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THE DETERMINATION OF OXYGEN IN SODIUM

By

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Index No. ORNL-1286
This document contains 28 pages.
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Per Letter Instructions Of Category: Chemistry-General

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THE DETERMINATION OF OXYGEN IN SODIUM

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April 30, 1952

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Abstract

A method has been developed for the determination of sodium monoxide in sodium which depends upon the reaction between sodium and n-butyl bromide in hexane solution. The sodium monoxide does not react with the reagent and can be determined, after the addition of water, by titration. The method is comparatively rapid, requires only the simplest of equipment, and it has the advantage that both oxygen and other impurities can be determined on the same sample.

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THE DETERMINATION OF OXYGEN IN SODIUM

INTRODUCTION

Attention has recently been given to the determination of oxygen in sodium, particularly in low concentrations. At room temperature, oxygen can exist in sodium as sodium monoxide, sodium peroxide, sodium hydroxide, or sodium carbonate. Pepkowitz and Proud[5] have shown that the peroxide and hydroxide are converted to monoxide at higher temperatures and that the carbonate is not present in sodium which has been heated to 400°C or above. Thus, if the sodium to be analyzed is heated above 400°C before sampling, sodium monoxide is the only oxygen-containing compound present and is the only one which will be considered in this report.

The oxygen content of sodium is of interest because of the extreme reactivity of sodium monoxide at elevated temperatures. The oxide reacts with all the common metals (including the platinum group metals), graphite, and ceramic materials, and because of this extreme reactivity, other impurities besides oxygen are often determined in sodium. Ideally, determinations of both oxygen and impurities should be made on the same sample, thus providing a sounder interpretation of data as well as economy of sample.

A method which has been previously developed for this determination is that of Pepkowitz and Judd.[4] Essentially, this method depends upon the extraction of sodium under an inert atmosphere with mercury and the separation of the residual Na_2O, which is insoluble in mercury. With this method, however, it is not possible to determine

oxygen and impurities on the same sample. A modification of the Pepkowitz and Judd method has been reported by Williams and Miller.[6]

The determination of oxygen and impurities on the same sample of sodium and the desirability of improving upon the method of Pepkowitz and Judd in other respects have been considered of sufficient importance to merit a search for an alternate method for this determination. In addition to making possible analyses for oxygen and impurities on a single sample, such a method should, compared with the Pepkowitz and Judd procedure, have the following attributes: (a) require less elaborate and fragile apparatus; (b) depend to a lesser extent on the technique of the operator; (c) yield results of equal or better precision and accuracy; and (d) require the same or less time per determination.

These studies have led to the development of a method which meets the above requirements. It is based upon the fact that n-butyl bromide, C_4H_9Br, reacts with sodium to form the neutral salt, sodium bromide, but does not react with sodium monoxide. Following this reaction, dissolution of the residue in water yields titratable sodium hydroxide (from the monoxide) in a sodium bromide solution. The development of this method has, accordingly, entailed a study of the rate of reaction between n-butyl bromide and sodium and between n-butyl bromide and sodium monoxide.

THE REACTION OF N-BUTYL BROMIDE WITH SODIUM

The Wurtz reaction[1] is a common method for the preparation of paraffinic hydrocarbons from alkyl halides. In this reaction, sodium is used as a coupling agent to link the alkyl groups in an inert, dry solvent, generally ether, as follows:

$$RX + 2Na + R'X = R - R' + 2NaX \qquad (1)$$

This reaction (1) is extremely rapid when R is less than four carbon atoms long. The rate of reaction varies directly with the atomic weight of the halide.

