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ARMY TROPIC TEST CENTER

JULY 1975

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METHODOLOGY INVESTIGATION

AN IMPROVED ANALYTICAL METHOD FOR ATMOSPHERIC CHLORIDES IN TROPIC TESTS

FINAL REPORT

by
J. F. SPROUSE

JULY 1975

Approved for public release; distribution unlimited.

UNITED STATES ARMY
TROPIC TEST CENTER
FORT CLAYTON, CANAL ZONE

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A methodology investigation was recently completed at the US Army Tropic Test Center in the Canal Zone to develop an improved analytical method for rapid determination of water-soluble chlorides. For the past 8 years, ambient salt has been measured for corrosion studies by wet-candle sampling and determining water-soluble chlorides by manual mercuric nitrate titration using diphenylcarbazone-bromphenol blue indicator.

Two experimental methods, select ion electrode and flame emission for sodium, were evaluated against the standard mercuric nitrate method. Flame emission for sodium, using an empirical chloride to sodium ratio of 1.69, provides the best estimate of chloride concentration to the mercuric nitrate method and results were well within the error limitations of the wet-candle sampling method. The investigation showed that by using flame emission, instead of the mercuric nitrate titration, time for laboratory work was halved.

It was recommended that the new method be adopted as standard operating procedure at the Tropic Test Center, thereby realizing a savings/investment ratio of 1.17 and a 17 percent rate of return of the initial cost of the investigation.

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SUMMARY

The US Army Tropic Test Center conducted a methodology investigation from September 1974 through February 1975 in the humid tropic environment of the Canal Zone. Objective was to develop an improved analytical technique for rapid determination of total chloride in wet-candle samplers.

For the past 8 years atmospheric salt has been measured at tropic test sites by the wet-candle method. Ambient salt naturally impinges upon a wet gauze wick which transports and holds it over a 30-day exposure period. The candle is then returned to the laboratory and analyzed for water-soluble chloride. The past analytical procedure for chloride has used the manual mercuric nitrate titration using diphenylcarbazone-bromphenol blue as an indicator.

Two instrumental methods were evaluated against the mercuric nitrate method for reducing supply requirements, speed of analyses, and achieving comparable accuracy of results. The two methods evaluated were chloride select ion electrode and flame photometry for sodium concentration. Chloride to sodium ratios were used as a basis for chloride determination in the latter method. Flame emission for measuring sodium concentrations was found to provide an estimate of chloride concentrations well within the error limitations of the wet-candle sampling method. The chloride to sodium ratio found satisfactory for calculating chloride concentration was 1.69. By using the flame emission analysis for sodium instead of chloride measurements by mercuric nitrate titration, time for laboratory work was halved. The new method of analysis will result in a savings/investment ratio of 1.17, and yield a 17 percent rate of return on the initial cost of the methodology investigation.

PREFACE

During the preparation of this final report, significant technical contributions were made by M. A. Johnson and J. C. Bryan of the US Army Tropic Test Center staff. Mr. Johnson provided the statistical analyses of the data and Mr. Bryan completed the economic analysis. During the experimental portion of the study, significant contributions were made by Elizabeth Tejeira and George Lindahl, also of the USATTC staff.

This project was conducted under the technical supervision of Dr. D. A. Dobbins, Chief, Analysis Division, US Army Tropic Test Center.

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SECTION I. INTRODUCTION

BACKGROUND

In coastal regions where atmospheric salt plays an important role in corrosion processes, the requirement exists to measure the ambient salt content for correlation with materiel performance. Ambient salt measurements have been performed at US Army Tropic Test Center sites on a regular basis since 1967. The atmospheric sampling method currently used employs the "wet-candle technique" which provides a relative comparison of ambient saltfall between test sites. Saltfall is reported as average daily chloride impinging on an exposed surface area of wet gauze during a given field exposure period. The water-soluble chloride is determined by a titrimetric technique, very time consuming and requiring a large amount of reagents, supplies, and laboratory space. Individual samples are still manually processed for analysis including digestion, chemical treatment, and titration. This investigation was initiated to develop a faster analytical technique that would reduce the man-hour requirement for analysis, the amount of support chemicals and supplies, and allow automatic sample handling without sacrificing accuracy of analysis.

