquid nitrogen and pounding with a hammer. To avoid the introduction of heavy metals, Kirk and Sumner (4) used a porcelain burr mill to grind jack beans in the preparation of urcase. An attempt was made to use this mill in the present study. Although preliminary results indicated no contamination, the design is such that whole grains and stemmy materials cannot be satisfactorily ground. It seems likely that a similar porcelain burr mill could be designed which would be suitable for general plant tissue grinding. Chrome or cadmium plating of the inner surfaces of a hammer or Wiley mill might also be possible. It is commonly recommended (1) that for iron or other micro element analyses, plant samples should be ground in a porcelain jar mill using flint pebbles, instead of in a Wiley or hammer mill. The basis of this recommendation is not known, since flint is of marine origin and contains appreciable amounts of carbonaceous material (2). The results obtained here, showing its mineral content and rate of wear during grinding, would not support this recommendation. It has been further recommended (1) that any contamination arising during grinding in a Wiley or hammer mill may be compensated by subtracting a grinding blank. The results presented in Table VII do not substantiate this recommendation.

The grinding of plant samples for analysis for certain elements in a particular mill may be possible, but each mill and each type of plant material would have to be examined individually for each element to be determined.



Figure 2. Contamination of Oat Grain Samples as a Function of Sample Size

30-, 120-, and 480-gram samples of oat grain (bars A, B, and C, respectively) were ground for 66 hours in a jar mill using flint balls. The 480-gram sample was not completely ground in this length of time. The content of each element is denoted by the heights of the bars. The shaded area represents the content of the element in the unground sample.

The data presented further indicate that many of the previous analyses and conclusions regarding micro element content of plants should be re-examined in light of the grinding procedures used.

SUMMARY

In an investigation of contamination resulting from grinding plant tissues in the common grinding mills, the effects of type of grinding methods, type of plant material, duration of grinding, and size of plant sample upon contamination of thirteen elements during sample preparation were studied.

Grinding plant material in Wiley mill and hammer mill produced iron and copper contamination. Jar mill grinding with flint balls resulted in contamination of iron, zinc, copper,

Table VIII. (Comparison of Composition Contamination in a Plant	of Flint Rock Flour with Sample®
Element	Micrograms of Element per 0.03 Gram of Flint Rock Flour	Contamination of Plant Tissue, 7/g.
Zn Na Fe Cu Co	185.1 141.0 13.7 0.8 0.01	137.4 130.0 23.4 1.0 0.01
Table IX.	Comparison of Composition	of Single Flint Ball and Flint
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	Rock Flour Produced during	Jar Mill Grinding

Element	Flint Flour	Single Pebble
Ca	Mg./g.	Mg./g.
Mg	0.06	0.06
K	6.6	1.5
P	5.0	0.2
5	0.0	0.0
Fe	458	770.
Źn	6170.	20.9
Mn	25.7 6.3	49.3 98.8
Co	0.35	1.71
10	10.0	0.4

cobalt, and sodium. The use of porcelain or Mullite balls during jar mill grinding gave rise to appreciable contamination of iron, zinc, copper, cobalt, sodium, and in some cases calcium, sulfur, and phosphorus. Flint, porcelain, and Mullite balls all wear appreciably during jar mill grinding. The contaminating elements in flint rock flour are present in about the same proportions as in the contamination of a plant sample ground in the jar mill, using flint balls.

Hand grinding with a mortar and pestle resulted in no appreciable contamination of iron, zinc, copper, boron, cobalt, manganese, molybdenum, calcium, sodium, magnesium, phosphorus, sulfur, or potassium.

Grinding contamination is erratic for both jar and iron mills. A several-fold variation in iron contamination resulted from uniform Wiley mill grinding technique. While iron contamination of samples ground in a jar mill using Mullite balls is almost a straight-line function of loss of weight of the balls during grinding, the loss in weight is not uniform with time.

Large increases in contamination of zinc, iron, copper, cobalt, and sodium resulted from decrease in size of plant samples ground in a jar mill using flint pebbles.

For the types of mills studied, less contamination resulted from the grinding of vetch seed than from the grinding of oat grain.