In the Wurtz synthesis, an excess of sodium is always present. A series of tests was conducted to determine whether the reaction proceeds to completion under the reverse of these conditions, that is, when an excess of the alkyl halide is present. Small amounts of sodium were added to large excesses of the halides: propyl, butyl, and amyl chlorides, bromides, and iodides. In all cases, the initial reaction was characterized by rapid formation of a blue crust on the sodium and subsequent evolution of heat. In several minutes, if the crust was left undisturbed, the sodium burst violently with complete conversion to sodium halide accompanied by the evolution of much heat. When the blue crust was disturbed, resulting in the exposure of fresh sodium, a similar violent reaction occurred. The rate of reaction varied little with the halide used, although a somewhat longer time was required in the case of the amyl halides. Various hydrocarbons which are inert with respect to sodium were added to the halides in varying proportions in order to study their effect upon the reaction rate. It was observed that if the boiling point of the added hydrocarbon was

greater than that of the halide, a violent, uncontrollable reaction occurred, especially when the reaction mixture was agitated. This was true even when the proportion of halide was as small as 10 percent by volume. When solvents with lower boiling points than the halide were tested, the reaction proceeded smoothly, without violence, to the complete conversion of the sodium to the halide salt. Hexane (C_6H_{14}, b.p. 67 to 71°) proved to be particularly effective in controlling the reaction rate. It became evident that the reaction is controllable when the boiling point of the solvent is sufficiently low so that the heat evolved by the reaction between halide and sodium is dissipated in boiling away the solvent. When the heat of reaction is great enough to boil the halide, a violent reaction is inevitable.

The selection of a suitable halide was based on availability, ease of drying and preparation, and reaction rate with sodium. According to these criteria, n-butyl bromide, C_4H_9Br, b.p. 101.6^{o}C, is satisfactory. A hexane solution of 40 to 60 volume percent n-butyl bromide gives a suitable reaction with 0.1 to 20 grams of sodium. When the bromide concentration is increased to 80 percent, by volume, all of the hexane is volatilized and the reaction eventually becomes uncontrollable. Concentrations much lower than 20 percent by volume produce too slow a conversion of the sodium to the salt for analytical application.

Studies of the effect of excess butyl bromide over the stoichiometric quantity needed for the sodium taken showed that a five- to seven-fold excess is optimum for less than 5 grams of sodium. For

larger samples a three-fold excess is optimum. In general, when the quantity of bromide is appreciably less than optimum, the time required for complete reaction is of the order of 10 to 15 hours. Greater excesses than the upper optimum value offer little advantage.

THE REACTION OF N-BUTYL BROMIDE WITH SODIUM MONOXIDE

The reactivity of n-butyl bromide with sodium monoxide was studied. Literature sources yielded little information, but it was postulated that the following reactions were possible:

$$Na_2O + C_4H_9Br = C_4H_9ONa + NaBr \qquad (2)$$

$$C_4H_9ONa + C_4H_9Br = C_4H_9OC_4H_9 + NaBr \qquad (3)$$

Reaction (3) represents the Williamson [2] synthesis of ethers whereby an alcoholate and an alkyl halide are caused to react under special conditions to form an ether. In the proposed method, following the reaction of sodium with alkyl halide, the residue of sodium bromide and other products is dissolved in water, and from the basicity of the solution, the monoxide content can be calculated. The formation of any organic compound which yields an equivalent amount of hydroxide upon hydrolysis will not affect the results.

$$Na_2O + H_2O = 2NaOH \qquad (4)$$

$$C_4H_9ONa + H_2O = NaOH + C_4H_9OH \qquad (5)$$

$$C_4H_9OC_4H_9 + H_2O = \text{No reaction} \qquad (6)$$

No oxygen is lost in (5) since it can all be recovered by hydrolysis and a basicity titration. A loss of oxygen would occur, however, if dibutyl ether, which is not hydrolyzed by water, were formed.

To determine the extent of ether formation 10 to 50 mg of sodium monoxide was placed in a solution of 50 percent butyl bromide in hexane and allowed to stand for various periods of time at 60 to 65°C. The conditions of the test were selected to approximate those under which the reaction with sodium is conducted. The residual Na_2O, which was visibly unchanged even after 72 hours contact, was filtered, dissolved in water, and the sodium hydroxide formed was titrated. The results of these tests are shown in Table I.

