volve calculations only, based on reference to results of existing official methods.

Bleaching Methods Committee. This committee continues to be rather inactive as there is no specific problem before them although one member of the committee is making a spectroscopic study of bleaching response of various oils. In view of the problems on standard bleaching earth presented in the first of this report, the committee may soon have a very active problem.

Vitamin Committee. This committee is rather inactive pending action that the U. S. Pharmacopoeia may take in their contemplated consideration of the physicochemical methods of Vitamin "A" assay that the committee has previously developed.

Glycerine Analysis Committee. Revision in tentative method Ea-6-46 for the periodic acid determination of glycerine was adopted (November, 1948).

Spectroscopy Committee. A spectrophotometric method of analysis for constituent fatty acids was adopted (November, 1948) as tentative.

General. The foregoing reviews of committee activities are in most cases as complete as information has been made available to the Uniform Methods Committee. It is entirely complete with respect to all official actions of the Society on analytical methods.

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The Determination of Potassium in Soap and Mixed Caustic Lye*

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A MODIFICATION of the method for the determination of potassium as the periodate, suggested by Willard and Boyle (34), is presented. The modification increases the accuracy and sensitivity of the original method and at the same time contributes to its usefulness as an industrial control procedure. A literature survey is presented as an aid for those who wish to evaluate the proposed method by comparison with other methods.

Review of Methods

Cobaltinitrite. The determination of potassium with sodium cobaltinitrite, as first suggested by de Koninch (11), has disadvantages that cannot be overlooked when extreme accuracy is desired. The precipitate of dipotassium sodium cobaltinitrite has been studied quite completely by Robinson and Hauschildt (22). Their investigations show the composition of the precipitate to vary, depending upon the conditions of the precipitation; the most important is the sodium and alcohol concentrations of the precipitating medium and the temperature at which the precipitation is made. Others (19, 25, 26, 30) have confirmed this work insofar as agreeing with the qualitative effect of these variables. There is wide discrepancy, however, in the literature, concerning the quantitative effects of Na:K ratio, temperature, and concentration.

Sodium cobaltinitrite reagent is generally prepared by mixing a solution of sodium nitrite with a solution of cobaltous acetate in acetic acid. Since precipitation by this reagent usually gives high results, it is felt that a reagent containing less extraneous materials would be desirable. This is accomplished by Wilcox (33), who employs an aqueous solution of trisodium cobaltinitrite as the precipitating reagent, the reaction being carried out in a nitric acid medium. The precipitate is crystalline and allegedly of constant composition regardless of the sodium concentration.

The precipitate of dipotassium sodium cobaltinitrite obtained through any scheme of precipitation may be finally determined either gravimetrically or volumetrically. One of the best known methods is that of Kramer and Tisdall (18), who decompose the precipitate with alkali, oxidize the liberated nitrite with potassium permanganate, and back titrate the excess with oxalate.

There are certain disadvantages in this method, and these are outlined by Brown, Robinson, and Browning (5), who have suggested an alternative procedure. They dissolve the precipitate in ceric sulfate and back titrate the excess with ferrous ammonium sulfate, using ortho-phenanthroline as the indicator. An average error of 2% is reported in determinations of potassium from 0.2 to 1.0 mg.

A variation of the cerium procedure is presented by Kaye (16). Potassium iodide is added to the excess ceric sulfate, and the liberated iodine is titrated to a starch endpoint using sodium thiosulfate. The obvious advantage of such procedure lies in the sharpness of the endpoint, even in very dilute solutions.

Further variations of the cobaltinitrite method include the use of silver cobaltinitrite reagent and the final determination made with ceric sulfate and ferroin (17). Determination of the precipitate formed from the same reagent is also made through the estimation of silver in the insoluble complex using the Volhard method (14). An alternative procedure is the determination by distillation and titration of ammonia (10). The formation of the silver complex is preferred by some because of its greater insolubility, more constant composition, and ease of manipulation.

Colorimetry. Colorimetric methods applicable to the determination of potassium are many and include further variations of the precipitation of the cobaltinitrite. One of these is suggested by Eden (12) and is a variation of the method of Jacobs and Hoffman (15), in which a brilliant green complex is formed with choline hydrochloride and potassium ferrocyanide. Wander (31) suggests the oxidation of dipotassium sodium cobaltinitrite with dichromate and

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sulfuric acid followed by measurement of the resultant yellow-green color.

Sideris (27) determines potassium indirectly by precipitating the cobaltinitrite and colorimetrically measuring the amount of cobalt in the acid solution of the precipitate using nitroso-R-salt (disodium salt of 1-nitroso-2-hydroxy-3:6-naphthalene disulfonic acid).