All the mechanical grinding methods used resulted in serious contaminations of one or more elements. Although a particular mill may be used in the preparation of plant samples for the analyses of certain elements, it is concluded that marked errors would be involved in using the common mills for grinding plant tissue for general or extensive micro element analyses.

ACKNOWLEDGMENTS

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Glass Electrode Assembly for Titrating Microbiological Vitamin Assays

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N THE titration of microbiological vitamin assays it is often more desirable to use a glass electrode pH meter to determine the end point than to use an indicator and note the color change. A simple assembly, using a well-known commercial glass electrode pH meter (Beckman, Laboratory Model G) and standard laboratory equipment, has proved very satisfactory in this laboratory, furnishing a simple and rapid accurate titration procedure.

A 7.5-cm. (3-inch) glass funnel with the stem cut off 1.25 cm. (0.5 inch) from its body and fitted with rubber tubing long enough to reach to a drain is supported about 7.5 cm. (3 inches) from the laboratory bench. A small piece of glass tubing connected to the compressed air line through a trap is placed in the funnel, so that the bottom tip of the tube is just in the stem of the funnel. The tip of a 25-ml. buret is inserted halfway down the funnel and over to one side. An external glass electrode and calomel electrode are suspended in the funnel about 2.5 cm. (1 inch) from the bottom and slightly off center. A pinchclamp is inserted in the rubber tubing line just below the stem of the funnel.

To titrate an assay, the pinchclamp is put in place and the air turned on, so that a steady stream of bubbles will emerge from the air tube. The assay medium is poured into the funnel and the assay tube is washed with 10 to 12 ml. of distilled water, The electrometric ner. The funnel is which is also added to the funnel content. titration is carried out in the customary manner. then drained by opening the pinchelamp, and the assembly is ready for the next titration.

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CHLOROMETRY

A Titrimetric Procedure Available for Microanalysis

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Standard sodium hypochlorite solution is recommended as a general titrimetric reagent for microanalytical work. The solution must be made with sufficient excess of sodium hydroxide so that the pH is about 12.5 and must be stored in brown, glass-stoppered bottles. Under these conditions, sodium hypochlorite solution is remarkably stable and compares favorably with other titrimetric reagents. With the use of this reagent, chlorometric determinations can be made at room temperature with ease, precision, accuracy, and a sharpness of the end point that leaves nothing to be desired in an analytical reagent.

T IS a popular misconception that because sodium hypo-chlorite is a highly reactive substance it is too unstable to be used as a standard titrimetric reagent. Because of this belief, it has almost never been used for this purpose.

"Chlorometry" is the term used to designate the quantitative estimation of various substances by use of standard hypochlorite solution, in a manner entirely analogous to iodometry and bromometry. Although chlorometric determinations have not achieved any degree of practical application, there are references to the use of hypochlorite as a macroanalytical reagent in the literature.

As early as 1824, Gay-Lussac estimated the strength of chlorinated lime by permitting a fine suspension of chlorinated lime to flow from a buret into a hydrochloric acid solution of an arsenite and obtained the end point of the reaction by using indigo as the indicator. Denigès (3) using a similar modifica-tion turned to potassium bromide as the indicator. However, Lunge-Berl (9) showed both of these determinations to be rather inaccurate.

inaccurate. In some respects, chlorometry has as venerable a history as iodometry, introduced by Bunsen and Schwarz in 1853, the bromate methods of Koppeschaar (8) and the bromometric methods of Manchot (10). Jackson and Parsons (4) advocated the use of sodium chlorite as a volumetric oxidizing agent. Jellinek and Kresteff (5), continuing a series of studies of newer methods in volumetric analysis, presented chlorometry as a valuable volumetric aid. They prepared a standard solution of sodium hypochlorite by passing chlorine gas from a small tank of chlorine into N sodium hydroxide solution until the solution was approximately 0.13 N with respect to sodium hypochlorite content. They kept this solution in a clear trans-parent bottle connected to a buret, using rubber connections, and found that with an excess of alkali the titer of the standard sodium hypochlorite solution kept surprisingly constant. Thus, their original titer, using the potassium iodide-hydrochloric sodum hypochlorite solution kept surprisingly constant. Thus, their original titer, using the potassium iodide-hydrochloric acid method of estimation, was 0.1350 to 0.1351 N. After 7 days, the strength of this solution was practically unaltered, for their estimations gave the normality a value of 0.1351 to 0.1352. After an additional 10 days, the titer had been re-duced to 0.1330 to 0.1328. They attributed this loss of about 1.5% to the fact that they had made no attempt to shield the solution from sunlight. Jellinek and Kuhn (6) prepared a standard solution of sodium