Table I

Recovery of Sodium Monoxide After Contact with n-Butyl Bromide

Contact Time, Hr.	Sodium Monoxide, mg			
	Added (A)	Found (B)	Difference (B-A)	Recovery Percent
2	13.2	14.0	0.8	106
2	17.5	17.0	-0.5	97
16	20.9	20.7	-0.2	99
16	25.0	25.9	0.9	103
16	48.9	49.0	0.1	100
24	19.6	19.8	0.2	99
24	52.6	52.2	-0.4	99
36	22.2	22.0	-0.2	99
36	21.5	21.3	-0.2	99
36	27.2	26.5	-0.7	97
72	20.7	20.3	-0.4	98
72	34.0	33.4	-0.6	98
72	27.1	26.4	-0.7	98
72	13.3	11.4	-1.9	86

The precision was not as high as might be desired because of the difficulties encountered in the handling of sodium monoxide. The

monoxide was weighed by difference and kept over phosphorus pentoxide to prevent hydration insofar as possible. The reagent when received was 97.5 percent Na_2O and 2.5 percent Na_2O_2. To eliminate the effect of possible changes in the oxide upon standing, however, total basicity determinations were carried out simultaneously with the butyl bromide tests.

On the basis that there was no significant loss of basicity up to 36 hours, the results indicated no formation of dibutyl ether. In only isolated cases was the quantity of base found less than that which was added. However, in all tests when the contact time exceeded 24 hours, the base found was less than that added, although the losses were slight and can hardly be considered significant under the conditions of the tests. No dibutyl ether could be detected in the filtrate.

The possible loss of basicity in the filtrate was checked by titrating the hydrolyzed filtrate. In no case was any basicity found, even for the trials of 72 hours contact. It seems evident that no soluble alcoholate is formed under these conditions.

It may be concluded from these tests that sodium monoxide and 50-percent n-butyl bromide in hexane do not react to lose any titratable basicity over a period of at least 24 hours.

THE METHOD

Description of the Procedure

Ordinarily, samples of metallic sodium are contained in sealed glass tubes or bulbs. The normal procedure is to immerse the container in hexane in a tray or trough and break off and discard the sealed end or ends. The sample can be manipulated into the reaction vessel in such a way that it always remains immersed in hexane. n-Butyl bromide is then added to the hexane covering the sample. In cases, however, in which the sample tubes are sealed with a material which is soluble in hexane, it has been found convenient to break off the ends of the sample tubes under dried and degassed mineral oil and immediately transfer the sample to a tube containing 50 volume percent n-butyl bromide in hexane. The film of mineral oil apparently protects the exposed ends of the sample during this brief exposure to the atmosphere so that no monoxide is formed as a result of the transfer. The sample weight is normally approximately two grams, although it can be from 1 to 20 grams. The reaction is carried out in a 4 x 20-cm tube containing 50 volume percent n-butyl bromide in hexane. For large samples, a proportionately larger tube is used. The density of sodium being greater than that of the reagent solution, the sample sinks to the bottom where it is crushed by means of a heavy glass rod. The reaction soon begins, as is evidenced by the formation of a blue crust on the exposed sodium. The rate

of reaction is increased considerably by exposing fresh surface by mulling the sample with the glass rod. Boiling of the mixture occurs as the reaction proceeds, but at no time does the sodium rise to the surface. The reaction is complete in 1 to 2 hours, especially when the mixture is heated on a sand bath at 60° to 70°C after the start of the initial reaction. The need for the addition of external heat is dependent upon the size of the sample; the reaction of 2 grams of sodium generally supplies enough heat to obviate any external heating. If time permits, the reaction may be allowed to go unattended over-night with no adverse effects.

Upon completion of the reaction, the precipitate of sodium bromide is finely crushed in the reaction mixture with the glass rod to expose any small particles of unreacted sodium to the reagent. It is important that the reaction be complete, since the amount of hydroxide formed upon addition of water to even one small particle of sodium may be large compared with the quantity of monoxide originally present. Water, which has been boiled to expel carbon dioxide, is then added. A two phase system results with the organic layer consisting of excess butyl bromide, hexane, and octane, above the aqueous phase, which is a solution of sodium bromide and sodium hydroxide. The volume of this phase should be of the order of 100 to 200 ml. Although an indicator can be used, the titration with acid is best carried out potentiometrically with a pH meter. A glass electrode which responds satisfactorily in solutions of high sodium ion concentration is used. The amount of basicity found is a direct determination of the oxygen present.

