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**GLOVEBOX AMALGAMATION FOR THE
DETERMINATION OF OXYGEN
IN ALKALI METALS**

by

Ben D. Holt

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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SUMMARY

The use of a new type of amalgamation vessel for the determination of oxygen in sodium and potassium is described. The metal is amalgamated immediately after sampling inside a helium-filled glovebox, thereby terminating the risk of significant oxygen contamination by subsequent handling and exposure to the glovebox atmosphere. End-point sensitivity is enhanced by titrating the oxide residue in the same vessel, thus avoiding dilution by wash water that would be required in the transfer to a titration flask. The described technique yielded generally lower and more reproducible values in the low-ppm range than did the older, vacuum-line, amalgamation procedures.

INTRODUCTION

In early versions of the apparatus used for the determinations of oxygen in alkali metals by the amalgamation method, the extraction chamber was stationary and was permanently attached to a supply of mercury, a source of purified inert gas, and a vacuum line for the duration of the extraction.^{1,5,6} Goldberg² used a reaction chamber that could be detached from the rest of the system. His model could be loaded with a freshly-cut sample inside a glovebox, and, after connection to the vacuum line for the addition of mercury, could again be detached for manual shaking to ensure rapid and complete amalgamation.

By a later approach to the method, the entire mercury extraction is carried out inside the glovebox in which the sample is prepared.³ Sources of sample contamination that may arise from handling in vacuum systems, such as the degassing of container walls and the minute leaks of moisture and/or air through freshly-prepared stopcocks and glass (or O-ring) joints, are thereby avoided.

This report describes a newly-designed, greaseless, extraction bottle that has been tested for the glovebox amalgamation procedure and discusses the results obtained in the analysis of sodium and potassium,

as compared to results obtained by the vacuum-line procedure. The newer technique yielded generally lower and more reproducible values for oxygen concentrations in the low-ppm range.

APPARATUS

The apparatus consisted of a 90-ml extraction bottle (Fig. 1), supplementary glassware for handling the extracted amalgam, a glovebox of low moisture concentration, and the necessary equipment for titrating the alkali oxide after extraction.

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Fig. 1. Extraction Bottle

The neck of the extraction bottle was made of an outer, standard-taper joint so that an inner joint could serve as a vent and spatter chimney during the initial amalgamation. Each bottle and stopper were matched before use (by lightly grinding with a water-suspended, fine abrasive) to avoid the danger of harboring particles of amalgam within the ground surfaces of the joint during mercury washings.

It was important that the heavy-walled spout on the extraction bottle have an inside diameter no less than 3 mm, which tapered abruptly down to 1 mm at the end. Fabrication was best accomplished by thickening the 3-mm-ID tubing to about 1 mm or less, and then sawing the tubing in two at the point of 1-mm diam. The drain rate of mercury from such a bottle was about 20 ml/min. The 1-mm orifice caused a slug of mercury about 10 mm high to remain in the spout, even when the bottle was tilted to the vertical position of the spout and held until no further drainage occurred.

A glass-stoppered, 250-ml bottle was used inside the glovebox to collect the drainings from the initial extraction and subsequent washings. Outside the glovebox, this amalgam was emptied into an excess of standard 1N HCl solution in a 1-liter flask for back-titration with standard 1N NaOH solution to determine the sample size.

The glovebox contained helium, which was continuously circulated through a charcoal-bed cold trap that held the moisture content down to about 15 ppm and the oxygen to about 5 ppm. A transfer chamber that could be evacuated was attached to the box for introducing and withdrawing samples, mercury, and glassware. The oxygen concentration of the helium was determined by a mass spectrometer, and the moisture concentration by a moisture monitor, Model 2G-303ME, manufactured by Consolidated Electrodynamics Corp., Pasadena, California.

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Fig. 2. Steps of the Procedure

PROCEDURE

Figure 2 illustrates the essential steps of the procedure.

Preparation

Place in the transfer chamber an adequate supply of clean, dry mercury, the necessary tools for cutting sodium samples, and six or less of each of the following: extraction bottles with matching glass stoppers, $\text{T } 27/21$ inner joints, and 250-ml drain bottles. Evacuate the transfer chamber for 1 hr, and then move the equipment into the glovebox.