OBJECTIVE

Develop an improved analytical method for rapid determination of total chloride in wet-candle field samplers.

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SECTION II. DETAILS OF INVESTIGATION

GENERAL

This investigation was initiated to develop an improved analytical technique for rapid determination of water-soluble chloride collected in the tropics. The "wet-candle technique" for sampling ambient concentrations of salt has long provided a simple means of comparing saltfall among remote test sites without electric power. Its primary disadvantage has been the time required for chemical analysis in the laboratory. Total time required for digestion, chemical treatment and titration has been approximately 8 hours. Typically, six to eight samples have been handled by one technician during this period. Chemical treatment and titration have required approximately 5 hours of the total. Therefore an analytical technique has been sought that will shorten the time consuming process. The basic requirement for field sampling has been satisfied by the wet-candle method, but presently available analytical techniques can save dwindling man-hour resources.

Since 1967, the Tropic Test Center has provided wet-candle salt measurements for numerous tests by the US Army Frankford Arsenal. Ambient salt measurement test support has also been furnished for the HAWK Missile System (US Air Force Systems Command), Tropical Service Life of Electronic Parts (US Army Electronics Command), and the External Cargo Sling (US Army Aviation Systems Command). Support is currently active for Frankford Arsenal, ECOM and AVSCOM.

Wet-candle measurements also have been used to support the Tropic Test Center's test methodology program. Past methodology investigations supported include Determination of Optimum Tropic Storage and Exposure Sites, FY 70–73; Mobility in Natural Environments, FY 73–74; and Exposure/Performance Tests of Selected Materiel Items, FY 74–75.

RELATED LITERATURE

The measurement of ambient salt concentrations requires that salt be collected from the air, then a suitable analytical technique must be used to measure the quantity collected. Several methods have been employed for both sampling and analyses, each of which has its advantages and disadvantages. A bibliography on sampling methods, analytical techniques, and salt related corrosion studies by Brierly[1] provides a convenient source of reference material.

Field Sampling

Two methods are presently used at the Tropic Test Center for measuring atmospheric chloride; wet candles[2] and high-volume air filtration.[3]

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[1] Brierly, W. B., *Bibliography on Atmospheric (Cyclic) Sea-Salts*, US Army Natick Labs, Technical Report No. 70-63-ES, April 1970.

[2] Foran, M. R., E. V. Gibbons, and J. R. Wellington, *The Measurement of Atmospheric Sulfur Dioxide and Chlorides*, Chemistry in Canada, Vol 10 (5), p 33–41, May 1958.

[3] ASTM-STD, D 2009–65, part 23, *Collection by Filtration and Determination of Mass, Number, and Optical Sizing of Atmospheric Particulates, Recommended Practices, for*, pp 854–862, Philadelphia, PA, 1967.

The wet-candle method is used more widely in the Canal Zone because it is simple to operate and does not require electrical power. While this method does not provide an absolute means of measuring ambient levels of chlorides, it provides a measure of relative quantities of saltfall among different test sites. The wet candle, figure 1, provides a sampling method for collecting salt spray and crystals that are deposited by impingement on a surface. The same mechanism for deposition applies to surface deposits incident to materiel located near coastal regions.

