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A METHOD FOR THE QUANTITATIVE ANALYSIS OF THE SILVER OXIDE CATHODE

23 June 1965

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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This report presents a method to analyze quantitatively the mixtures of silver oxides and silver metal that occur in the silver oxide cathode. Verification of a reaction between argentic oxide and silver metal in the dry state is also presented. This work was performed under Task RUTO 3E000/217.

The results should be of interest to manufacturers and users of silver oxide-zinc batteries.

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A Method for the Quantitative Analysis of the Silver Oxide Cathode

Prepared by:
Regina D. Wagner

ABSTRACT: A method has been developed to quantitatively analyze mixtures of the silver oxides and silver metal such as occur in the silver oxide cathode of primary and secondary alkaline silver-zinc batteries. The detailed procedure is given and data verifying its accuracy presented. The occurrence of a reaction between argentic oxide and silver metal is also verified.

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A Method for the Quantitative Analysis of the Silver Oxide Cathode

This report presents a method to analyze quantitatively the mixtures of silver oxides and silver metal that occur in the silver oxide cathode. Verification of a reaction between argentic oxide and silver metal in the dry state is also presented. This work was performed under Task RUTO 3E000/2121/F008-06-02, PA 217.

The results should be of interest to manufacturers and users of silver oxide-zinc batteries.

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INTRODUCTION

The silver oxide cathode at various states of charge and discharge contains argentic oxide (AgO), argentous oxide (Ag_2O), and silver metal.[1] At certain stages, all three components are present simultaneously. At the maximum state of charge obtained by Wales[2], the presence of silver metal as well as argentic oxide was shown by X-ray diffraction.

Many methods have been proposed for determining the percentages of silver oxides and silver in the silver oxide cathode. Two of the most notable involve X-ray diffraction and thermogravimetric analyses. The analyses obtained by X-ray diffraction techniques are empirical and have an inherent inaccuracy of approximately 5% for that component which is present in the greatest quantity in the sample. The proposed thermogravimetric method of analysis[3] was shown to be unsuitable for the analysis of silver and its oxides, due to the simultaneous decomposition of argentic and argentous oxides.[4]

DISCUSSION

The method presented herein utilizes wet chemical techniques to analyze homogeneous mixtures of silver and silver oxides. The procedure consists of two steps. The first step involves the determination of the metallic silver and the silver present in the oxides. The second step involves the determination of the oxidizing power of another portion of the mixture. From these data the composition of the mixture is calculated. (Appendix A)

Each of these steps should be carried out in duplicate. Therefore, for the analysis of one mixture, a minimum of four portions are required, and it is necessary to have a mixture which is as homogenous as possible. Vigorous grinding or milling must be avoided because this alters the composition. Two reactions which may occur on grinding are: (1) thermal decomposition of argentic oxide due to locally generated heat; and (2) reaction between argentic oxide and silver metal to form argentous oxide. The latter reaction will be discussed later.

In the determination of silver metal and total silver in the oxides (Step I), the oxides of silver are dissolved in ammonium hydroxide to form a soluble silver amine complex. The metallic silver remains as a solid phase and the solution containing the dissolved oxides is separated from it by filtration. The silver amine complex is unstable and explosive and, for this reason, the filtrate is collected in dilute nitric acid, thereby instantly decomposing the unstable complex.

The oxidizing power of the sample (Step II), is determined by a modification of the iodometric method developed by Jirsa.[5] When the **mixture** is treated with a saturated solution of potassium iodide, iodine is liberated due to the oxidation of the iodide by the argentic oxide according to reaction (1); and the argentous oxide reacts with the iodide according to reaction (2).

(1) $AgO + 3I^- + H_2O \longrightarrow AgI_2^- + 1/2I_2 + 2OH^-$

(2) $Ag_2O + 4I^- + H_2O \longrightarrow 2AgI_2^- + 2OH^-$

In the resultant basic solution the iodine reacts according to reaction (3) and a nearly colorless solution results.[6]

(3) $I_2 + OH^- \longrightarrow HOI + I^-$

However, upon acidification, the iodine is again liberated.

