added to distinct alkalinity. From this point on the procedure was identical with the one already described in connection with the determination of gallium in the original solution of gallium chloride. The results are recorded in Tables I and II.

At the completion of the determinations the oxides of iron and gallium were examined spectroscopically[8] with the following results. The oxides of iron, as already mentioned, were invariably found to be free from gallium. The oxides of gallium contained negligible quantities of iron, a fact established by the presence only of the more persistent spectral lines of this element, $\lambda\lambda$ 2382.0, 2395.6, 2596.4 and 2599.4 Å.

Summary

A quantitative method is described for the separation of iron from gallium by means of α-nitroso-β-naphthol.

It is proved spectroscopically that the iron separated by this method is free from gallium.

It is proved spectroscopically that the gallium obtained from such a separation contains negligible traces of iron.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE MOORMAN MFG. CO.]

AN ACCURATE METHOD FOR THE DETERMINATION OF IODINE IN MINERAL MIXTURES[1]

BY M. D. KNAPHEIDE AND ALVIN R. LAMB

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The addition of potassium or calcium iodide to mineral mixtures to be fed to farm animals has made necessary the accurate estimation of iodine in such mixtures, both by the manufacturer and by the feed control chemist. The volatility of iodine under certain conditions, its probable adsorption upon the charcoal which is commonly found in such mixtures and the very small amounts which are permissible, tend to complicate the situation.

Simple extraction methods, using water, alcohol or alkali, were tried by the authors and found to be entirely inadequate. Except in freshly prepared mixtures, less than half of the iodine was recovered by extraction. Using samples of mixtures containing charcoal, it was found that the sum of the iodine in the alcoholic extract and in the residue approximated the total amount present, 40 to 50% of this amount being found in the extract.

Combustion of the sample in a silica tube and determination of the iodine by the method of McClendon[2] or by a combination of this method with

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[8] See Papish and Holt, ref. 4, for the arc spectrographic method employed.

[1] Presented at the St. Louis meeting of the American Chemical Society, April 18, 1928.

[2] McClendon, *J. Biol. Chem.*, **60**, 289–299 (1924).

that of Kendall[3] was laborious and produced rather low results. Fusion of the sample in a special Parr sulfur bomb with sodium peroxide and potassium chlorate, followed by determination of the iodine according to Kendall, gave very low results. Fusion with a mixture of sodium carbonate, potassium carbonate and potassium nitrate in molecular proportions was not satisfactory on account of the high temperature necessary and the short life of the nickel crucible.

Extraction of the sample with sodium hydroxide in aqueous solution, followed by fusion of the evaporated extract with sodium hydroxide in a nickel crucible according to Kendall gave concordant and fairly good but still low results.

Finally the fusion of the original sample with sodium hydroxide and potassium nitrate, followed by a modification of Kendall's procedure was found to yield the most nearly quantitative results. The working out of the proper conditions and the testing of various modifications have involved running several hundred determinations. The method is still rather laborious, but six or eight determinations can easily be completed each day, the entire procedure extending most conveniently over three days. The details of the method and typical results follow.

Twenty grams of sodium hydroxide and 10 g. of potassium nitrate are fused together in a 100cc. nickel crucible. After cooling, a 10g. sample of the mineral mixture is placed evenly on top of the fused alkali and completely moistened with 5 cc. of saturated sodium hydroxide solution and 10 cc. of 80% alcohol. The crucible is then placed on a cold three-heat hot plate and the alcohol evaporated by the low heat. After half an hour the heat is cautiously increased until the crucible has been subjected to the highest temperature of the hot plate for about one and one-half to two hours. Thorough heating at this time prevents most of the trouble from effervescence of the material during the fusion. The crucible is then placed in a crucible furnace or one similar to that used by Kendall and Richardson,[4] which heats evenly both the sides and the bottom of the crucible. An ordinary electric furnace might be used, if it were not necessary to watch and sometimes cool the crucible to avoid bubbling over.

Mineral mixtures containing charcoal will require more attention during the fusion, on account of the violent reaction between the charcoal and the potassium nitrate. There is, however, no loss if the crucible is carefully watched. If the reaction becomes too violent the crucible is lifted from the furnace for a moment, and if necessary the bottom of the crucible is cooled in a beaker of water.