solution from sunlight. Jellinek and Kuhn (6) prepared a standard solution of sodium hypochlorite in the manner described by Jellinek and Kresteff and found it practically constant for a number of weeks. Kolthoff and Stenger (7) found that "H.T.H." calcium hypo-chlorite yielded stable solutions. They added excess bromide to the sample to be titrated, so that in their titrations the added hypochlorite actually behaved as hypobromite. They stand-ardized their hypochlorite solutions by titration against arsenic trioxide in acid or weakly alkaline solution, using Bordeaux as the indicator. the indicator.

Chapin (2) in a study of the decomposition of hypohalites found that potassium hypochlorite solution had its maximum stability at pH 13.1.

PREPARATION OF STANDARD SODIUM HYPOCHLORITE SOLUTION

Undoubtedly one reason for the lack of enthusiasm among analysts for the use of sodium hypochlorite as a titrimetric reagent is the apparent difficulty of preparing such solutions. The authors discarded the cumbersome method of Jellinek and Kresteff (5) and prepared a standard solution in the following simple manner.

Transfer 8.0 ml. of a commercial preparation of sodium hypo-chlorite solution containing 5% of available chlorine to a glass-stoppered brown-glass bottle, and dilute with water to about 2 liters. If necessary, add sufficient sodium hydroxide (1 gram) to raise the pH to about 12.5, the optimum pH for stability. To ascertain if the proper pH has been reached, the customary colorimetric methods for the determination of pH in the range 12 to 14 may be used. The authors used Chlorox as the source of sodium hypochlorite. Obtain the titer of the solution by titration against a primary standard of sodium asserite made as titration against a primary standard of sodium arsenite made as follows:

Weigh 0.2473 gram of arsenious oxide (arsenic trioxide, As₂O₄, National Bureau of Standards) and dissolve in 25 ml. of 10% sodium hydroxide solution. Transfer to a 1-liter volumetric flask, make slightly acid with sulfuric acid (1 to 6), and dilute with water to 1 liter. This solution is 0.005 N.

The solution of sodium hypochlorite made as directed above is generally somewhat stronger than 0.005 N. Its exact titer can be determined by titration against the standard arsenite solution. Its normality may be adjusted to exactly 0.005 N by the usual procedure.

TITRATION PROCEDURE

To estimate the strength of the sodium hypochlorite solution the following simple procedure may be used.

Transfer a known aliquot of standard arsenite solution to a 125-ml. Erlenmeyer flask or a 150-ml, beaker: a 4-ml, aliquot if a microburet is to be used for the standard hypochlorite solution and a 5-ml, aliquot if a semimicroburet is to be used. A standard solution of tartar emetic, [potassium antimony] tartrate, $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O_1$ containing 1 mg, of antimony per 10 ml, of solution may also be used. Add 5 ml, of concentrated hydrochloric acid and adjust the volume of the solution to 35 to 40 ml, by adding distilled water. Fill a microburet or semimicro buret with the standard hypochlorite solution. Add 1 drop of 0.05% methyl orange indicator solution to the test solution and titrate directly with the sodium hypochlorite solution. Add another drop of methyl orange indicator solution near the end point and continue the titration until the color of the methyl orange is destroyed. Make a blank titration using exactly the same volume of hydrochloric acid, water, and 2 drops of methyl orange indicator solution. drops of methyl orange indicator solution, replacing the volume of arsenite or antimony test solution by additional distilled water. The blank should run about 0.12 to 0.14 ml.

