20 February 1935 NRL Report No. P-1126

NAVY DEPARTMENT
BUREAU OF ENGINEERING

Report on

Submarine Storage Batteries: Emergency Analysis for Chlorine Content of Electrolyte

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Number of Pages: Text - 5 Tables - 1

Authorized by: BuEng.let. A2-2/EN8(3-22-Y1) of 22 Dec. 1934.

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BuEng (5)

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ABSTRACT

This report studies a method of analyzing for chlorine: (a) in battery water suspected of having been contaminated by chlorine, and (b) in storage battery electrolyte. For battery water, the procedure of chloride analysis of boiler water in the M.E.I. is directly suitable. But for electrolyte, none of the standard methods of analysis having proved applicable, a simple method based upon visually comparing the amount of silver chloride precipitated in the suspected electrolyte with that in a readily prepared standard, was devised.

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APPENDIX

INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Engineering letter, ref.(a); other references pertinent to this report are given as refs. (b) and (c).

Reference: (a) BuEng.let.A2-2/EN8(3-22-Y1) of 22 Dec.1934.
(b) Revision, Chapter 28, M.E.I.
(c) Article 6-102(2), M.E.I.

(b) Statement of Problem

2. During the operation of submarines, sea water or other chlorine-containing water may by accident get into the cells of the main storage batteries. The presence of chlorine in the cells is dangerous to personnel and deleterious to the health and life of the cells. The problem is to find a method for the rapid approximate analysis of the electrolyte in the cells to determine if the chlorine content is greater than the limit which experience has shown should not be exceeded. This analysis is to be made by the personnel of the submarine by using the standard Navy boiler water testing outfit; and the analysis is designed to guide the emergency treatment of the battery to remove chlorine pending such time as samples of the electrolyte can be sent to a Navy Yard where a complete analysis of them can be made by a qualified chemist to decide whether further treatment is necessary. Incidentally, the analysis is to be used in determining the suitability of water for use in watering the storage batteries either when the water is suspected of containing chlorine or as routine procedure when watering batteries or receiving battery water from tender or base.

(c) Known Facts Bearing on the Problem

3. When sea water gets into a storage cell, the salt, NaCl, therein is converted at once to hydrogen chloride,

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$

Some of this HCl gets out into the air of the battery compartment, and as it is an irritating gas, the personnel is immediately warned that sea water has been admitted to the battery. As the HCl is very soluble, most of it, however, remains in the electrolyte where it soon becomes in contact with the plates. Here some of the chloride is precipitated out as lead chloride and falls into the sediment space at the bottom of the jar. Some of it is oxidized by the lead peroxide of the positives to give free chlorine, a poisonous yellow colored gas which escapes into the air of the battery compartment. The remainder stays in solution in the electrolyte as chloride-ion. Charging and cycling the cell tend ultimately to drive most of the chlorine out of the cell as free chlorine gas. But during the time that any chlorine remains, it is deleterious to the health and life of the plates and experience shows that any concentration of the chloride greater than the limit of 0.012% set by ref.(b) should not be permitted.

4. The Bureau of Engineering suggested that the operating personnel of a submarine should have means to analyze the electrolyte for chlorine to determine whether accident has resulted in the chlorine contamination exceeding this limit and suggested that the boiler water testing outfit be used to make such analysis.

5. The boiler water testing outfit analysis for chlorine depends upon titrating a measured sample with a standard solution of silver nitrate. It precipitates out the chloride as silver chloride

$$Cl^- + Ag^+ \longrightarrow AgCl \downarrow$$

As an indicator to determine when all of the chloride has been consumed, potassium chromate is put into the solution and this causes a characteristic red precipitate of silver chromate when all of the chloride is gone.

6. Unfortunately this method of analysis can not be directly employed for storage battery electrolyte since the large quantity of acid present prevents the action of the indicator. It is, therefore, necessary to modify the procedure employed in testing boiler water. The boiler water procedure can, however, be directly used for analyzing battery water suspected of containing chlorine.