Other colorimetric procedures (29) which may be utilized after precipitation of the potassium with sodium cobaltinitrite include direct development of the cobalt chloride, development with dimethyl glyoxime and sodium sulfide, development with salicylic acid and α-naphthylamine and development with cysteine hydrochloride and hydrogen peroxide.

When the concentration of sodium is constant in all samples, a colored complex of potassium may be developed directly with dipicrylamine (2). A similar procedure may be used in the absence of sodium and sulfates in which the color of a solution of potassium picrate is measured (7). For low concentrations the colorimetric determination of a solution of potassium chloroplatinate has been suggested (1). Even more sensitive is the same type of measurement using iodoplatinate (8).

Chloroplatinate. It has been stated (9) that the classical gravimetric procedure using chloroplatinic acid (13), which is the official A.O.C.S. method, is the most accurate method for the determination of small amounts of potassium. Schohl and Bennett (24) have modified the chloroplatinate precipitation procedure and have developed a volumetric method based on the following reactions:

$$K_2PtCl_6 + 6KI = K_2PtI_6 + 6KCl$$
$$K_2PtI_6 + Na_2S_2O_3 = K_2PtI_4 + 2NaI + Na_2S_2O_6$$

The method is reported to have an accuracy of 2% on samples containing as little as 0.4 mg. of potassium.

Variations on the chloroplatinate method are few as compared with the cobaltinitrite method. One which is of interest, however, employs metallic magnesium to reduce the platinum in a neutral solution of the chloroplatinate precipitate. After the platinum has been reduced to the metallic state, the liberated chlorine is titrated with silver nitrate using dichlorofluorescein indicator (6).

Although the chloroplatinate method is more accurate or at least more stoichiometrically positive than the cobaltinitrite method, the latter may be preferred by many since the cost of chloroplatinic acid may be prohibitive where large numbers of samples are handled. Recovery of the platinum is not completely satisfactory in addition to the further time involved in this step.

Perchlorate. The original perchlorate method for the determination of potassium as introduced by Schloessing (23) and modified by Smith (28) is so familiar that it will be given only passing mention.

Ammonium salts and sulfates must not be present. A little phosphate does no harm, but large quantities produce high results. This need for the absence of sulfates and fairly large amounts of phosphates makes the method a poor one to use in the analysis of synthetic detergents.

A complete bibliography of the perchlorate method, including its shortcomings, is given by Morris (20).

Flame Photometry. Unfortunately, potassium determination of flame photometry (4) leaves much to be desired. Even with the newer apparatus, in which an internal standard, such as lithium, is employed, the results are somewhat erratic. Dilution is necessary so that measurements may be made in parts per million, and since these results may be in error by several parts per million, the final results may show extremely large errors indeed.

Instruments of the internal standard and direct intensity type have been studied quite completely by the authors. The conclusion reached was that the individual instrument is no better than the sensitivity of its photocell and its device for atomizing the sample. Recently others (35) have borne out the inaccuracy of the flame photometer, especially the interference of common metals, acids, and solvents.

It has been reported, however, that a photometric measuring instrument such as that supplied for use with the Beckman Spectrophotometer will produce results of more desirable accuracy (3).

Polarography. One of the newer schemes of instrumentation applicable to the analysis of potassium is the use of the polarograph (32). Good accuracy on samples containing as little as 0.001% potassium is obtainable in the absence of sodium. A c. v. curve is obtained with the sample in an electrolyte of aqueous tetraethyl ammonium hydroxide, and the height of the wave compared with a previously prepared calibration curve.

Discussion

The determination of potassium as periodate, KIO_4, offers a number of attractive advantages. The salt has a high molecular weight; it lends itself well to volumetric determination by a very exact titration of liberated iodine; it is only slightly soluble and contains about the same percentage of potassium as the chloroplatinate and cobaltinitrite. Determinations are sensitive to 0.1 mg. of potassium and may be carried out quite rapidly. Since satisfactory methods are now available for the manufacture of periodic acid, the reagent is comparatively inexpensive and readily available.

The solvent used in the method is that chosen by Willard and Boyle (34). A mixture of ethyl alcohol and ethyl acetate is not oxidized by periodic acid during the time required for the analysis. It is miscible with over 10% of water and dissolves sodium periodate and other salts while leaving the potassium salt completely out of solution.

The reaction used by Willard and Boyle to titrate the periodate was first suggested by Müller and Friedberger (21).

$$IO_4^- + 2I^- = IO_3^- + I_2$$

The reaction is quantitative only in neutral solution, preferably buffered by boric acid-borate. The free iodine is titrated with standard arsenite. The only advantage of this over the proposed method of completely reducing the periodate to iodine is that iodate will not interfere. Müller and Friedberger used this reaction to determine periodate in the presence of iodate. Since precautions are taken in the proposed method to preclude the presence of iodates, there is no reason why the periodate should not be completely reduced and the liberated iodine titrated with thiosulfate. The most obvious advantage is that the sensitivity of the method is increased by a factor of four. The advantage of using thiosulfate rather than arsenite and the elimination of buffers is not to be overlooked.