The sample weight is determined by titrating an aliquot of the aqueous phase for bromide content with standard silver nitrate using

eosin as the indicator. Sodium can be calculated from the bromide content of the solution. The sample weight thus obtained is in error by the amount of sodium hydroxide formed, but this error is insignificant and may be disregarded in practically all cases. If the quantity of oxide is significant, it may be added to the sample weight.

The remainder of the aqueous solution, minus the aliquot taken for the bromide determination, is then available for the determination of other impurities besides oxygen.

Purification of Reagents

The success of this method necessarily rests upon the degree to which the reagents can be freed from water and oxygen. Hexane, as the inert diluent, exhibits little tendency to pick up water and the commercial grade is essentially water-free as received. n-Butyl bromide, although immiscible with water, does contain traces of water. These reagents can be successfully dried and maintained in an anhydrous condition for satisfactory periods of time.

Hexane was treated by drying over sodium in the form of ribbon, distilling from this medium, and storing in a dark bottle over sodium. In order to prevent possible oxygen contamination, an atmosphere of oxygen-free argon was maintained in the hexane container. Some lots of hexane were observed to discolor the sodium upon long standing (several weeks). To correct this difficulty, a step to remove unsaturates, by a sulfuric acid wash, was added to the purification procedure. Hexane treated in this manner could be stored for several weeks without evidence of change.

n-Butyl bromide was purified by washing the commercial grade material with concentrated sulfuric acid, to remove unsaturated compounds, until the acid layer was clear. The residual sulfuric acid in the reagent was neutralized with sodium bicarbonate, and the reagent was subjected to a preliminary drying with calcium chloride. It was then distilled and stored in a dark bottle in an oxygen-free argon atmosphere in contact with activated alumina. n-Butyl bromide treated in this manner remained sufficiently dry and free of oxygen for use in the determination for several weeks.

The quantity of water in the reagents following such purification was determined by the Karl Fischer method.[3] The results are given in the following table:

Table II

Water in Purified n-Butyl Bromide and n-Hexane

Material	Water, ppm
n-Butyl bromide	< 2
Hexane	< 2

Modification for Samples in Metal Containers

Attention has been given to the application of this method to samples of sodium contained in metal tubes or cups. It was found by experiment that the action of n-butyl bromide on sodium in such containers is excessively slow, because of the limited surface exposed, and there was some indication that the metal catalyzes the decomposition of the reagent. The technique which proved successful for removing sodium from this type of container, without contaminating the sample, was to submerge the container in an inert liquid and melt out

the sodium by raising the temperature of the liquid. The requirements for such a liquid are: (a) that it be completely inert to Na or Na_2O; (b) that it have a low affinity for water and oxygen; (c) that its boiling point be higher than the melting point of sodium; and (d) that it have a lower density than sodium, in order that the metal remain submerged.

A review of the available information in the literature indicated that some of the paraffinic hydrocarbons probably meet these requirements as well or better than any other readily available compounds, and several of these hydrocarbons were tested. The liquids were purified by washing with concentrated sulfuric acid to remove unsaturated compounds, neutralizing with sodium bicarbonate, and desiccating over sodium in ribbon form. The solvent was then distilled and kept over sodium in dark bottles. Other desiccants used were alumina, calcium chloride, and phosphorus pentoxide.

The water content of hydrocarbons treated in this manner was determined by the Karl Fischer method.[3] The results are given in Table III.

Table III

Water Content of Solvents After Drying Treatment

Material	Desiccant	Water, ppm
n-Hexane	Sodium	<2
"	Phosphorus pentoxide	<2
"	Alumina	<2
"	Calcium chloride	10
Decalin	Sodium	10
"	Phosphorus pentoxide	5
n-Nonane	Sodium	<2
	Alumina	<2
2,2,5 trimethylheptane	Sodium	<2
	Phosphorus pentoxide	<2
	Alumina	<2

In a number of cases, the water content of these liquids was probably considerably less than the lowest figure given, since the limit of determination was of the order of 2 ppm for the size of sample available for this test.