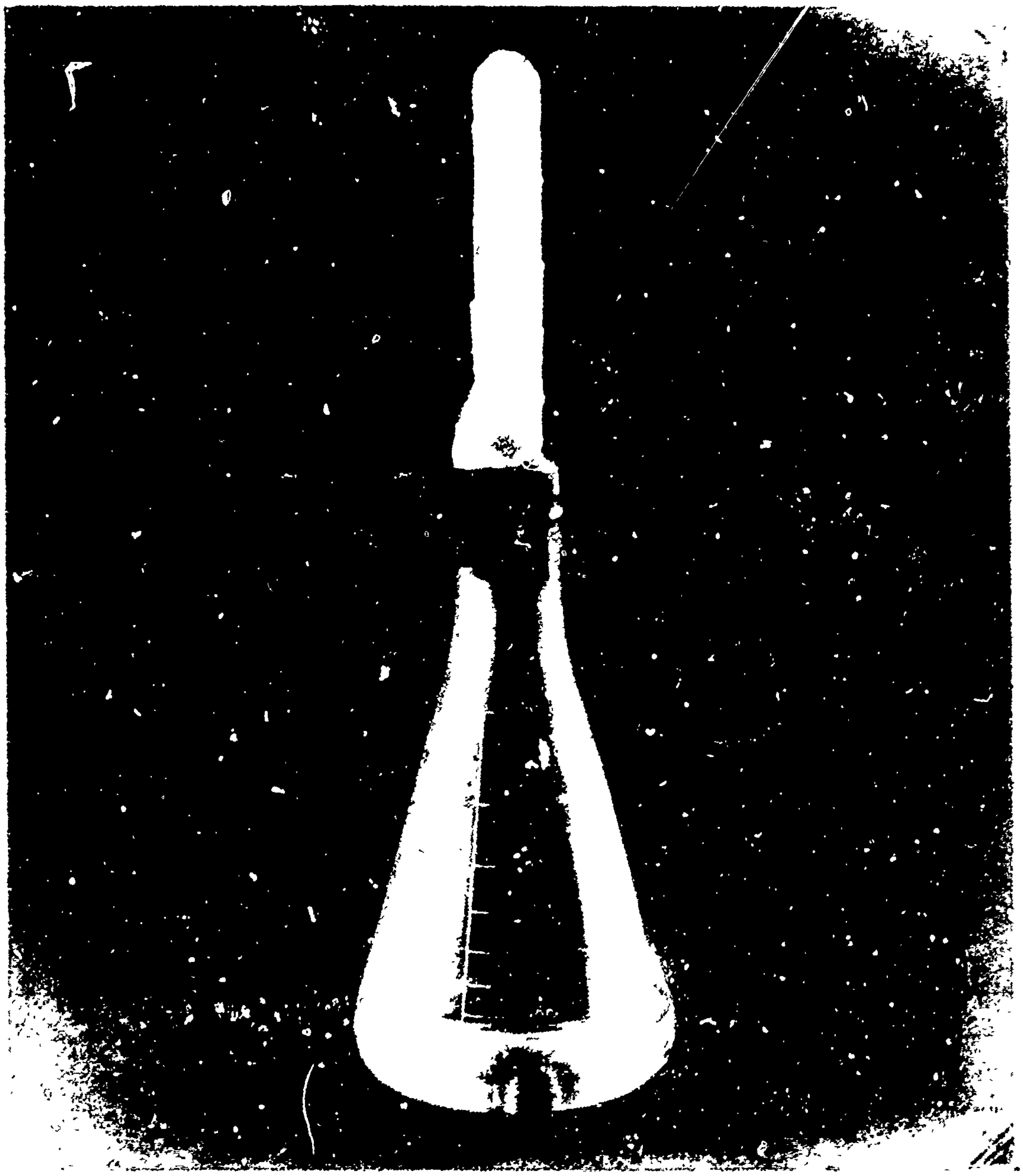

Figure 1. Wet Candle for Sampling Ambient Salts.

The wet-candle method by Ambler and Bain[4] was used for measuring ambient salt concentrations in Canada.* Candles used at the Tropic Test Center are identical to those used for the Canada corrosion studies and the only maintenance required in the tropics is adding distilled water during the dry season. Average daily salt levels are determined by exposing the candles for approximately 30 days, then determining the number of milligrams (mg) of chloride that accumulated during that period. Results are reported in mg chloride per square meter of exposed gauze per day. In this manner, the value reported represents the average saltfall per day of exposure.

The second method of measuring saltfall is a choride-free filter pad through which a known volume of air is passed. The filter pad is then digested in water and the solution analyzed for total chloride by the same wet analysis procedure used for the wet candles.[5] Thus far, only one tropic test site has been monitored by this technique. The method allows measurement of particulate and aerosol chloride concentration in the air, and will be used further where absolute measurements are required for supporting tropic tests. The method has the disadvantages of requiring electrical power for driving an air pump and collects only those salt particles greater than the pore size in the filter pad.