(d) Narrative of Original Work

7. In the experimental work, samples of storage battery electrolyte with known amounts of chloride as an impurity were prepared and used to study various methods of analysis. It was found that most of the standard methods of analysis are inapplicable to electrolyte, containing as it does such a high concentration of a strong acid. It was found that recourse had to be made to a simple colorimetric method of estimating the silver chloride precipitated out on the addition of silver nitrate solution.

METHODS

(a) Preparation of Materials

8. In the experiments 1.280 sp.gr. (wartime gravity) electrolyte was used since any methods applicable to this can be

used with 1.210 sp.gr. Samples of this electrolyte were made up containing 0.006, 0.009, 0.012, 0.015% chloride respectively and these were used in testing the suitability of the several methods of analysis. A Navy standard boiler water testing outfit and its standard solutions were used.

(b) Description of Experiments

9. It was soon found that the standard boiler water testing procedure could not be used in the presence of the strong sulphuric acid of the electrolyte, as it would dissolve any silver chromate indicator which formed. Hence, the attempt was made to neutralize the acid with submarine air-purification carbon dioxide absorbent, as this is the alkaline material most readily available aboard a submarine. By so neutralizing the acid, it was hoped to make the boiler water analysis method directly applicable; but owing to the insolubility of the products of the neutralization, this scheme proved to be impracticable.

10. Next, equal volume samples of several test electrolytes were put in long test tubes and to each of these was added a 10 ml sample of silver nitrate from the boiler water test kit. The test tubes were then corked up and inverted; the silver chloride precipitate thus formed made the several solutions "milky" and it was found that a rough estimate of the relative concentration of the chloride could be obtained by comparing the "milkiness" of the sample. By this means it is possible to determine readily whether or not the chloride concentration in a given sample is greater or less than the limit percentage of 0.012%.

DATA OBTAINED

11. The results of these experiments suggest the following directions for analysis of: (a) battery water and (b) storage battery electrolyte for chloride to determine in an emergency whether or not the chloride concentration exceeds the specified limits.

(a) Battery Water

In case it is suspected that the battery water contains chlorine, an analysis of it should be made. To a small sample of the suspected water add some silver nitrate solution and shake the mixture. If the solution remains clear it contains no chlorine. If a milky precipitate is formed, the water should be analyzed in exactly the manner used for testing the chloride in boiler water in M.E.I. 6-102(2), using a 50 ml sample. The chloride will thus be obtained in grains per gallon and the corresponding percentage is given in Table 1.

(b) Electrolyte

To test for the presence of chlorine in electrolyte, add a few drops of silver nitrate solution from the boiler water test outfit and shake. If the electrolyte remains clear it contains no chlorine. If a milky precipitate of silver chloride is formed, chlorine is present and it is necessary to determine the amount of chlorine in order to determine whether it is present in sufficient amount to be dangerous. To do this measure out a 50 ml sample of the electrolyte into the 50 ml graduate from the hydrometer syringe. Put this sample into one of the big test tubes provided. In another test tube put 50 ml of electrolyte from some cell which contains no chlorine and add to this 0.3 ml of sea water and shake; this latter solution will contain 0.012% chloride and will be used as a standard to check against the other. To each of these test tubes add 10 cc of silver nitrate solution from the boiler water test kit. Stopper the two tubes with the rubber stoppers provided, invert, and shake them. Next, compare the "milkiness" of the two tubes. If the suspected sample is less "milky" than the standard it contains less than the specified limit of chlorine and is not, therefore, dangerous.

Water in harbors, etc., may contain less chloride than normal sea water; if such water were used in making the comparison, the results would be somewhat in error but the error would be on the side of safety. As an alternative, a standard solution containing chloride could be carried in the boiler water testing outfit. This could be made by dissolving 29.5 grams of pure sodium chloride in 1000 ml of water and would be equivalent to sea water in chloride content. Or a sample of water from the open sea could be carried in a bottle.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

12. The results of this study show that the standard methods of analyzing for chlorine fail in strong electrolyte solution. A simple method was devised of analyzing for chlorine by comparing visually the amount of precipitate of silver chloride formed in a suspected electrolyte with that contained in a standard solution containing the limiting percentage of chlorine, the latter being prepared by the simple expedient of using sea water as a known source of chlorine. The service use of this suggested method would require the addition to the standard Navy boiler water testing outfit of: (a) several 100 ml test tubes with rubber stoppers, and (b) a 0.3 ml pipette, stowage space for which can probably be made in the testing outfit cabinet.

