9 March 1943

NRL Report No. P-2021

NAVY DEPARTMENT

FR-2021

Report on

Determination of Perchlorates in Submarine Storage Battery Electrolyte

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

Number of Pages: Text - 5 Tables - II Plates - 1

Authorization: Bureau of Engineering letter SS/S62 (9-S-Ds) of 28 September 1939, and Bureau of Ships Letter SS179/S62(350) of July 24, 1942.

Date of Test: April 1940 to August 1940 - September 1942 to November 1942.

Prepared by:

Edward J. Peebles, Assistant Chemist

Reviewed by:

J. C. White, Senior Chemist, Head of Section

P. Borgstrom, Head Chemist, Superintendent
Chemistry Division

Approved by:

A. H. Van Keuren, Rear Admiral, USN, Director

Distribution: BuShips (10)
Materiel Lab. (1)

hsl

TABLE OF CONTENTS

ABSTRACT

Methods have been devised for the determination of perchlorates in submarine storage battery electrolyte based on the reduction of perchlorate to chloride. The reduction is accomplished by the fusion of the dry salt or by heating the electrolyte with titanous sulfate.

The reduction with titanous sulfate is faster and more convenient but is subject to errors due to volatilization of a part of the chlorine as hydrochloric acid while the solution is being heated with concentrated sulfuric acid. A distillation procedure has been worked out in which these errors are avoided by absorption of the hydrochloric acid in alkaline solution. Total chlorine is determined by titration.

I. REFERENCES

(a) Bureau of Engineering letter SS/S62 (9-S-Ds) of 28 September 1939.
(b) J. Am. Chem. Soc. 34, 812 (1912)
(c) Chem. News 119, 8 (1919)
(d) Bull Soc. Chem. Biol. 19, 739-46 (1937)
(e) Enclosure of NRL ltr. to BuShips SS/19 Eng. of 11 May 1942.
(f) BuShips ltr. to NRL SS179/S62(350) of 24 July 1942.
(g) NRL Report No. P-1608.

II. AUTHORIZATION

1. This work was authorized by references (a) and (f).

III. STATEMENT OF PROBLEM

2. The purpose of this work was to devise a method for the quantitative determination of perchlorates in submarine storage battery electrolyte.

IV. KNOWN FACTS BEARING ON THE PROBLEM

3. A number of methods have been reported in the literature for the determination of perchlorates but few of these are sensitive enough for use in detecting the small amounts which may be found in battery electrolyte. The only practical procedure consisted in the reduction of perchlorate to chloride and determination as chloride. Preliminary tests indicated that the method described in reference (b) might be suitable. This consists in the reduction of perchlorate to chloride by fusing the dry perchlorate salt in a flask, the neck of which contains a glass wool plug to prevent loss of material by spattering. Another method was reported in reference (c) in which the perchlorate is reduced by titanous chloride in hot concentrated sulfuric acid solution. The excess of standard titanous ion is titrated with ferric alum using potassium thiocyanate as an indicator. This method is suitable only when there are no other oxidizing agents present in the solution. The direct determination as chloride by this procedure is difficult due to the introduction of chloride by the reducing agent. Reference (d) reports a method which has been used in determining small amounts of perchlorate present in biological materials. Sulfur and concentrated sulfuric acid are heated with the dry salt and the evolved gases containing sulfur dioxide and hydrochloric acid are absorbed in a 20% sodium sulfite solution and chloride is determined as silver chloride.

4. A procedure for the determination of perchlorate based on the method of reference (b) was devised for use in the study of the salted SQUALUS cells and was reported by letter in reference (e). This method was used in the analysis of electrolyte from the pilot cells of the after battery of the USS PLUNGER which had been found to be contaminated with chlorine. Reference (f) enclosed a report by the Yard Testing Laboratory, Navy Yard, Pearl Harbor, on the analysis of battery electrolyte for perchlorate and the request that this method be studied at this Laboratory.