Analytical Methods

After wet candles are exposed to the environment for approximately 30 days, they are returned to the laboratory and the chloride is extracted from the gauze and combined with the solution removed from the candle flask. Total milligrams of chloride in the solution is equal to that deposited during the field exposure except for a small amount residual to the candle.

A standard method for measuring dissolved chloride is to titrate it with a dilute solution of mercuric nitrate in the presence of a mixed diphenylcarbazone-bromphenol blue indicator.[5] This method is currently used at the Tropic Test Center for determining dissolved chloride from wet candles and filters from the high-volume air samples.

Dissolved chlorides also may be analyzed using instrumental methods. Specific ion electrodes[6] (SIE) are being used in practically every application where the requirement to monitor chloride exists. While the measurement is very simple and fast, specific ion electrodes are subject to erroneous measurements because of interfering ions in certain applications, thereby limiting their usefulness.

It is possible to closely approximate ambient salt concentrations by measuring the quantity of metallic ions composing the water-soluble salt. While a theoretical ratio may not be acceptable for converting cation to anion concentration, an experimentally determined value offers a convenient method if the ratio remains constant with time. In coastal areas where the salt origin is from seawater sprays and aerosols, the chloride-to-sodium ratio should remain fairly constant. Therefore, a convenient analytical method for sodium, flame emission spectroscopy (FE), was evaluated for determining chloride concentration.

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* See reference 2.

[4] Ambler, H. R., and A. A. J. Bain, *Applied Chemistry*, No. 5, p 436, 1955.

[5] Intersociety Committee, *Methods of Air Sampling and Analysis, Method 201, Analysis for Chloride-Content of the Atmosphere (Manual Method) (12203-01-68T)*, p 243, American Public Health Association, Washington, DC, 1972.

[6] *Orion Specific Ion Electrodes, Bibliography*, Orion Research Incorporated, Cambridge, MA, 15 January 1 70

EXPERIMENTAL METHODS

Two experimental analytical techniques for dissolved chloride were evaluated with respect to the standard mercuric nitrate titrimetric method during this investigation. Samples used for evaluating the experimental procedures with respect to the standard mercuric nitrate method were acquired from three sources. Wet candles already located at field test sites, and analyzed monthly using the standard method, were also analyzed using the experimental methods. Finally, two sets of wet candles were used for checking reproducibility of the wet-candle sampling method in the Canal Zone tropics, and they provided additional candles for evaluating the analytical methods. Measuring reproducibility of the wet-candle sampling method provided information for assessing the required accuracy of the analytical technique for measuring chloride.

Field Exposure of Candles

To evaluate the reproducibility of wet candles and to provide samples for developing an improved analytical method for water-soluble chlorides, 16 candles were placed adjacent to one another in an open field. The candles were fabricated according to standard operating procedure (table C-1). Candles were placed on racks in the field as shown in figure 2. Data were collected at two different field sites; (1) Chiva Chiva open field inland site on the Pacific side of the Isthmus, and (2) Fort Sherman open field inland site on the Atlantic side of the Isthmus. These two sites were selected on the basis of historical salt measurements that show the Chiva Chiva site is characteristic of low ambient salt concentrations and Fort Sherman site is characteristic of high salt concentrations. However, continuous saltwater spray is not characteristic of the Fort Sherman site.

Figure 2. Field Exposure of 16 Identical Wet Candles.

Sixteen wet candles were exposed at Chiva Chiva from 13 September through 15 October 1974. The candles were exposed with two candles per rack and racks were 3 feet apart. All eight racks were placed in a straight line, northeast to southwest, that was perpendicular to the prevailing wind direction characteristic of the Chiva Chiva site during that time of the year. The candles were checked on a weekly basis to insure that water levels were sufficient for wetting the gauze wick. At the end of the 32-day exposure the candles were returned to the laboratory for analyses.

Sixteen wet candles were exposed at the Fort Sherman open field inland site from 19 December 1974 through 20 January 1975. The candles were exposed in the same manner as those at Chiva Chiva. The racks were located on a line, running northwest to southeast, perpendicular to the prevailing wind direction. The candles also underwent weekly maintenance to insure sufficient water level for wetting the gauze wick. After the 32-day exposure period the candles were returned to the laboratory for analyses.