The silver metal present in the **mixture** is oxidized by the iodine according to reaction (4).

(4) $Ag^\circ + 1/2I_2 \longrightarrow AgI$

Reaction (4) is quantitative when the concentration of potassium iodide is high enough to keep all the silver iodide dissolved (Appendix B). If the silver iodide is not in solution, a protective coating of the iodide forms on the silver metal particles and reaction (4) does not go to completion.

The silver metal oxidation must take place quantitatively if the determination of the oxidizing power of the **mixture** is to be accurate. The addition of a wetting agent, such as Sterox, increases the rate at which the silver metal oxidation occurs.

ANALYTICAL PROCEDURE

Reagents. Use nitric acid, hydrochloric acid, sulfuric acid and ammonium hydroxide which are analytical quality reagents, and potassium iodide which is iodate free analyzed-grade reagent.

Prepare a 0.1-N sodium thiosulfate solution by adding 25 g. reagent grade sodium thiosulfate crystals to 1 liter of freshly boiled distilled water containing 2-3 g. borax crystals as a preservative. Standardize this solution with pure potassium iodate.

Prepare a 0.1-N iodine solution by adding 6.5 g. of resublimed iodine to 500 ml. of distilled water containing 12 g. of potassium iodide. Standardize this solution just prior to or immediately after its use.

Prepare a Sterox solution by adding approximately 0.5-1.0 ml. Fisher 1% Sterox solution to 500 ml. distilled water.

Sample Preparation. Wrap the cathode in an envelope of glassine paper and work the active material loose from the grid. Transfer the silver-silver oxide mixture into an agate mortar and break the agglomerates by gentle crushing with an agate pestle. Transfer the sample to a small glass container with a tight fitting cap and shake vigorously to thoroughly mix the sample. The mixture should be shaken prior to the removal of each aliquot to preserve the homogeneity of the sample.

It is not necessary that the sample be moisture free prior to analysis, since the determination of the silver containing components is not affected by the presence of water and the amount of impurities and moisture can be obtained later by difference. However, the sample must be dry enough for the accurate determination of weight. When the cathode is removed from an activated battery, i.e., one containing electrolyte, the plate should be rinsed thoroughly with distilled water and dried to a constant weight in an evacuated desiccator over a suitable desiccant. Do not dry the sample above room temperature because the argentic oxide slowly decomposes.

Step I. Weigh a 0.25-0.4 g. aliquot of the sample directly into a 30 ml. fine porosity filter crucible, which has previously been brought to a constant weight. Seat the crucible above a 500 ml. filtering flask containing 10 ml. 1:1 HNO_3 in a manner which permits the quantitative recovery of the filtrate (Figure 1). Slowly pour 15 ml. of 1:30 NH_4OH into the crucible and allow the mixture to stand while the oxides of silver dissolve. After approximately 1/2 hour, apply a gentle suction to the filtering flask and remove most of the NH_4OH solution from the crucible. Slowly pour another 15 ml. of 1:20 NH_4OH into the crucible and allow the mixture to stand for an hour. The solids in the crucible should be stirred with a stream of distilled water occasionally to facilitate the dissolution of the silver oxides. (Caution: Do not stir the mixture in the crucible with a stirring rod; this may cause an explosion of the silver amine complex. The removal and replenishment of the NH_4OH solution should be continued until all the silver oxides have dissolved. Two 15 ml. portions of the NH_4OH solution should be sufficient for dissolving the oxides in most samples, however, when the sample contains large amounts of Ag_2O, additional quantities of

NH_4OH solution are required.) When the silver oxides have dissolved, wash the silver metal in the crucible twice with 10 ml. of 1:20 NH_4OH and several times with distilled water. Dry the crucible to a constant weight and determine the weight of the silver metal by difference.