Amalgamation

Pour 50 ml of mercury into each extraction bottle, and insert a chimney tube in the $\text{T } 27$ joint. Prepare a clean-surfaced sample of sodium (about 2 g), and drop it immediately through the chimney into the mercury. Swish the mercury around on all sides of the bottle (not up into the chimney) several times to ensure an immediate and complete amalgamation. (A delay in this step may lead to the rapid formation of a solid phase, on the surface of the mercury, that is difficult to break up for complete liquid solution.) Let the solution set for 10 min.

Extraction

Empty the amalgam through the spout of the extraction bottle into a 250-ml, glass-stoppered bottle. The 1-mm orifice of the spout causes a slug of mercury to remain in the 3-mm section, thus retaining in the bottle the micro quantity of extracted, solid oxides. Rotate the bottle to its upward position, allowing the mercury slug to fall back inside. Replace the chimney with a matched glass stopper, being careful not to entrap droplets of amalgam in the ground-glass surfaces of the joint.

Add 10 ml of mercury from a supply of 40 ml, measured out in a pharmaceutical graduate. Place a loosely-fitting, $1/2$ -in.-long, soft, rubber bulb (cut from the end of a medicine-dropper bulb) over the end of the spout; grasp the bottle in one hand in such a way as to hold the rubber wall of the bulb firmly against the 1-mm orifice and to hold the glass stopper in place; thoroughly shake the bottle several times. (Vigorous shaking is necessary to thoroughly wash the inside surfaces of segments of stainless-steel tubing, if such segments have been used to enclose the alkali-metal sample.) Lift the stopper slightly to provide vent; remove the rubber cap, carefully avoiding loss of the mercury that may be lodged in the spout; and drain the mercury through the spout into the 250-ml amalgam bottle. Repeat the steps of this paragraph three times.

Titration

Replace the rubber bulb on the spout of the stoppered extraction bottle, and move both the extraction bottle and the stoppered amalgam bottle out of the glovebox. Using a wash bottle containing freshly-boiled, distilled, deionized water, immediately direct a squirt of water through the spout into the extraction bottle (with the glass stopper loosened to provide vent), and attach a clean, rubber hose to the spout to direct a stream of CO₂-free nitrogen into the bottle. With a minimum amount of water from the wash bottle, rinse the bottom surface of the glass stopper and the inner walls of the extraction bottle. Add a drop of phenolphthalein solution, and titrate with standard 0.01N HCl solution.

RESULTS AND DISCUSSION

Samples of sodium and potassium were analyzed both by the present technique and by that described by Goldberg.² Table I compares the results on fresh-surfaced sodium samples, carved from two 1-lb chunks (A and B)

TABLE I. Comparison of Oxygen Results on Carved, Reagent-grade Sodium

Material	Procedure					
	Glovebox Helium		Present		Goldberg ²	
	Moisture, ppm	Exposure, min	Weight, g	Oxygen, ppm	Weight, g	Oxygen, ppm
Sodium (A)	30 ^a	10	3.2	7		
Sodium (A)	30 ^a	10	3.4	4	2.4	25
Sodium (A)	30 ^a	10	2.1	5	2.5	12
Sodium (A)	30 ^a	10	1.7	6	2.0	74
		70	2.1	7	2.4	34
		145	2.0	32	2.5	91
		205	1.5	74	2.1	111
		265	1.8	107		
		325	2.0	361		
Sodium (B)	15 ^b	10	1.6	6	1.6	6
		70	1.3	10	1.5	46
		130	1.7	22	1.3	58
		190	1.7	28	1.5	61
		250	2.0	51	1.4	144
		310	1.5	51	1.5	258

^aEstimated. The flow rate through the moisture monitor had not been calibrated.

^bMeasured by a CEC, Model 26-303ME, moisture monitor at prescribed flow rate.

of reagent-grade metal supplied by General Chemical Division of Allied Chemical, Morristown, New Jersey. After the data listed on the first three

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Fig. 3. Sample Contamination vs Time of Exposure to Glovebox Helium

lines of Table I (analyzed on separate days) were obtained, two series of several samples each were analyzed some weeks apart. For each series, the samples were cut into separate pieces within a few minutes, and then, on each succeeding hour, one piece was dropped into the mercury in an extraction bottle of the present technique, and one was sealed in a reaction chamber of the design used by Goldberg. Figure 3 shows the concentrations of oxygen plotted against time of exposure to the glovebox helium for the two series of samples. A fairly smooth variation of oxygen concentration versus time of exposure was indicated in both series by the present procedure; the vacuum-line technique yielded generally higher and more erratic values over the observed range of time. The lower rate of contamination appearing in the series of analyses of chunk B was apparently due to a lower moisture content of the helium. The higher values obtained by the older procedure were not necessarily assumed to be in error, although the available sources of contamination and the time of exposure to such sources were significantly greater than those for the procedure of immediate amalgamation, by which the reactivity of the alkali metal to the environmental oxygen and moisture was essentially terminated.