A further test of these dried solvents was made by determining the length of time the surface of molten sodium remained bright in contact with the solvent. When the solvent was decalin, discoloration of the surface occurred after 15 to 20 minutes if the decalin was in contact with the atmosphere. However, if a dry, inert atmosphere was maintained over the decalin, the sodium retained its brightness for nearly 24 hours. n-Nonane and its isomer, 2,2,5 trimethylheptane, proved exceptionally stable and exhibited practically no tendency to absorb moisture or oxygen. Several hours passed before any discoloration of the sodium occurred, and, when a blanket of inert gas was maintained, it was several days before a slight discoloration took place.

These findings indicate that n-nonane and 2,2,5 trimethylheptane can be dried and will remain dry for significant periods of time. Although these solvents cannot replace hexane as a diluent for n-butyl bromide in this method, because of their high boiling points, they are useful when sodium must be melted from metal containers without introducing oxygen contamination.

RESULTS

The procurement of standard samples containing known amounts of oxygen is difficult, if not impossible, because of the extreme reactivity of sodium with oxygen and the tendency of the metal to be heterogeneous with regard to the distribution of the oxide it contains. The range of oxygen concentration of greatest interest extended from 0.001 to 0.1 percent. In an attempt to obtain sodium with an oxygen content in the lower part of this range, the metal was double distilled under high vacuum. Published results for oxygen in sodium prepared in this manner vary somewhat, the general average being about 0.02 percent. The results of determinations on these samples are given in Table IV.

Table IV

Oxygen Content of Double Distilled Sodium

Group	Sodium, Grams	Oxygen, Milligrams	Oxygen, Percent
A	2.103	1.12	0.053
A	2.212	1.15	0.052
B	1.362	0.344	0.025
B	1.340	0.420	0.031
B	0.946	0.166	0.018
B	1.323	0.327	0.025
B	0.895	0.188	0.021

Standard deviation = 0.004 percent.

Other samples containing known amounts of oxygen were prepared by adding known quantities of high purity sodium peroxide, Na_2O_2, to sodium at 300° to 400°C to form sodium monoxide quantitatively:

$$Na_2O_2 + 2Na = 2Na_2O \qquad (11)$$

This reaction proceeds with considerable violence if the temperature is increased rapidly. In the tests performed, however, the use of a sand bath for heating and the high ratio of sodium to sodium peroxide (approximately 100 to 1) decreased the explosion hazard. Mineral oil, previously conditioned by heating under argon to 400°C in contact with sodium, was used as an inert medium for the reaction. Intimate contact between the reactants was found to be necessary to obtain complete reaction. Typical results are shown in Table V.

Table V

Recovery of Known Amounts of Oxygen in Sodium

(Oxygen Added as Sodium Peroxide)

Oxygen, Percent				
Added	Blank*	Total (Blank + Added)	Found	Difference
0.224	0.054	0.278	0.285	+ 0.007
0.101	0.054	0.155	0.158	+ 0.003
0.110	0.054	0.164	0.161	- 0.003
0.218	0.054	0.272	0.282	+ 0.010
0.145	0.054	0.199	0.210	+ 0.011
			Average	0.007

* Average of 3 determinations.

The method was also tested by comparison with results obtained by the Pepkowitz and Judd method. The differences obtained are shown in Table VI.

Table VI

Oxygen in Sodium

Comparison of Results by the n-Butyl Bromide and

The Pepkowitz and Judd Methods

Sample	Oxygen, Percent A n-Butyl Bromide		Oxygen, Percent B Pepkowitz		A - B
1	0.043		0.034		0.009
2	0.012		0.011		0.001
3	0.019		0.025		-0.006
4	0.047		0.043		0.004
5	0.022		0.038		-0.016
6	0.024		0.010		0.014
7	0.017		0.022		-0.005
8	0.028		0.018		0.010
9	0.020		0.025		-0.005
10	0.029		0.018		0.011
11	0.027		0.026		0.001
12	0.028		0.069		
	0.036	0.037	0.037	0.052	-0.015
	0.037		0.049		
13	0.042		0.029		
	0.032	0.034	0.028	0.043	-0.009
	0.030		0.062		
14	0.025		0.010		
	0.031		0.018		
	0.018	0.024	0.021	0.017	0.007
	0.025				
	0.021			Algebraic Sum	0.001

Number of cases in which A > B = 8
Number of cases in which A < B = 6

In another attempt to obtain a series of samples of uniform oxygen content, a cylindrical block, or ingot, of sodium weighing two pounds was sampled and analyzed for oxygen. The block was cut under mineral oil into 14 slices and 3 to 6 samples were taken from each slice. The results are shown in Table VII.