After the mixture is in a quiet state of fusion the crucible is tipped on all

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[3] Kendall, *J. Biol. Chem.*, **43**, 149–159 (1920).

[4] Kendall and Richardson, *ibid.*, **43**, 164 (1920).

sides in an open flame to wash down the sides of the crucible with the fusion mixture. Next a few small crystals of potassium nitrate are added until no more gas is liberated by further additions and the sides of the crucible are again washed down in the flame.

The melt is then poured out into the clean crucible cover to cool or the crucible is turned while cooling so that the material solidifies on the sides of the crucible. The cooled melt and the crucible are placed in a 600cc. beaker, covered with water and heated below the boiling point for a short time. After standing overnight at room temperature, the crucible and cover are rinsed off and removed. In order to neutralize part of the alkali and facilitate filtering, 10 cc. of sirupy phosphoric acid is added and the beaker placed on a steam-bath for about three or four hours with occasional stirring to break up the mass and insure complete solution of the iodine.

The beaker is cooled[5] and the insoluble residue filtered off in a 10cm. funnel and washed with cold water into an 800cc. beaker, adjusting the volume to about 550 to 600 cc. At this time the solution should be clear and colorless.

In order to destroy nitrites, which interfere with the titration with methyl orange, 10 cc. of 20% sodium bisulfite solution is now added, the solution brought just to the boiling point and then cooled. About 30 cc. of 85% phosphoric acid is run in from a buret, a few drops of methyl orange solution added and the addition of phosphoric acid continued to the neutral color of the methyl orange, after which 1.5 cc. of the phosphoric acid is added in excess. The total amount of phosphoric acid required is generally not over 35 cc., except when the presence of considerable charcoal in the sample has necessitated the use of more potassium nitrate, which is thus mainly reduced to carbonate. Care must be taken not to run appreciably over the end-point, since excess acid gives low results. However, the addition of the acid must be fairly rapid, as the color of the methyl orange has a tendency to fade, due to incomplete destruction of the nitrites.

After neutralization, a small lump of anthracite coal[6] (0.5 cm. in diameter) is put in and the solution is boiled for at least twenty minutes, the volume being reduced to about 400 to 500 cc. This length of time is essential in order to remove all traces of sulfurous acid. The solution is cooled again and bromine water added until a distinct and permanent yellow color is produced. The solution is then boiled until colorless by reflected light and then for exactly five minutes longer. A few crystals of salicylic acid are added to assure the removal of the last traces of brom-

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[5] A galvanized iron pan with sides about 10 to 12 cm. high and outlets at different levels is a very convenient means of cooling beakers of solution, which is necessary several times during this determination.

[6] Kendall, *J. Biol. Chem.*, **43**, 151 (1920).

ine, and the solution is cooled, after which 5 cc. of 20% reduced phosphoric acid[7] and 0.5–1.0 gram of chemically pure potassium iodide are added. The solution is then titrated in the usual manner with 0.005 *N* sodium thiosulfate solution, adding starch solution when the brown color of the liberated iodine is nearly gone. The volume of the solution at the final titration should be 400 to 500 cc.

The thiosulfate solution is standardized according to Kendall, by dissolving approximately 1 g. of pure iodine in a liter of 0.5% sodium hydroxide solution. This solution is then diluted ten times, 25 cc. is pipetted into a flask, diluted to 200 cc. and 10 cc. of 30% sodium hydroxide added. The solution is then neutralized with phosphoric acid and the iodine determined as in the method here outlined.

The thiosulfate solution may also be standardized by pipetting into a beaker or flask 25 cc. of a solution containing 0.1308 g. of potassium iodide per liter, adding 200 cc. of water, 5 cc. of 20% sodium bisulfite and 2 or 3 g. of sodium hydroxide. This is neutralized with phosphoric acid, adding 1.0 cc. of the concentrated acid in excess and proceeding further as in the regular determination described above. To calculate the milligrams of iodine to which 1 cc. of the thiosulfate solution is equivalent, the following formula is used

$$\frac{2.5}{\text{cc. of Na}_2\text{S}_2\text{O}_3\text{ soln.}} = \text{mg. I equiv. to 1 cc. of Na}_2\text{S}_2\text{O}_3\text{ soln.}$$

It is well to keep the volume of the solution used in standardization down to about 200 cc. for better and more comparable end-points in the final titration.