In accordance with common practice in the use of this method, the results were calculated on the basis that all the oxygen was present as the alkali-metal oxide, M_2O . Certainly, if most of the contamination had been present as MOH , the reported results are low by a factor of 2.

Table II compares values of oxygen found in sodium and potassium samples (C, D, and A), all of which were contained in segments of stainless-steel tubing that were cut from longer sections of alkali-metal-filled tubing with a metal-tubing cutter. The better agreement of results, obtained by the two techniques, shown in Table II, compared to Table I, may be attributable to better protection of the samples, by the stainless-steel tubing, between the time of sampling and the time of amalgamation.

A simple test of the efficiency with which floating, finely-divided powder is separated from mercury, by draining from the extraction bottle through the spout orifice, was made by adding a few milligrams of talcum powder and 50 ml of mercury to such a bottle and following the prescribed

steps of the procedure. Even though the bottle remained "loaded" with powder, the scant, visual evidence of powder on the mercury collected in the drain bottle indicated that the loss by entrainment was probably less than 5%, which is an insignificant error in low-ppm data.

TABLE II. Comparison of Oxygen Results on Sodium and Potassium in Sections of Stainless-steel Tubing

Material	Glovebox Helium		Procedure			
	Moisture, ppm	Exposure, min	Present		Goldberg ²	
			Weight, g	Oxygen, ppm	Weight, g	Oxygen, ppm
Sodium (C)	15	10	0.96	60	0.91	407 ^a
		10	0.89	70	0.96	113
Sodium (D)	11	5	1.3	11	1.3	11
	13	5	1.4	10	1.3	12
	15	5	1.2	11	1.8	32 ^b
Potassium (A)	18	5	1.1	16	1.4	14
	18	5	1.1	11	1.2	30 ^b

^aLeak developed in stopcock during analysis.

^bOne of the end segments of the stainless-steel tubing.

It was not convenient to make alkalinity tests on the mercury washings that followed the initial amalgamation and extraction of every analysis. Reliance was placed upon preceding experiments that confirmed that the four 10-ml mercury washes were sufficient to remove all of the original alkali-metal sample from the extraction bottle.

The curves in Fig. 3, showing the effect of the duration of sample exposure to the glovebox atmosphere, indicate that during the first few minutes, the gas contaminants in the helium had a negligible effect on the oxygen results (even though the helium was of mediocre purity) with respect to moisture. By extrapolation to zero time of exposure, it may be observed that the "true" oxygen content was only one part per million, or so, below that measured when the sample was exposed for 5 to 10 min to helium containing about 15 ppm of water.

Although the purpose of this experimentation was not to study the mechanism of oxidation of the metal by the oxygen-bearing contaminants of the glovebox helium, it may be of interest to note that the rate of oxidation appeared to increase with time, as well as to exhibit a dependence on the moisture content of the helium. This phenomenon may indicate that a rate-determining factor to oxidation is the magnitude of the effective

surface area, which is continually increased by the growth of a reactive hydroxide (or oxide) layer. Such a mechanism has been attributed by Kofstad to a similar pattern of oxidation of tantalum by oxygen (0.001 to 1 Torr) at 1400°C.⁴

The chief advantages of the new extraction bottle are (1) it has no stopcock or greased joint to provide a grease film that may harbor alkali-rich amalgam particles; (2) it is compact and easily handled through a vacuum transfer chamber, so that a group of about six bottles can be processed together through the procedure; and (3) it serves well as the air-free titration vessel, thus conserving wash water (that would otherwise be needed for transfer to another vessel) and leaving the aqueous volume at a minimum to enhance the sensitivity of the end point. Six analyses could be completed in one day.

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