(b) Recommendations

13. It is recommended that the Bureau consider the feasibility of the suggested method for chlorine analysis as an emergency measure aboard submarines.

SUMMARY AND DISCUSSION

14. Study of several methods of analyzing for chlorine in electrolyte shows that the usual methods are inapplicable to electrolyte. A simple "colorimetric" method was devised using a standard prepared from sea water for comparison. The suggested method is designed solely to guide personnel in an emergency in the treatment of the contaminated storage battery pending such time as the submarine can obtain the services of a qualified Navy Yard chemist to make detailed analyses. For the analysis of battery water, the M.E.I. procedure, ref.(c), for boiler water is applicable.

TABLE 1

Conversion of Chloride Analysis

In following the instructions of M.E.I. 6-102(2), a 50 ml sample is used and tested with a reagent silver nitrate of which 1 ml corresponds to 2 grains chloride per gallon. If this same reagent is used in testing a 50 ml sample of electrolyte or battery water, the percentage of ~~chloride~~ chlorine * is found in the following tables from the amount of reagent used.

ml of silver nitrate used	percent ~~chloride~~ chlorine * by weight
1.280 specific gravity	
0.2	0.0005%
0.4	0.0011
0.6	0.0016
0.8	0.0022
1.0	0.0027
2.0	0.0054
3.0	0.0081
4.0	0.011
5.0	0.013
1.210 specific gravity	
0.2	0.0005%
0.4	0.0011
0.6	0.0017
0.8	0.0023
1.0	0.0028
2.0	0.0057
3.0	0.0075
4.0	0.011
5.0	0.014
Battery Water	
0.2	0.0004%
0.4	0.0009
0.6	0.0014
0.8	0.0019
1.0	0.0023
2.0	0.0047
3.0	0.0062
4.0	0.0091
5.0	0.012

* Determined as chloride

See attached

FORM N. R. L. 19

Cl_2 Cl

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

DATE

OBSERVER

TIME

TEST

	COL. 1	COL. 2	COL. 3	COL. 4	COL. 5	COL. 6	COL. 7	COL. 8
		Reported			Rechecked			
		1.28	1.21	H_2O	1.28	1.21	H_2O	
1	0.2	0.0005	0.0005	0.0004	0.00054	0.00057	0.00069	
2	0.4	0.0011	0.0011	0.0009	0.00107	0.00113	0.00137	
3	0.6	0.0016	0.0017	0.0014	0.00161	0.00170	0.00206	
4	0.8	0.0022	0.0023	0.0019	0.00214	0.00227	0.00274	
5	1.0	0.0027	0.0028	0.0023	0.00268	0.00283	0.00343	
6	2.0	0.0054	0.0057	0.0047	0.00536	0.00566	0.00686	
7	3.0	0.0081	0.0075	0.0062	0.00804	0.00849	0.01029	
8	4.0	0.011	0.011	0.0091	0.01073	0.01133	0.01372	
9	5.0	0.013	0.014	0.012	0.01340	0.01415	0.01715	
10								

11 Sample calc. 1 cc. Titration for 50 cc sample.

12 1 cc = 2 grains Cl / gallon

13–15 $1 \times \frac{2}{7000} \Big/ \frac{1}{3.7854}$ (cc/gallon) $\Big/ 454$ (cc/liter) $\Big/ 100 = 0.00343\%$ Cl (cc/liter)

16 1 grain = 0.0648 grams

17–18 $\frac{2 \times 0.0648}{3.7854} = 0.03426$

19

20

SHEET ___ OF ___ SHEETS COMPUTED BY ________ CHECKED BY ________

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