RESULTS

In order to determine the stability of the standard sodium hypochlorite solution prepared in the manner directed above, titrations were performed as detailed at intervals during 3 years. In all, five series of experiments were run. Titrations were performed in triplicate and the results averaged. The results obtained in three of these series are representative. In the first the initial normality was 0.004970; after 102 days it was still 0.004970; the maximum variation within this period was +0.000008. In the second series, initial normality was 0.005572; after 175 days this had degraded to 0.005543, the maximum variation within the period being -0.000021. In another series, the initial normality was 0.00500 and at the end of 56 days was 0.004977 with a maximum variation of -0.000020. The other two series gave comparable results.

As a check on the accuracy of sodium hypochlorite solution as a titrimetric reagent, arsenic and antimony were determined in standard solutions, using both the potassium bromate and the sodium hypochlorite methods.

DISCUSSION

In the determination of microquantities of antimony, the potassium bromate method (1) was not entirely satisfactory for a number of reasons, the principal ones being that titrations had to be performed almost at the boiling point in strong hydrochloric acid solution with the consequent production of relatively copious and irritating fumes of hydrogen chloride and that the blank, using methyl orange as the indicator, was large. The blank obtained using some of the indicators suggested by Smith and Bliss (11) was even larger.

Standard sodium hypochlorite solution has several marked advantages. It is an economical reagent. One can perform direct titrations with it. It is unnecessary to perform the titrations at elevated temperatures, eliminating any danger from the irritating fumes of hydrochloric acid. The blank is smaller than that obtained with potassium bromate titrations. Hypochlorite titrations can be performed under conditions of low acid concentration without apparent decrease in accuracy. From 0.1 to 1 mg. of antimony or arsenic per 10 ml. of sample solution can easily be estimated. Titrations can be made in glass-stoppered bottles,

glass-stoppered Erlenmeyer flasks, or iodine flasks, if desired, to minimize losses attributed to volatility. Many of the indicators mentioned by Smith and Bliss, and Kolthoff and Stenger can be used instead of methyl orange without increase of the blank. The precision compares favorably with that of other methods, as can be seen from the reproducibility of results.

Several precautions must, however, be observed in using sodium hypochlorite solution as a titrimetric reagent. It must be preserved in brown, glass-stoppered bottles. It may be kept at room temperature without deterioration over considerable periods of time. Keeping the solution at lower temperatures is perhaps preferable.

The optimum conditions for the titrations are a volume of at least 35 to 40 ml. with an acid concentration equivalent to 5 ml. of concentrated hydrochloric acid.

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Thiosulfate Washers in Alkoxy Microdeterminations

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Determinations of methoxy and methylimide groups in which thiosulfate alone is used as a washer give values considerably lower than theoretical. This is due to the solubility of the methyl iodide in the washer, and a subsequent reaction. Ethoxy and ethylimide determinations are not subject to this loss. The effect of thiosulfate can be eliminated by using as washer thiosulfate dissolved in saturated sodium chloride, or by adding cadmium sulfate as in the standard gravimetric procedure. The minor errors in determinations using as washers water, phosphorus suspension, or 0.5% sodium carbonate, are insignificant in comparison with that due to thiosulfate. A rapid distinction between ethoxy and methoxy can be made by doing a determination with a good washer, such as 0.5% carbonate, then with 5% thiosulfate; the methoxy value will be reduced to 55 to 70% of the original, while ethoxy remains unchanged.

WORK on alkaloids in this laboratory required the de-velopment of micromethods of alkoxy and alkimide determination. The apparatus used was that of Pregl for alkoxy and that of Friedrich for alkoxy and alkimide determinations, and the procedure was essentially that of modern textbooks of microchemistry. Three to 5 mg. of material were weighed on tinfoil, dissolved in phenol and acetic anhydride, heated with hydriodic acid, and passed through a washer of 5% thiosulfate containing 0.5% sodium carbonate. Final estimation was by the Viebock-Brecher method. Preliminary experiments with the Friedrich apparatus showed that the values obtained with vanillin and several alkaloids did not agree with theory, calculation being from first principles. The titration obtained with all methoxy-containing substances was only 50 to 70% of the theoretical, while ethoxy values agreed closely with theory. The method was then examined in detail and many

of the more obvious possible sources of error were eliminated. The same effect was found in the Pregl apparatus. The only factor not eliminated appeared to be the washing solution. Consequently, red phosphorus suspension, the original washer of Pregl (9), as well as water and 0.5% sodium carbonate was tried. These gave theoretical results in the Pregl apparatus, and values some 5% low in the Friedrich apparatus. The use of thiosulfate as a washer was then investigated, and the literature searched for counterindications to its use. Thiosulfate washers are almost universally used and recommended by the later workers in microchemistry.