Experimental

Since the proposed method was to be applied to control laboratory work where many samples would be handled simultaneously, the original method calling for mechanical stirring was impractical. A number of determinations were made to compare the effects of mechanical versus hand stirring (Table I). As a result, hand stirring was recommended and many later observations have borne out the validity of the alternate procedure.

TABLE I

% Na Present	% K Added	% K Found				
		Mechanical Stirring, 30 min.		Hand Stirring, 5 min. Intervals		
		Low Speed	High Speed	30 min.	45 min.	60 min.
10.00	3.00	2.99	2.98	2.99	2.98	3.02
15.00	3.00	2.98	2.99	2.97	3.00	2.99
20.00	3.00	3.01	2.99	3.01	2.98	2.99
5.00	12.60	12.60	12.59	12.60	12.60	12.61
10.00	12.60	12.61	12.59	12.60	12.60	12.61
20.00	12.60	12.61	12.60	12.60	12.61	12.59

Reagents

1. *Periodic Acid.* The reagent must be free of iodic acid and may be tested as follows: Dissolve 0.5 gm. of periodic acid in 25 ml. of water. Add a few drops of N/4 silver nitrate and warm to dissolve the yellowish-brown silver periodate. If iodic acid is present, a white flocculent precipitate of silver iodate will form. The grade manufactured by the G. F. Smith Chemical Company, Columbus, Ohio, was used in all work and showed no trace of iodate.

2. *Solvent.* Mix equal parts of 95% 3A ethyl alcohol and anhydrous ethyl acetate. One gram of periodic acid dissolved in 100 ml. of solvent should show no more than a trace of free iodine after standing at room temperature for one hour. If aldehydes are present in the alcohol, treat it before mixing with the ethyl acetate, by refluxing 2-3 hours over 0.5 gm. of NaOH and 2.5 gm. of $AgNO_3$ per liter. Distill after refluxing.

3. *Sodium Thiosulfate.* 0.1 N standard solution.
4. *Potassium Iodide.* 30% water solution.
5. *Nitric Acid.* C. P., concentrated.
6. *Indicator.* Starch paste.

Preparation of the Sample

Soap. Dissolve 5.000 gm. of soap in warm water, decompose with 20 ml. of 1-3 nitric acid, clear and filter through wet paper into a 250-ml. volumetric flask. Wash with hot water, cool, dilute to mark and remove a 50-ml. aliquot (or one of such size as to contain no more than 30 mg. of K_2O). Evaporate to dryness in a 150-ml. beaker on a steam bath. To the residue add 10 ml. of conc. nitric acid and again evaporate to dryness. Chlorides will reduce periodic acid and must be removed in this manner. If more than traces of ammonium salts are present, the dried nitrate salts should be gently heated over a flame to decompose any ammonium nitrate. The residue should then be treated once more with enough nitric acid to wet the salts and again taken to dryness on the steam bath.

Caustic Lye. Transfer 5.000 gm. of sample to a 500-ml. volumetric flask and make to volume with water. Place an aliquot containing no more than 30 mg. of K_2O in a 150-ml. beaker and neutralize with conc. nitric acid. Evaporate to dryness and treat with nitric acid, taking the same precautions as directed for soap.

Precipitation of KIO_4

To the dried nitrate salts, add *not more than* 5 ml. of water and swirl to dissolve as completely as possible. Add 3 ml. of water (from a small graduate) in which 1.0 gm. of periodic acid has *just* been dissolved. Swirl at frequent intervals for 3 or 4 minutes to permit complete precipitation of the KIO_4. Add 90 ml. of the alcohol-ethyl acetate solvent and allow the mixture to stand in an ice bath for 30 minutes with vigorous hand stirring at 5-minute intervals. Filter through a Gooch crucible and wash with about 50 ml. of anhydrous ethyl acetate at 0°C.

It is essential that the precipitation be carried out as indicated. If the periodic acid is added after the addition of the solvent, the precipitate will be gelatinous and difficult to filter, whereas if it is first formed in aqueous solution, the periodate will be crystalline.

Titration of the Liberated Iodine

Place the crucible and contents in a 250-ml. beaker, add 100 ml. of water and 5 ml. of conc. HCl. With a stirring rod, loosen the asbestos mat and tip the crucible into its side. Add 10 ml. of the 30% KI solution and titrate with N/10 sodium thiosulfate. After some of the iodine color has disappeared, carefully lift the crucible above the liquid with the stirring rod. Rinse it with water from a wash bottle into the beaker and remove it. Continue the titration to the starch endpoint.