Manual Method for Chloride ($HgNO_3$)

The standard mercuric nitrate ($HgNO_3$) analytical procedure for determining total amount of chloride collected in a wet candle requires digesting to dissolve the salt, filtering, oxidation, volumetric dilution, then titration. The standard analytical procedure used for the past eight years is given in table C-1. During this investigation the procedure was changed to provide sufficient sample sizes for all analyses performed. After digesting and filtering, each sample was evaporated to approximately 75 milliliters (ml), then it was volumetrically diluted to 100 ml. The sample was divided equally into 50-ml aliquots. One aliquot was used for chloride determinations by using a selective ion electrode (SIE) and sodium analyses by flame emission (FE) spectroscopy. The second 50-ml portion was analyzed according to the mercuric nitrate procedure in table C-1 beginning with paragraph 6, step 7. Volumes were adjusted to smaller quantities, where necessary, to maintain concentration ranges for maximum accuracy for each respective analytical method during this investigation. Results from a wet candle are usually expressed as mg chloride/m^2/day, i.e., milligrams of chloride deposited on one square meter of wick averaged over a 30-day exposure period. For evaluation of the experimental analytical techniques with respect to the standard method, all results are reported as total milligrams of chloride. This allows direct comparison of analytical method without regard to time of exposure. In order to convert from milligrams chloride to mg Cl/m^2/day, it is only necessary to divide total chloride in mg by ($0.01\ m^2 \cdot T$). "T" is the length of candle exposure in days.

Select Ion Electrode (SIE)

Chloride concentration was measured directly on the 50-ml aliquot of solution using an Orion Model 92-17 chloride ion electrode and Orion Model 90-01 standardized reference electrode using potassium chloride standard solutions between 1 and 500 ppm for calibration. Samples that did not fall within this concentration range were concentrated by evaporation or diluted until they were within the operating range. Total chloride for the wet candle was calculated by multiplying the concentration in ppm by the appropriate volume of solution.

Water-soluble chloride concentrations measured using the above select ion electrode are typically completed from 10^{-5} to 10^{-1} (moles/liter) or 0.35 to 3500 ppm. Precision is dependent on parameters such as the presence of interfering ions, total ionic strength of the sample, temperature, and pH. Precision is generally good to ± 1 percent of the chloride activity in the sample when the electrode is frequently calibrated.[7]

Flame Emission (FE) for Sodium

After chloride concentration was measured using the chloride select ion electrode, the same aliquots were analyzed for sodium using flame emission spectroscopy. Analyses were completed on a Beckman Model 440 Atomic Absorption instrument with a flame emission accessory. Total milligrams of sodium were calculated by multiplying the measured concentration in ppm by the appropriate volume of solution.

Sodium analysis by flame emission spectroscopy in this laboratory has a minimum detection limit of 0.06 ppm. The upper limit of measurement is not defined because a very concentrated solution can be volumetrically diluted until its concentration falls below the typical instrument operating maximum of 50 ppm for daily laboratory analyses. Precision of analysis for sodium using flame emission spectroscopy is generally ± 1 percent of the sodium concentration.

RESULTS AND STATISTICAL ANALYSES

The data in tables 1 through 4 list the milligrams of chloride determined by select ion electrode (SIE) and standard mercuric nitrate ($HgNO_3$), and milligrams of sodium measured by flame emission (FE).

Developmental work and initial analyses were completed on wet candles undergoing exposure at tropic test sites located throughout the Canal Zone. The data in table 1 are the results of chloride and sodium analyses for wet candles exposed at these sites for support of presently assigned tropic tests. Ambient salt concentrations vary among these sites depending upon their location. The Fort Sherman breakwater site is located in a almost continuous salt spray from the Caribbean Sea, as opposed to the Fort Sherman jungle site (Skunk Hollow) which is located in a dense tropical moist forest.

Chemical analyses for 16 identical wet candles exposed at Chiva Chiva during the period 13 September through 15 October 1974 (32 days) are shown in table 2.