Table VII

Determination of Oxygen in Bulk Sodium - N-Butyl Bromide Method

Section	Oxygen, Percent Sample					
	1	2	3	4	5	6
1	0.033	0.034	0.033	0.033	---	---
2	0.046	0.047	0.048	0.048	---	---
3	0.055	0.048	0.053	---	---	---
4	0.073	0.070	0.081	---	---	---
5	0.055	0.056	0.064	0.047	---	---
6	0.064	0.063	0.067	0.058	---	---
7	0.050	0.060	0.050	0.042	---	---
8	0.042	0.057	0.055	---	---	---
9	0.033	0.067	0.059	0.070	---	---
10	0.052	0.044	0.076	0.049	---	---
11	0.065	0.093	0.076	0.070	0.072	0.073
12	0.063	---	0.052	0.052	0.049	0.055
13	0.038	0.036	0.037	---	---	---
14	0.042	0.032	0.030	---	---	---

A further evaluation of the method has been made on the basis of the results of 31 duplicate determinations, the results of which are shown in Table VIII. These samples were contained in two-bulb glass sample tubes which were filled by drawing molten sodium into the tubes. The designations "upper" and "lower" refer to the position of the bulbs during filling; the sodium entered the tube, passed through the lower bulb and on into the upper bulb. The two bulbs were then separated to provide duplicate samples.

Table VIII

Oxygen in Sodium - Duplicate Determinations

Sample	Oxygen, Percent A Upper Bulb	Oxygen, Percent B Lower Bulb	Difference A-B
1	0.022	0.020	0.002
2	0.024	0.023	0.001
	0.023	0.025	-0.002
3	0.024	0.026	-0.002
4	0.027	0.025	0.002
5	0.025	0.027	-0.002
6	0.024	0.030	-0.006
7	0.028	0.027	0.001
8	0.029	0.029	0.000
9	0.029	0.029	0.000
10	0.027	0.031	-0.004
11	0.026	0.033	-0.007
12	0.030	0.030	0.000
13	0.030	0.030	0.000
14	0.029	0.032	-0.003
15	0.030	0.031	-0.001
16	0.032	0.029	0.003
17	0.035	0.030	0.005
18	0.032	0.036	-0.004
19	0.034	0.034	0.000
20	0.035	0.034	0.001
21	0.035	0.038	-0.003
22	0.038	0.043	-0.005
23	0.047	0.039	0.008
24	0.051	0.039	0.011
25	0.053	0.052	0.001
26	0.055	0.054	0.001
27	0.052	0.064	-0.012
28	0.063	0.057	0.006
	0.052	0.061	-0.009
	0.059	0.052	0.007
		Algebraic Sum	-0.012
		Average Difference	0.003

Number of cases in which A > B = 13
Number of cases in which A < B = 13

Standard Deviation:
Calculated from average range - 0.0030
Calculated from sum of variance - 0.0034

DISCUSSION

The results for the determination of oxygen in distilled sodium (see Table IV) are in the range of those found by previous investigators. The average for five determinations was 0.024 percent. Pepkowitz and Judd[2] found the average of three determinations to be 0.02 percent. In the present case, the sodium was melted under vacuum and filtered by gravity into a flask after which it was distilled twice before being collected in small evacuated glass bulbs. The standard deviation for the results on these samples was 0.004 percent.

The recovery of oxygen added as sodium peroxide provides a check on the method at higher concentrations of oxygen. In general, such high values (see Table III) would rarely be encountered in high grade sodium. The average difference of 0.007 percent is satisfactory under such conditions.

Another test of the present method is a comparison of the results with results obtained on identical samples by the Pepkowitz and Judd method. The differences found are shown in Table VI. It is assumed that the samples were identical with respect to oxygen content. The average difference is 0.008 percent, and in only a few cases was the difference greater than 0.01 percent. In general, there is no indication that one method tends to yield higher or lower results than the other. The fact that both methods yield the same results, on the average, is a confirmation of the accuracy of the n-butyl bromide method, since the Pepkowitz and Judd method is believed to be an accurate one.