Gravimetric Determination of KIO_4

An alternate procedure is to filter the precipitated KIO_4 through a Gooch crucible that has been previously dried at 105°C. and weighed. After washing the precipitate with ethyl acetate as directed, dry for 10 minutes at 105°C. and reweigh.

Calculations

$$\%\ K_2O = \frac{\text{ml. of thiosulfate} \times \text{normality} \times 0.00589 \times 100}{\text{Weight of sample}}$$

$$\%\ K_2O = \frac{\text{Weight of precipitate} \times 0.2047 \times 100}{\text{Weight of sample}}$$

Cooperative Work

Cooperative work has been done to establish the reproducibility of this method. As a result it has been adopted as a standard control method and has shown none of the difficulties usually encountered with new methods, even in the hands of comparatively inexperienced analysts. Table II shows the results obtained by four independent laboratories using the proposed method on three cooperative samples. All laboratories and analysts were completely unfamiliar with the method.

Interferences

Willard and Boyle have shown the effect of the presence of other metals and of free acids. Results are unsatisfactory in the presence of iron, manganese, chromium, rubidium, cesium, and ammonium.

TABLE II

	Sample No. 1	% K$_2$O Sample No. 2	Sample No. 3
Made to contain	2.61	2.61	2.53
Laboratory A	2.62	2.61	2.54
Laboratory B	2.60	2.61	2.50
Laboratory C	2.60	2.58	2.54
Laboratory D	2.61	2.61	2.54

If both calcium and sulfates are present, results may be low as a result of the formation of a double potassium calcium sulfate. It is possible to separate potassium from as much as 70 times as much sodium. Free acids, other than hydrochloric, may be present, but large quantities produce a precipitate that filters only with difficulty. Perchloric acid will produce a precipitate of $KClO_4$ which will not be converted to periodate with 30 minutes of stirring.

The presence of large amounts of glycerine, ethanolamines, and similar organic compounds that may nitrate will interfere with the results. The samples, in such cases, should be prepared by ashing.

Summary

The method of determining potassium as KIO_4, as suggested by Willard and Boyle, has been modified and applied to the analysis of soap and caustic lye. The precipitated periodate is completely reduced, and the liberated iodine is titrated with standard thiosulfate. The determination is sensitive to 0.1 mg. of potassium and the analysis of large numbers of samples may be carried out simultaneously in a relatively short time. This, along with the low cost of the reagents, makes the method applicable to industrial control work. An extensive literature search was made and the complete list of references is included.

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Report of the Color Committee May, 1949

Introduction

THIS report covers work completed since the 1948 report printed in the Journal of the American Oil Chemists' Society, Volume XXVI, No. 2, 45-51, February, 1949. At the meeting of the Color Committee, held in New York in November, 1948, it was decided to continue the investigation of the reproducibility of the Coleman Junior spectrophotometer and to set up a method that could be recommended for adoption by the Uniform Methods Committee of the Society. The work reported herein is aimed at completing this program.

Work Completed

The Committee submitted to 20 collaborators four oil samples and a nickel sulfate solution, together with a proposed spectrophotometric color method. Each collaborator was requested to

1. Follow the method as given, except no dilutions should be made
2. Report both densities and transmissions
3. Be sure the instrument was calibrated exactly
4. Use Type B cuvettes
5. Read oils at 525 and 550 mμ., using CCl_4 as a blank
6. Read nickel sulfate at 400, 470, 510, 525, 550, and 700 mμ., using both water and CCl_4 as blanks
7. Read Lovibond colors on the oil samples.

The data obtained are shown in Tables I, II, and III. Complete spectral information on the four oils is given in Table IV and Fig. 1. The Barrow-Agee laboratories obtained Lovibond red readings on a large number of oils in process and read spectrophotometric transmissions on the same oils at several wavelengths. These data are plotted in Figs. 2 and 3.

Discussion of the Data

A total of 20 sets of samples were sent out to the Color Committee collaborators. Sixteen reported results using the Coleman Junior spectrophotometer and one using the Coleman Universal Model 11. Agreement was generally good except for Laboratory 6, which was extremely erratic on the nickel sulfate solution. Instruments in Laboratories 11 and 19 appear to be out of wavelength calibration. The instrument in Laboratory 12 gave too high results at all wavelengths for some unexplained reason. Laboratory 13 was slightly high because a 20.5 mm. cell was used for all measurements. All of these results (Table II) are excluded, leaving 12 sets of results, which have been assembled in Table I.

While all of the instruments, except the one in Laboratory 15, were supposed to be calibrated against the instrument maker's didymium filter, instruments in 6, 11, 12, and 19 are out of calibration if the nickel