V. METHODS

A. By Fusion of the Dry Perchlorate Salt

5. Potassium perchlorate is reduced to chloride by fusion and the total chlorine is determined as chloride. Procedure: Pipette a sample of the electrolyte into a 200 cc. round bottom pyrex flask and add anhydrous potassium carbonate of reagent grade, with shaking, until the solution is slightly alkaline. Evaporate the solution to dryness in an oven and ignite at dull red heat using a baffle in the neck of the flask to prevent loss of salt by spattering. The baffle may consist of a glass wool plug or a glass tube wound with a glass rod spiral which has been ground to fit loosely into the neck of the flask. After all cracking has ceased, allow the flask to cool, wash down the baffle and dissolve the residue in water making the solution slightly acid with nitric acid. Warm the solution and add a measured excess of 0.05 Normal silver nitrate solution. Filter off the precipitate, wash with hot water, and to the combined filtrate and washings, add 3 cc of a saturated solution of ferric alum to which a few drops of nitric acid have been added. Titrate the excess silver nitrate with 0.05 Normal ammonium thiocyanate until a permanent pink color is secured. Then, for a 25 cc sample of electrolyte

$$\text{Total chlorine in mg. per liter} = 71\ (\text{cc } 0.05\ N\ AgNO_3 - \text{cc } 0.05\ N\ NH_4\ CNS)$$

A blank analysis should be run on the pure electrolyte of the same specific gravity in order to determine the concentration of chlorine in the potassium carbonate and other reagents. The blank determination can generally be neglected if a good grade of potassium carbonate is used.

B. Nephelometric Method

6. The procedure reported in reference (f) is as follows: Heat a 5 cc sample of the electrolyte to boiling with an equal volume of concentrated sulfuric acid and containing a measured volume of titanous sulfate (20% solution) in excess. After cooling, dilute the solution with water, add silver nitrate to precipitate the chloride and compare the turbidity with standards prepared in the same way. The method is recommended for concentrations of chlorine of 0.002 - 0.012%.

7. Standard solutions of potassium chloride and potassium perchlorate were prepared, each containing 50 mg per liter of chlorine. These solutions were treated by the above procedure and the percent transmission of the silver chloride suspensions were measured with Cenco Photelometer using a standard blue filter. The turbidity increases following the precipitation with silver nitrate as shown in Plate 1. The same effect has been observed with silver chloride suspensions in water and was reported in reference (g) where transmission curves were plotted for various concentrations of chloride. In order to compare the amounts of silver chloride precipitate by this method it is necessary to compare the turbidity at the same time following the additions of silver nitrate. Various

concentrations of chlorine were tried but it was not possible to establish any relationship between concentration of silver chloride and transmission of light which is sufficiently accurate for quantitative work. The method is also subject to error due to a loss of chlorine as hydrochloric acid by volatilization during the heating of the sample with titanous sulfate.

C. Reduction with Titanous Sulfate by Heating in an Open Flask and Determination of Chlorine by Titration.

8. Procedure: To a 25 cc sample of the electrolyte add 25 cc of concentrated sulfuric acid and an excess of titanous sulfate solution. Heat the mixture to boiling, cool, add 100 cc of water and 5 cc of concentrated nitric acid and precipitate the chloride by a measured excess of 0.05 Normal silver nitrate. Filter out the silver chloride and proceed as in paragraph 5. A blank run must be made using the same volume of titanous sulfate solution as in the test sample. The results of these analyses are recorded in Table 1. With concentrations of 100 mg/liter or less of chlorine, good results were obtained although the end point of ferric thiocyanate was rather indistinct due to the high concentrations of sulfuric acid. With concentrations much in excess of 100 mg/liter low results were obtained due to a loss of chloride by volatilization of hydrochloric acid. Tests carried out by the same procedure on samples of electrolyte containing 500 mg/liter of chlorine as chloride gave similarly low results.