Data for analyses of 16 identical wet candles exposed at Fort Sherman from 19 December 1974 through 20 January 1975 (32 days) are presented in table 3.

The data in table 4 show chloride analyses for 12 control wet candles which were fabricated and analyzed, but not exposed to the environment. The control candles allowed measurements of residual chloride from fabricating materials, reagents, and distilled water. Chloride collected in the field is the difference between total chloride measured in the candles after exposure and that measured in the control candles.

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[7] *Instruction Manual for Model 92-17 Chloride Ion Electrode,* Orion Research Incorporated, Cambridge, MA.

Table 1. Chemical Analysis of Wet Candles Exposed at Tropic Test Sites

Sample	Test Site	Chloride, mg SIE	Chloride, mg $HgNO_3$	Sodium, mg FE
1*		5.80	2.40	0.83
1†		2.80	2.22	1.65
1‡	Fort Sherman Forest (Skunk Hollow)	5.60	2.82	1.95
1§		2.20	2.09	1.00
2*		3.50	2.60	0.53
2†		3.15	2.70	1.55
2‡	Galeta Open Field (Laboratory)	6.00	3.78	2.65
2§		4.30	3.78	2.35
3*		6.00	3.08	0.82
3†		2.00	1.39	0.80
3‡	Galeta Forest	2.10	1.71	0.92
3§		1.90	1.61	0.86
4*		20.00	15.98	8.84
4†		43.00	44.53	25.00
4‡	Galeta Coastal	165.00	156.18	91.00
4§		190.00	178.58	105.00
5*		7.60	2.60	1.64
5†		6.20	5.15	3.10
5‡	Fort Sherman Open Field	20.00	16.60	9.70
5§		29.80	28.44	15.70
6*		60.00	55.49	33.66
6†		190.00	169.99	103.00
6‡	Fort Sherman Coastal (Toro Point)	660.00	698.11	442.00
6§		800.00	825.81	515.00
7*		2.30	2.90	1.04
7†		9.40	5.85	4.20
7‡	Fort Gulick Open Field (Ammo Dump)	7.20	4.77	3.05
7§		1.95	1.54	0.70
8*		3.70	2.27	0.83
8†		3.60	2.54	1.50
8‡	Coco Solo Open Field (POL Farm)	3.10	2.17	1.23
8§		7.20	3.63	3.05

* Samples exposed from 7 October to 7 November 1974
† Samples exposed from 7 November to 6 December 1974
‡ Samples exposed from 6 December 1974 to 10 January 1975
§ Samples exposed from 10 January to 10 February 1975

Table 2. Chloride Analyses of Wet Candles Exposed at Chiva Chiva Open Field Site for 32 Days*

Candle Number	Chloride, mg SIE	Chloride, mg $HgNO_3$	Sodium, mg FE
1	2.85	1.02	0.52
2	5.00	1.14	0.57
3	3.90	0.71	0.58
4	4.00	1.10	0.47
5	3.00	0.93	0.56
6	5.80	1.39	1.16
7	3.30	1.31	0.98
8	2.85	0.99	0.66
9	3.10	1.21	0.66
10	3.55	1.16	0.58
11	3.10	1.23	0.71
12	4.25	1.27	1.12
13	6.20	1.25	0.30
14	3.55	0.89	0.50
16	6.20	1.41	0.40
16	3.90	1.10	0.52

* Exposure period was 13 September through 15 October 1974.

Table 3. Chloride Analyses of Wet Candles Exposed at Fort Sherman Open Field for 32 Days*

Candle Number	Chloride, mg SIE	Chloride, mg $HgNO_3$	Sodium, mg FE
1	21.00	18.72	10.60
2	17.00	15.73	9.30
3	23.00	18.86	10.80
4	14.30	11.83	7.10
5	23.00	19.36	11.10
6	26.00	23.71	12.40
7	27.00	22.60	12.20
8	25.00	20.69	11.60
9	15.00	11.52	7.00
10	19.00	15.68	9.50
11	19.00	15.21	9.20
12	19.80	19.81	11.20
13	20.50	19.98	10.60
14	24.80	19.30	12.10
15	16.00	14.95	8.50
16	15.00	12.08	7.30