Quantitatively transfer the filtrate to a 400 ml. beaker. The solution should be acidic; if not, acidify with 1:1 HNO_3. Add 2 ml. of concentrated HCl to precipitate the silver as silver chloride. Heat the suspension nearly to boiling and then allow it to stand in the dark for a minimum of 1 hour. Collect the precipitate quantitatively in a previously weighed fine porosity filter crucible. Dry the crucible to a constant weight and determine the weight of the silver chloride.

Step II. Weigh a 0.25-0.4 g. aliquot of the sample into a 100 ml. volumetric flask. Add 10 g. of potassium iodide and rinse down the sides of the flask with approximately 5 ml. of Sterox solution. Swirl the flask until all the black silver oxide powder has dissolved. Add 10 ml. of 1-N H_2SO_4 and swirl the flask in subdued light for about 3-5 minutes to allow the oxidation of the silver metal to silver iodide to occur.

Begin the addition of $Na_2S_2O_3$ titrant. Stop the titration prior to its completion and examine the solution to determine if all the silver metal has been oxidized. If particles of silver metal can be seen on the bottom of the flask, swirl the flask until they are dissolved and then continue the titration until one drop of titrant removes the iodine color.

If the number of milliequivalents of silver metal present in the sample is greater than or equal to the number of milliequivalents of AgO, it will be necessary to pipet a known volume of the standardized 0.1 N iodine solution into the flask. If silver metal remains unoxidized when the iodine color becomes pale, the addition of iodine is necessary. When iodine solution is added to the unknown, an additional quantity of KI (approximately 5 g. KI for each 10 ml. of iodine solution) must also be added in order to keep all of the AgI in solution. The iodine can be added at any stage in the above procedure after the silver oxides have dissolved.

Because of the air oxidation of KI in acid solution, the volume of $Na_2S_2O_3$ used must be corrected for the volume necessary to titrate a blank. A blank should be run with each of the duplicate analyses.

VERIFICATION OF THE ANALYTICAL PROCEDURE

The accuracy of the analytical procedure was determined by analyzing known mixtures of the three components: AgO, Ag_2O, and Ag. The argentic oxide used was supplied by the Power Sources Division of Whittaker Corporation and contained 97.38% AgO and 2.60% Ag_2O as determined by analysis for oxidizing power by the method of Jirsa[5] and for total silver content by gravimetric chloride. The argentous oxide and the silver metal (Silpowder 120) were supplied by Handy and Harman and were each analyzed for total silver and for weight loss on heating at 500°C. Each sample was found to contain less than 0.1% impurities.

Neither of the oxides contained any silver metal impurity as demonstrated by complete solubility in 1:20 NH_4OH. The silver metal sample had no silver containing impurities soluble in 1:20 NH_4OH. Neither the argentous oxide nor the silver metal contained any impurity which oxidized iodide to iodine.

Experimental. In order to determine whether the described analytical procedure could be used to analyze quantitatively for each of the silver containing components in the presence of the other two, the following experiments were performed: Portions of AgO, Ag_2O and Ag^o were individually weighed directly into a filtering crucible. This mixture was then analyzed according to the procedure outlined under Step I. Identical portions were also weighed directly into a flask and analyzed according to the procedure outlined under Step II. Repetitive analyses of aliquots of samples prepared by thoroughly mixing weighed quantities of AgO, Ag_2O and Ag^o were made according to the procedures outlined under both Steps I and II.

Results and Discussion. The results of the analyses of several known mixtures according to Step I are given in Table I. These results show that the silver metal content and the total silver content of the oxides can be determined by this procedure with an accuracy of 0.5%. The results of the analyses according to Step II are shown in Table II. These results show that the argentic oxide present can be accurately determined in the presence of both argentous oxide and silver metal when the silver metal content of the sample is known.

In order to test the precision of the method, known amounts of AgO, Ag_2O and Ag^o were thoroughly mixed to obtain a homogeneous sample. The results of three separate analyses of aliquots of this sample are given in Table III and show that the precision is acceptable.