D. Distillation Method

9. Because the reduction with titanous sulfate is faster and more convenient than the other methods tried, it was considered advisable to devise a procedure using this method of reduction which would be applicable over a wide range of concentrations. It was found that by distilling the sample with concentrated sulfuric acid and titanous sulfate the chlorine is evolved as hydrochloric acid which can be absorbed in alkali and analyzed as chloride. The only special equipment necessary is a distilling apparatus of the type used in Kjeldahl nitrogen determinations. All the connections should be of ground glass to avoid attack by the sulfur trioxide mist.

10. The following procedure was devised:

Pipette a 25 cc sample of the electrolyte to be analyzed into a 300 cc Kjeldahl flask and add 25 cc of concentrated sulfuric acid. Add a measured excess of titanous sulfate (20% solution) and connect immediately to the distilling apparatus. Distill slowly to avoid bumping until the residue contains only fuming sulfuric acid and absorb the vapors and distillate in 50 cc of approximately 1% sodium hydroxide solution. The tip of the condenser should dip into the alkaline solution and after the reducing mixture in the Kjeldahl flask begins to boil, the level of the liquid should rise and fall in the condenser. The solution in the Kjeldahl flask loses its blue color near the end of the distillation and becomes first green, then straw colored. Allow the system

to cool, wash down the trap and condenser into the distillate, and neutralize the excess sodium hydroxide with concentrated nitric acid adding approximately 5 cc in excess. Warm the solution and add a measured excess of 0.05 Normal silver nitrate. Filter out the precipitate and wash with hot water and to the combined filtrate and washings add 3 cc of a saturated solution of ferric alum to which a few drops of nitric acid has been added. Titrate the excess silver with ammonium thiocyante until a permanent pink color is secured. It is necessary to run a blank distillation using an equal volume of titanous sulfate. Then for a 25 cc sample of electrolyte

$$\text{Total chlorine in mg/liter} = 71\ (\text{cc } 0.05\ N\ Ag\ NO_3 \text{ used for sample} - \text{cc } 0.05\ N\ Ag\ NO_3 \text{ used in blank}$$

$$\% \text{ Chlorine} = \frac{\text{mg/liter chlorine}}{\text{Spec. Grav. x } 10000}$$

The distillation method was tested on a number of standard solutions and samples of battery electrolyte containing chloride and perchlorate. Typical analyses are recorded in Table 2.

E. Rapid Methods of Titrating Chloride

11. It is possible to titrate the excess silver nitrate without filtering out the silver chloride precipitate by first adding approximately 10 cc of nitrobenzene and titrating with ammonium thiocyanate as before. If the solution contains an excess of sulfuric acid, however, the red ferric thiocyanate color fades rapidly making the end point difficult to detect.

12. The titration can also be carried out as follows: Neutralize the sodium hydroxide solution, containing the absorbed chloride, with approximately 0.1 Normal sulfuric acid using bromo cresol purple as an indicator (pH 5.2-6.8). Add 1 cc of 1 Normal potassium chromate and titrate with 0.05 Normal silver nitrate solution until a permanent pink color is obtained. This end point is very sensitive to pH and in general is not as accurate as the thiocyanate titration.

F. Determination of Chloride

13. In order to determine the concentration of perchlorate when total chlorine is known, it is necessary to analyze the electrolyte for chloride. Dilute a 25 cc sample of the electrolyte to approximately 100 cc, add 5 cc concentrated nitric acid, and precipitate the chloride with an excess of 0.05 Normal silver nitrate. Filter out the precipitate and titrate the excess silver as before with 0.05 Normal ammonium thiocyanate. The chlorine present as perchlorate is obtained by subtracting the concentration of chloride from the total chlorine.

VI. DISCUSSION OF DATA AND RESULTS

14. In detecting small amounts of perchlorate by fusion of the salt the principal difficulty is in the large amount of potassium sulfate formed during the neutralization of the electrolyte.