* Exposure period was 19 December 1974 through 20 January 1975

Table 4. Chloride Analyses of Wet Candle Controls Not Exposed to the Environment

Candle Number	Chloride, mg SIE	Chloride, mg $HgNO_3$	Sodium, mg FE
1	0.80	0.46	0.42
2	0.53	0.53	0.41
3	0.56	0.48	0.36
4	0.54	0.46	0.39
5	0.50	0.54	0.39
6	0.64	0.52	0.39
7	0.60	0.48	0.34
8	0.66	0.63	0.42
9	0.58	0.58	0.42
10	0.60	0.95	0.35
11	0.66	0.99	0.30
12	0.65	0.74	0.28

The percent errors between the standard and SIE methods, and between the standard and FE methods, were computed as a preliminary evaluation of the accuracy of the two experimental techniques. Milligrams of chloride by the FE method were calculated from the Cl.Na atomic ratio (1.54) for sodium chloride. SIE measurements were directly in ppm chloride. Table 5 generalizes these errors for the experimental data in tables 1, 2, and 3.

Table 5. Errors between Standard Mercuric Nitrate and Experimental Methods

	Table 1		Table 2		Table 3	
Error	$mgCl_{SIE}$	1.54•mgNa	$mgCl_{SIE}$	1.54•mgNa	$mgCl_{SIE}$	1.54•mgNa
Average absolute error, $\overline{\lvert E \rvert}$, %	40.20	18.01	259.29	23.99	16.91	11.05
Average error, $\overline{E}$, %	−38.17	+13.71	−259.29	−3.65	−16.90	+11.05
Standard deviation of $\overline{E}$, $\sigma_{\overline{E}}$	45.50	20.78	90.35	29.08	9.15	9.15

For additional comparisons between the standard and experimental methods of analyses, t-tests between paired means[8] were made to determine whether there were differences in average chloride measurements among all three methods. Also, F-tests between standard deviations were made to determine significant differences in variability of measurements.[8]

In an attempt to reduce the errors in table 5, correction factors for both experimental data sets were evaluated. From graphs of standard versus experimental data, it was determined that a linear correction factor should yield satisfactory results.

Two types of linear corrections were chosen for comparison. The first was:

$$Y_{corrected} = a + bY_{measured} \tag{1}$$

and the second was an abreviation of the first, namely:

$$Y_{corrected} = bY_{measured} \tag{2}$$

where a and b are constants to be computed for the best $Y_{corrected}$ results. "$Y_{measured}$" is either mg chloride as measured by SIE or mg sodium as measured by FE. To minimize the percent error between the experimental and standard methods, least squares curve fitting techniques were applied to the formula,

$$E = \frac{Y_{actual} - Y_{corrected}}{Y_{actual}} \tag{3}$$

or

$$E = \frac{Cl_{HgNO_3} - (a + bY_{measured})}{Cl_{HgNO_3}}$$

for the first correction equation, and, for the second;

$$E = \frac{Cl_{HgNO_3} - bY_{measured}}{Cl_{HgNO_3}} \tag{4}$$

The value of E, to be estimated using the least squares approach to finding empirical values for a and b, was zero for all pairs of measured data. This curve fitting procedure was applied to three different sets of data; all data, data $<$10mg Cl_{HgNO_3}, and data $>$10mg Cl_{HgNO_3}. The correction equations generated are as follows:

Based on all data in tables 1, 2 and 3;

$$\begin{aligned} mgCl &= 0.53 \cdot (mgCl_{SIE}) - 0.65 \\ &= 0.53 \cdot (mgCl_{SIE}) \\ &= 1.56 \cdot (mgNa) + 0.06 \\ &= 1.69 \cdot (mgNa) \end{aligned} \tag{5}$$

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[8] National Bureau of Standards, *Experimental Statistics,* Handbook 91, para 3-3.12, 4-2.1, Government Printing Office, Washington, DC, 1963.