During the preparation of known mixtures it became apparent that analyses of some mixtures changed during the mixing process. In mixtures containing both AgO and Ag^o the amount of these two components decreased during mixing and the amount of Ag_2O increased. Mixtures containing only Ag_2O and Ag^o or only AgO and Ag_2O showed no change in composition during mixing. These observations suggested that reaction (5) occurs

$$(5) \quad AgO + Ag^o \longrightarrow Ag_2O$$

The data in Table IV show that this reaction proceeds quantitatively. It is interesting to note that the extent of this reaction during 104 days stand at room temperature was approximately equal to that which occurred during 48 hours of mixing at room temperature. As a further check on the validity of reaction (5) the AgO and Ag^o that were mixed as shown in Table IV were analyzed by X-ray diffraction. Neither component showed any detectable amount of Ag_2O. The X-ray diffraction pattern of the sample after 48 hours of mixing did show the presence of approximately 30% Ag_2O.

The occurrence of reaction (5) in the silver oxide-zinc battery was first suggested by Denison[7] and has been mentioned many times by other workers. However, no proof that this reaction occurs in dry samples has been presented prior to this work.

SUMMARY

An analytical procedure for determining the composition of a sample containing both oxides of silver and silver metal has been developed.

By use of the analytical procedure, we have shown that a reaction occurs between argentic oxide and silver metal in dry samples.

This method will serve as a useful tool in the study of the silver oxide cathode which is of special interest due to its widespread use in high energy density batteries for missiles and spacecraft.

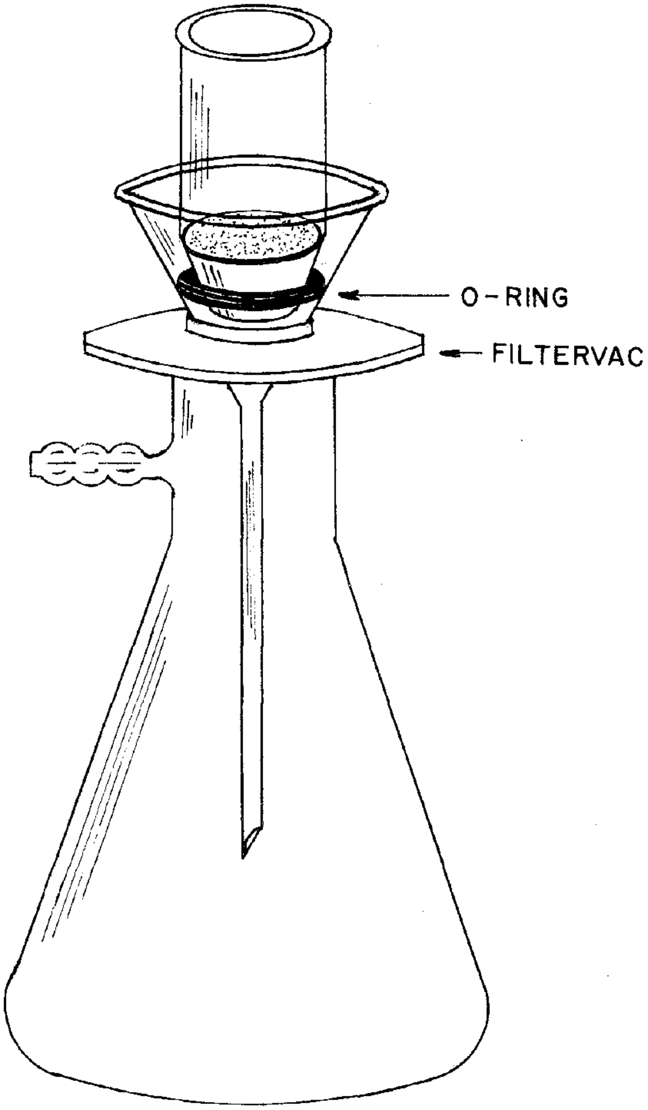

FIG. I APPARATUS FOR QUANTITATIVE RECOVERY OF THE FILTRATE

TABLE I.