This salt may dry in the flask as a hard cake which is troublesome during the fusion and causes the end point of the chloride titration to be less distinct. A small sample of electrolyte should be used wherever possible.

15. The method for the determination of total chlorine by turbidity measurements did not give consistent results because the turbidity due to silver chloride changes with time. Perchlorate is completely reduced to chloride by titanous sulfate but low results may be obtained for these analyses due to the volatilization of hydrochloric acid especially at higher concentrations of chlorine. The best results were obtained by reducing with titanous sulfate, distilling the solution and absorbing the hydrochloric acid produced in sodium hydroxide solution. Loss of chlorine is avoided and the end point is much more distinct than in titrations of solutions containing a large excess of sulfuric acid. This method can be used for detecting small amounts of perchlorate in the presence of a large excess of chloride.

VII. CONCLUSIONS AND RECOMMENDATIONS

16. The distillation method described in paragraph 10 of this report is recommended for the quantitative determination of perchlorate over the entire range of concentrations of chlorine found in the electrolyte of a salted storage battery cell. This method is accurate, simple in operation, and is sufficiently rapid for routine laboratory analysis.

17. The method of fusion of the perchlorate salt can be used satisfactorily in determining perchlorate but is slower than the distillation method. In detecting minute traces of chlorine, large samples of electrolyte must be used and the precipitate of potassium sulfate becomes troublesome. Care must be taken during the evaporation and fusion in order to avoid a loss of salt by spattering.

18. With total chlorine concentrations of approximately 100 mg/liter, or less, perchlorate may be determined as chloride following reduction with titanous sulfate by heating in an open flask. No appreciable chlorine is lost by volatilization during the heating at these low concentrations.

19. The nephelometric method reported in reference (f) can be used as a rapid check when it is necessary to ascertain whether or not electrolyte conforms to the M.E.I. Specifications of 0.012% total chlorine, however, the reduction mixture must be heated carefully to avoid volatilization of chlorine and the comparisons must be made at the same time, following precipitation of the silver chloride.

TABLE I

Determination of Chlorine by Titration Reduction
of Perchlorate with Titanous Sulfate by Heating in an Open Flask

cc sample taken	chlorine present as	mg per liter chlorine	Spec. Gravity	% Chlorine	cc sulfuric acid added	cc $Ti_2(SO_4)_3$ Sol.	mg/liter chlorine found
25	CLO_4^-	500	1200	0.042	25	10	380
							370
25	CLO_4^-	500	1250	0.040	25	10	380
							340
25	CL^-	500	1200	0.042	25	10	340
							360
50	CLO_4^-	5	1250	0.0004	20	5	5
50	CLO_4^-	10	1250	0.0008	20	5	9
50	CLO_4^-	50	1250	0.0042	25	5	50
							50
50	CLO_4^-	100	1250	0.0084	25	5	98
							83
25	CLO_4^-	100	1250	0.0084	10	2.5	100

TABLE II

Determination of Chloride and Perchlorate

Distillation Method & Titration

Concentration of Chlorine as chloride		as perchlorate		Conc Chloride Found	Total Chlorine Found	Chlorine Present As Perchlorate Found
mg/liter	% Cl	mg/liter	% Cl	mg/liter	mg/liter	mg/liter
500	0.040	10	0.0008	496	507	12
250	0.020	250	0.020	247	488	241
100	0.008	100	0.008	97	202	105
10	0.0008	500	0.040	8	504	496
10	0.008	10	0.008	9	19	10