TABLE I

ANALYSIS OF MINERAL MIXTURE SAMPLES OF KNOWN IODINE CONTENT

Iodine added, mg.	Recovered, mg.	Remarks	Iodine added, mg.	Recovered, mg.	Remarks
2.0	1.96	10 g. of KNO_3 used	1.0	1.04	10 cc. of $NaHSO_3$ soln.
2.0	2.07	10 g. of KNO_3 used	2.0	1.99	15 cc. of $NaHSO_3$ soln.
2.0	1.97	10 g. of KNO_3 used	2.0	1.93	15 cc. of $NaHSO_3$ soln.
2.0	1.86	10 g. of KNO_3 used	2.0	2.01	15 cc. of $NaHSO_3$ soln.
2.0	1.96	3 g. of KNO_3 used	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	1.96	3 g. of KNO_3 used	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	2.00	3 g. of KNO_3 used	2.0	1.99	20 cc. of $NaHSO_3$ soln.
2.0	1.89	5 cc. of $NaHSO_3$ soln.	2.0	2.01	20 cc. of $NaHSO_3$ soln.
2.0	1.87	10 cc. of $NaHSO_3$ soln.	2.0	2.03	20 cc. of $NaHSO_3$ soln.
2.0	1.87	10 cc. of $NaHSO_3$ soln.	2.0	2.06	20 cc. of $NaHSO_3$ soln.
1.0	1.05	10 cc. of $NaHSO_3$ soln.	2.0	2.02	20 cc. of $NaHSO_3$ soln.
1.0	1.05	10 cc. of $NaHSO_3$ soln.	2.0	2.08	20 cc. of $NaHSO_3$ soln.
1.0	1.02	10 cc. of $NaHSO_3$ soln.			

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[7] Impurities in the phosphoric acid are reduced according to Kendall's method (*J. Biol. Chem.*, **43**, 150 (1920)) by diluting the 85% acid with four volumes of water and boiling for some time with aluminum strips.

The table shows some typical results obtained by this method with samples containing known amounts of iodine. The iodine was added in the form of potassium iodide to samples of mineral mixture containing no iodine or a very slight trace. Blanks were always run on the samples used and on the reagents.

Samples which contain no charcoal or bone meal may be fused with 20 g. of sodium hydroxide alone, omitting the potassium nitrate except for the addition of a few small crystals at the end of the fusion.

Summary

A method is described for the quantitative determination of small amounts of iodine in mixtures of mineral salts, charcoal, spent bone black, etc. The method is a modification of Kendall's and involves fusion with sodium hydroxide and potassium nitrate, removal of interfering substances, oxidation with bromine and determination of the iodine iodimetrically. Necessary conditions are outlined. Other methods were found very unsatisfactory for complex mixtures except when the samples were freshly prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ANTIMONY-ANTIMONY TRIOXIDE ELECTRODE AND ITS USE AS A MEASURE OF ACIDITY[1]

BY E. J. ROBERTS[2] AND F. FENWICK

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Increased realization of the importance of a knowledge of acidity in the control of chemical reactions has aroused a general interest in methods by which the activity of the hydrogen ion may be measured. If we dismiss from consideration the numerous and widely used color indicators, whose applicability rests upon comparative measurements with the hydrogen electrode, the latter at present constitutes by far the most important means of determining acidity. Under strictly defined conditions, it possesses a very high degree of accuracy and reproducibility; the maximum accuracy of the hydrogen electrode is not easy to attain, however, even approximately. The proper functioning of the platinum (or iridium) coating of the electrode is readily affected by traces of many substances not unlikely to be present in the system; reactions catalyzed by the platinum black may affect the hydrogen ion activity of the solution; the necessity of employing a gas phase of known partial pressure of hydrogen is awkward and presents serious difficulties in the investigation of

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[1] From the dissertation presented by E. J. Roberts to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1926–1927.