Results Indicating the Accuracy of Step I

Sample Composition	Ag° Determined	Error	Ag in Oxides Calculated	Ag in Oxides Determined	Error
Wt.AgO: - - - Wt.Ag_2O:0.1341 g. Wt.Ag°:0.3830 g.	0.3825 g.	-0.13%	0.1248 g.	0.1246 g.	-0.16%
Wt.AgO:0.0938 g. Wt.Ag_2O:0.0586 g. Wt.Ag°:0.1836 g.	0.1828 g.	-0.43%	0.1362 g.	0.1358 g.	-0.29%
Wt.AgO:0.0864 g. Wt.Ag_2O:0.0528 g. Wt.Ag°:0.1470 g.	0.1463 g.	-0.47%	0.1243 g.	0.1246 g.	+0.24%
Wt.AgO:0.0774 g. Wt.Ag_2O:0.0679 g. Wt.Ag°:0.1973 g.	0.1967 g.	-0.30%	0.1306 g.	0.1311 g.	+0.38%

TABLE II.

Results Indicating the Accuracy of Step II

Sample Composition	Meq. I_2 Found	Meq. I_2 used by the Ag°	Wt. AgO Determined	Error
Wt.AgO:0.3941 g. Wt.Ag_2O:0.0107 g. Wt.Ag°: - - -	3.1853 meq.	- - -	0.3946 g.	+0.13%
Wt.AgO:0.3323 g. Wt.Ag_2O:0.0643 g. Wt.Ag°: - - -	2.6819 meq.	- - -	0.3322 g.	-0.03%
Wt.AgO:0.2999 g. Wt.Ag_2O:0.0081 g. Wt.Ag°:0.0384 g.	2.0648 meq.	0.3560 meq.	0.2999 g.	0.00%
Wt.AgO:0.2991 g. Wt.Ag_2O:0.0080 g. Wt.Ag°:0.0356 g.	2.0824 meq.	0.3300 meq.	0.2988 g.	-0.10%

TABLE III.

Results Indicating the Precision of the Method

Aliquot	AgO	Ag_2O	Ag°
No. 1	29.8%	55.1%	14.2%
No. 2	29.8%	55.4%	14.0%
No. 3	29.6%	55.0%	14.2%
Average	29.7%	55.2%	14.1%

TABLE IV.

Change in Composition with Time of a Dry Mixture Containing AgO, Ag_2O and Ag^o

(Table entries given in moles per 100 grams)

Component	Composition			Change in Composition	
	Original (C_0)	After mixing for 48 hrs($C_{48\ hrs}$)	After standing for 104 additional days ($C_{104\ days}$)	$C_{48\ hrs}-C_0$	$C_{104\ days}-C_{48\ hrs}$
AgO	0.476	0.365	0.240	-0.111	-0.125
Ag_2O	0.007	0.119	0.241	+0.112	+0.122
Ag^o	0.364	0.253	0.131	-0.111	-0.122

CALCULATION OF SAMPLE COMPOSITION

1. Calculation of % Ag^{o}:

$$\% Ag^{o} = (\text{Wt. } Ag^{o} \text{ in g./Sample Wt.}^{I} \text{ in g.}) \times 100$$

2. Calculation of % AgO:

$$\% AgO = \frac{(\text{meq. } I^{o} \text{ liberated})(\text{g.}AgO/\text{meq.})}{(\text{Sample Wt.}^{II} \text{ in g.})} \times 100$$

$$\text{meq.}I^{o} \text{ liberated} = (\text{meq.}I^{o} \text{ found by titration}) + (\text{meq.}I^{o} \text{ used in } Ag^{o} \text{ oxidation}) - (\text{meq.}I^{o} \text{ added})$$

$$\text{meq.}I^{o} \text{ used in oxidation} = \frac{(\text{Sample Wt.}^{II})(\% Ag^{o}/100)}{(\text{g.}Ag^{o}/\text{meq.})}$$

$$\% AgO = \frac{\left[(\text{meq.}I^{o} \text{ found}) + \frac{(\text{Sample Wt.}^{II})(\% Ag^{o}/100)}{0.10787} - (\text{meq.}I^{o} \text{ added})\right](0.12387)}{(\text{Sample Wt.}^{II} \text{ in g.})} \times 100$$