U. S. NAVAL RESEARCH LABORATORY
BELLEVUE, D. C.

DATE

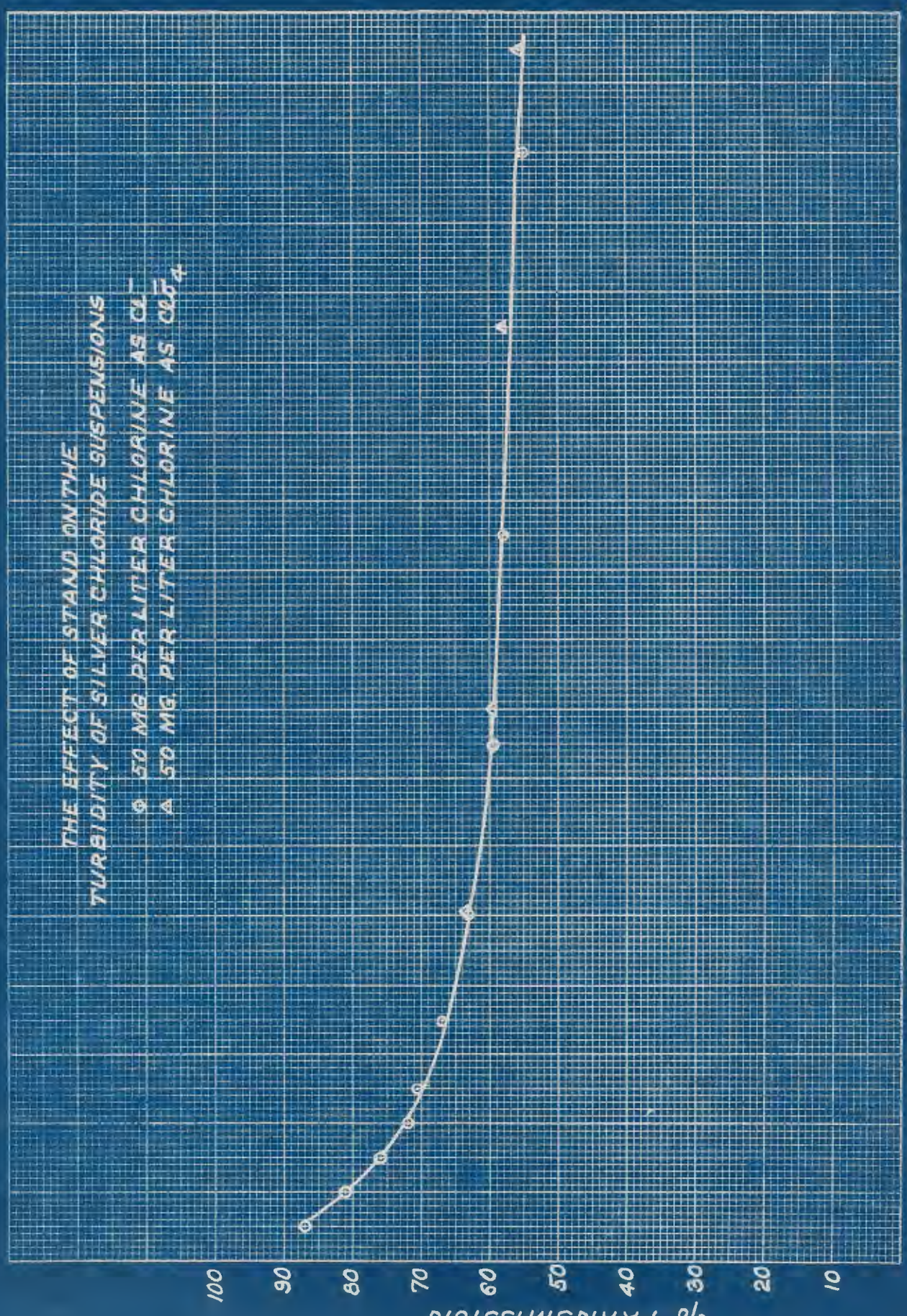

PLATE I

IF SHEET IS READ THIS WAY (HORIZONTALLY) THIS MUST BE TOP. IF SHEET IS READ THE OTHER WAY (VERTICALLY) THIS MUST BE LEFT-HAND SIDE.