EXPERIMENTAL

Known amounts of methyl iodide were introduced into the Friedrich apparatus without any hydriodic acid, drawn through various washers, and titrated in the ordinary way. With no washer, or with water, phosphorus suspension, or 0.5% carbonate the recovery was almost theoretical. With thiosulfate there was only 50 to 65% recovery, thus confirming the effect of thiosulfate.

A survey of results obtained with various washers in the Pregl apparatus is given for vanillin in Table I, and for phenacetin in Table II, which show that the effect of thiosulfate on the methoxy value is detected when 1 ml. of a 1.5% solution is used. This effect becomes much larger when 5 to 10% thiosulfate is used, while with very high concentrations (40%) theoretical values are again obtained. With ethoxy there was no detectable effect in any concentration.

DISCUSSION

The effect of thiosulfate is explained as a result of two factors: (1) the solubility of the alkyl halide in the washing solution, with Table I. Methoxy Values on Vanillin (Theory 20.36)"

Washing Solutions	Volume of Washing Solution Ml.	Sub- stance Mg.	Titration, 0.0188 N Thiosulfate Ml.	Methoxy %	Washing Solutions	Volume of Washing Solution <i>Ml.</i>	Sub- stance Mg.	Titration, 0.0188 N Thiosulfate Ml.	Methoxy %
Water	0.5 i.0	3.790 3.210 4.526 5.511 3.546	7.446.669.3911.807.49	19.1 20.1 20.2 20.7 20.5	5% thiosulfate 5% thiosulfate with 0.5% carbonate 10% thiosulfate	1.0	5.298 4.022 5.885 3.568 4.531	7.15 5.97 8.51 5.24 6.08	13.1 14.4 14.1 14.3 13.0
0.5% sodium carbon- ate	0.5	4.292 3.930 3.552 3.193 4.110	8.52 8.07 7.56 6.66 8.52	19.3 20.0 20.7 20.2 20.2	20% thiosulfate	i.0 1.0	5.284 4.172 3.600 3.692	7.89 6.61 5.80 6.05 5.60	14.5 15.4 15.6 15.9
bonate 1.5% sodium thiosul- fate	0.5	3.250 3.881 4.117 3.350 3.492 5.454	6.69 7.57 8.34 6.69 7.29 10.11	20.0 19.0 19.7 19.7 20.3 18.0	40% thiosulfate 80% thiosulfate 5% thiosulfate in satu- refed sodium sho-	1.0 1.0 1.0	3.767 3.892 5.252 5.470 3.780	8.08 8.30 10.39 10.80 7.87	20.2 20.7 19.2 19.2 20.2
5% thiosulfate	0.5	3.217 3.112 3.388 3.770 5.710	6.61 5.60 6.53 6.00 9.50	20.0 17.8 18.7 15.5	2.5% thiosulfate and	1.0	4.900 4:959 3.008 5.090 4.420	10.29 10.32 6.21 10.45 9 11	20.2 20.4 20.2 20.1 20.0 20.0
o / j this anate	1.0	4.038 4.026 3.668	7.68 7.49 5.80	18.5 18.0 15.4	fate		3.545 3.944 5.049	7.43 8.33 10.71	20.4 20.8 20.6

Table II. Ethoxy Values on Phenacetin (Theory 25.14)"

Washing Solutions	Volume of Washing Solution Ml.	Sub- stance Mg.	Titration, 0.0188 N Thiosulfate Ml.	Ethoxy %
Water	0.5	4.744 5.334 2.787	8.75 9.62 4.94	26.0 25.4 25.1
5 % thiosulfate	1.0	4.213 4.051 5.680	7.57 7.47 9.91	25.3 25.8 24.6
10% thiosulfate	1.0	4.815	8.65	25.3
20% thiosulfate	ilo	4.117 5.211	9.25	25.7 24.9