For the most part, the precision of the results shown in Table VII for the determination of oxygen in the block of sodium were good with respect to section. The standard deviation was calculated for each set of oxygen values pertaining to the individual sections, and these standard deviations are listed in Table IX. The over-all standard deviation calculated from all the results in Table IX is 0.008 percent. It seems probable, however, that an unusually high degree of segregation was encountered in sections 9, 10, and 11. If the results for these sections are disregarded, the standard deviation becomes 0.005 percent.

Table IX

Standard Deviation of n-Butyl Bromide Method For The Determination of Oxygen in Sodium

Section	Number of Determinations, N	Average, Percent	Standard Deviation, S
1	4	0.033	0.001
2	4	0.047	0.001
3	3	0.052	0.004
4	3	0.075	0.006
5	4	0.055	0.007
6	4	0.063	0.004
7	4	0.051	0.005
8	3	0.051	0.008
9	4	0.057	0.016
10	4	0.055	0.014
11	6	0.075	0.009
12	5	0.054	0.005
13	3	0.037	0.001
14	3	0.034	0.006

The standard deviation for the results of duplicate determinations listed in Table VIII is 0.0034 percent. The precision in this case was better than for any of the other results reported. The probable explanation is that the precision of the method is actually as good as is indicated and that the poorer precision observed for the other tests is a result of sample heterogeneities. It should be pointed out, however, that the duplicate determinations listed in Table VIII were made at the same time, side by side; such a procedure often effects an improvement, which is actually ficticious, in the apparent precision of a method. The question has often been raised as to whether the method of sampling employed in this case results in the segregation of sodium monoxide. It is evident from the data in Table VIII that there was no consistent tendency toward segregation; both upper and lower sample bulbs contained, on the average, the same quantity of oxide.

The results of the several series of tests which have been made indicate that the standard deviation of the present method is in the range 0.003 to 0.005 percent, which compares well with that for the Pepkowitz and Judd method. The reported mean deviation for the latter method is 0.005 percent,[2] which corresponds to a standard deviation of 0.006 percent.

The precision of the n-butyl bromide method may in fact be better than is indicated by the calculated standard deviation, owing to the difficulty in separating the effects of analytical errors from variations in results which represent real differences between supposedly identical samples.

The results obtained demonstrate that the precision and accuracy of the present method is satisfactory for samples of sodium containing more than 0.02 percent oxygen. Because of the lack of samples of suitably low oxygen content, the method has not been sufficiently investigated with respect to lower ranges of oxygen concentration. With this method, however, samples as large as 20 grams can be used, and no great difficulty is anticipated in the determination of oxygen concentrations down to 0.001 percent.

SUMMARY

A method has been developed for the determination of sodium monoxide in sodium which depends upon the reaction between sodium and excess n-butyl bromide in hexane solution. Sodium monoxide does not react with the reagent and can be determined, after the addition of water, by titration. Compared with the Pepkowitz and Judd method for the same determination, the present method has the advantage that both oxygen and other impurities can be determined on the same sample. In addition, the n-butyl bromide method requires only the simplest and most readily available equipment, and is easily adaptable to the analysis of large numbers of samples. The standard deviation of the method is 0.003 to 0.005 percent.

It has been shown that there is no reaction between n-butyl bromide and sodium monoxide which results in a loss of titratable basicity for periods of contact of at least 24 hours. Oxygen added to sodium in the form of sodium peroxide was recovered quantitatively, within the limits of error of the experiment.

This method is particularly suitable for application to samples of sodium in glass containers, although it can also be used for samples in metal containers. Although the determination of oxygen in the range 0 to 0.02 percent has not been sufficiently investigated, it is expected that the method will be applicable in this range if large samples are taken. A 2-gram sample is ordinarily used, but 20-gram samples present no difficulty.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of Mr. C. D. Susano and Mr. L. J. Brady, who made helpful suggestions, and of Mr. L. H. Jenkins and Mr. C. L. Stringfield, who performed a number of the determinations.

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