3. Calculation of % Ag_2O:

$$\% Ag_2O = \frac{\left[(\text{Wt.Ag in oxides}) - (\text{Wt.Ag due to AgO})\right]\left[\text{M.W.}Ag_2O/2(\text{At.W.Ag})\right]}{(\text{Sample Wt.}^{I} \text{ in g.})} \times 100$$

$$\text{Wt. Ag in oxides} = \text{Wt. AgCl}(\text{At.W. Ag/M.W. AgCl}) = \text{Wt. AgCl } (.7526)$$

$$\text{Wt. Ag due to AgO} = \left[(\text{Sample Wt.}^{I})(\% AgO/100)\right]\left[\text{At.W. Ag/M.W. AgO}\right]$$

$$\% Ag_2O = \frac{\left\{\left[(\text{Wt. AgCl})(.7526)\right] - \left[(\text{Sample Wt.}^{I})(\% AgO/100)(.8708)\right]\right\}(1.0643)}{(\text{Sample Wt.}^{I} \text{ in g.})} \times 100$$

NOTE: Sample Wt.^{I} = Wt. of aliquot used in Step I

Sample Wt.^{II} = Wt. of aliquot used in Step II

The average values obtained for % Ag^o and % AgO are used in the subsequent calculations.

SAMPLE CALCULATION:

Data obtained from a typical duplicate analysis:

Step I.

Sample Wt.^{I}	0.2546 g.	0.2565 g.
Wt. Silver Metal:	0.0357 g.	0.0362 g.
Wt. Silver Chloride:	0.2626 g.	0.2652 g.

Step II.

Sample Wt.^{II}	0.4214 g.	0.4040 g.
Meq. I_2 found:	0.4570 meq.	0.4419 meq.
Meq. I_2 added:	none needed	none needed

Calculated Results:

Sample Number:	Calculation	Average
No. 1	% Ag^o = (.0357/0.2546) X 100 = 14.0%	14.05%
No. 2	% Ag^o = (0.0362/0.2565) X 100 = 14.1%	

Sample Number:	Calculation	Average
No. 3	% AgO = $\dfrac{\left\{(0.4570)+\left[(.4214)(.1405)/.1079\right]\right\}(.1239)}{(.4214)}$ X 100 = 29.6%	29.65%
No. 4	% AgO = $\dfrac{\left\{(0.4419)+\left[(.4040)(.1405)/.1079\right]\right\}(.1239)}{(.4040)}$ X 100 = 29.7%	
No. 1	% Ag_2O = $\dfrac{\left\{(.1976)-\left[(.2546)(.2965)(.8707)\right]\right\}(1.0643)}{(.2546)}$ X 100 = 55.2%	55.3%
No. 2	% Ag_2O = $\dfrac{\left\{(.1996)-\left[(0.2565)(0.2965)(.9708)\right]\right\}(1.0643)}{(.2565)}$ X 100 = 55.4%	

APPENDIX B

EXPERIMENTAL VERIFICATION OF THE QUANTITATIVE OXIDATION OF SILVER METAL BY IODINE

Procedure. A sample of silver metal powder (99.9% pure) was weighed into a 125 ml. flask. Ten grams of potassium iodide, 5 ml. Sterox solution, and 25 ml. of standardized iodine solution were then added. The silver metal was given time to react with the iodine and the iodine remaining was determined by titration with sodium thiosulfate solution. The following results were obtained:

Sample	#1	#2	#3
Wt. Ag°	0.1068 g.	0.1038 g.	0.1067 g.
Meq. I° used	0.9851 meq.	0.9625 meq.	0.9875 meq.
Gms. Ag° oxidized	0.1063 g.	0.1038 g.	0.1065 g.

These results show that the reaction is quantitative and proceeds according to the equation:

$$Ag^{\circ} + 1/2 I_2 \longrightarrow AgI$$