^a Several blanks gave 0.05 to 0.07 ml. of thiosulfate with the washers used, though a few with high thiosulfate concentrations gave up to 0.20 ml. When bromine was removed by several drops of formic acid, the resulting solution gave no detectable liberation of iodine from potassium iodide. The phenol method of Nanji (8) was not needed.

a consequent dependence on the volume of washer used, and (2) the rate of reaction of the dissolved halide with thiosulfate. Methyl iodide and thiosulfate react in water according to a wellknown bimolecular reaction investigated by Slator (11). At 25° C. his data show for 0.035 N thiosulfate and 0.018 N methyl iodide a half-time of 10 to 12 minutes, with $K_2 = 0.85$. The ethyl iodide reaction is slower with K_2 at $25^\circ = 0.050$. This reaction is expected to occur in methoxy determinations because of the appreciable solubility of methyl iodide in water. At 20° 1.40 grams of methyl iodide dissolve in 100 grams of water (7). With very concentrated thiosulfate the solubility is apparently depressed, and little if any reaction can take place. The solubility of methyl iodide in concentrated neutral salt solutions would be expected to be much less than in water. With 1 ml. of 5% thiosulfate in saturated salt, no loss was found. Addition of an equal volume of 5% cadmium sulfate also completely suppressed any reaction, apparently through more than a solubility effect. In the case of ethyl iodide the lower rate of reaction and the lower solubility (at 20° 0.401 gram of ethyl iodide dissolves in 100 grams of water, 7) combine to give no detectable effect.

Satisfactory results were obtained by Pregl (9), using phos-phorus suspension as a washer for alkoxy and alkimide determinations by Viebock and Brecher (13), and by many later workers using modified apparatus. The main purpose of the washer appears to be to remove hydrogen iodide vapors, rather than iodine itself, and for this purpose an aqueous washer appears effective even in alkimide determinations. Phosphorus sus-pension was criticized by Friedrich (6) as it is incapable of re-moving iodine rapidly. He therefore used for the gravimetric method 3% thiosulfate to which was added an equal volume of

5% cadmium sulfate. The use of the latter material for removal of hydrogen sulfide was due to Edlbacher (3). Friedrich's values were correct, as would be expected from this study, but he does not insist on the admixture with cadmium sulfate. Friedrich (5) states that use of cadmium sulfate is not necessary Friedrich (b) states that use of cadmium sufface is not necessary if the acid is free from sulfide. The standard washer for the gravimetric method (Roth, 10) is 1 ml. of equal volumes of 5% thiosulfate and cadmium sulfate. As indicated in the table, this washer is perfectly satisfactory, and because of a chance effect which is not quite expected, the thiosulfate effect is elimi-nated, and results are free from error. This washer has also have used in modified volumetric methods by Elek (4) Christenbeen used in modified volumetric methods by Elek (4) Christensen, Friedman, and Sato (1), and Cooke and Hibbert (2) with good results.

Slotta and Haberland (12) used for the volumetric method 1 ml. of 1.5% thiosulfate to which was added 0.5% sodium car-bonate, and gave a few examples which were close to theory. From Table I it is seen that with 1 ml. of thiosulfate of this concontration a lowering is detected, but with 0.5 ml. little if any lowering. The washer for the volumetric method generally adopted by Friedrich (5) and by Roth (10) is 1 ml. of 5% thio-sulfate with optional addition of 0.5% carbonate. Roth states that this washer was used by Slotta and Haberland. The carbonate was found to have no effect on the thiosulfate reaction, and this washer was incapable of giving anything near the theoretical results. Friedrich (5) states that he used this washer for 5 years with completely satisfactory results. He gives no ex-ample of calculation and makes no mention of empirical corrections. In the volumetric methylimide determination he states that 1 ml. of 0.01 N thiosulfate = 0.1502 mg. of CH₃ (N), which, divided by 6, is in agreement with theory. Roth (10) also makes no mention of low results or empirical corrections. He gives 1 ml. of 0.02 N thiosulfate = 0.6204 mg. of OCH₃, which divided by 6 is theoretical. His feature in coloridation of methylic by 6 is theoretical. His factors given for calculation of methoxy, ethoxy, methylimide, and ethylimide are all in agreement with theory, assuming 100% recovery of alkyl iodide.

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