Based on data <10mg $ClHgNO_3$;

$$\begin{aligned} mgCl &= 0.14\cdot(mgCl_{SIE}) + 0.81 && (6)\\ &= 0.42\cdot(mgCl_{SIE})\\ &= 1.19\cdot(mgNa) + 0.36\\ &= 1.67\cdot(mgNa) \end{aligned}$$

Based on data >10mg $ClHgNO_3$;

$$\begin{aligned} mgCl &= 0.97\cdot(mgCl_{SIE}) - 2.37 && (7)\\ &= 0.88\cdot(mgCl_{SIE})\\ &= 1.68\cdot(mgNa) + 0.40\\ &= 1.72\cdot(mgNa) \end{aligned}$$

Application of the preceding formulas to the sets of data from tables 1 through 3 shows the following correction equations produced the least error:

Based on all data;

$$\begin{aligned} mgCl &= 1.69\cdot(mgNa) && (8)\\ mgCl &= 0.53\cdot(mgCl_{SIE}) - 0.65 \end{aligned}$$

Based on data <10mg $ClHgNO_3$;

$$\begin{aligned} mgCl &= 1.67\cdot(mgNa) && (9)\\ mgCl &= 0.14\cdot(mgCl_{SIE}) + 0.81 \end{aligned}$$

Based on data >10mg $ClHgNO_3$;

$$\begin{aligned} mgCl &= 1.72\cdot(mgNa) && (10)\\ mgCl &= 0.97\cdot(mgCl_{SIE}) - 2.37 \end{aligned}$$

The errors between the standard mercuric nitrate and experimental methods, after correcting the data in tables 1 through 3 with the above equations, are given in table 6.

Table 6. Errors between Standard Mercuric Nitrate and Experimental Methods After Using Correction Equations for Lowest Error

	Table 1		Table 2		Table 3	
Error	$0.53(mgCl_{SIE})-0.65$	$1.69\cdot(mgNa)$	$0.14\cdot mgCl_{SIE}+0.81$	$1.67\cdot mgNa$	$0.97\cdot mgCl_{SIE}$	$1.72\cdot mgNa$
Average absolute error, $\overline{\lvert E\rvert}$, %	46.94	15.5	24.44	25.0	6.67	4.4
Average error, $\overline{E}$, %	45.01	5.5*	−24.08	−12.1	0.82	0.8
Standard deviation of $\overline{E}$, $\sigma_{\overline{E}}$	23.82	22.8	22.16	31.5	8.08	5.2

* Average extent FE over estimated standard method.

As may be seen from tables 5 and 6, a significant reduction in error is achieved by application of correction equations to both experimental methods except for SIE in table 1 and FE in table 2. In these two cases, the direct measurements of chloride result in less error than results obtained using the correction equations. In addition, the flame emission method results produce an average error of at least half that obtained from SIE results, except for table 3 where the error is nearly equal for both methods.

Table 7 shows the results of significance tests based on the data in tables 2 and 3. Based on the two indicators of prediction for comparing the experimental methods with the standard method, [i.e., (1) t-tests between mean milligrams of chloride, and (2) F-ratios between the standard deviations of the chloride measurements], there were no significant differences in results from all three analytical methods for wet candles at Fort Sherman after applying the correction equations. Also, for the data in table 2, there was no significant difference in mean chloride measured by the standard and flame emission methods when the correction equations were applied to the FE data. The standard deviations were significantly different. Because the data in table 2 are among the lowest levels of chloride characteristic of tropic test sites in the Canal Zone, a high percentage variation in measurement should be insignificant when comparing its relative corrosiveness with test sites characterized by much greater saltfall.

Table 7. Significance Tests on Chiva Chiva Data (Table 2) and Fort Sherman Data (Table 3)

Significance Tests	Chiva Chiva (Table 2)					Fort Sherman (Table 3)				
(α = 05)	$mgCl_{HgNO_3}$	$mgCl_{SIE}$	0 14·$mgCl_{SIE}$ + 0 81	1 67·mgNa	1 69·mgNa	$mgCl_{HgNO_3}$	$mgCl_{SIE}$	0 97·$mgCl_{SIE}$ − 2 37	1 72·mgNa	1.69·mgNa
t-Test of Means										
mean	1 13	4 03	1 37	1 29	1.31	17 50	20 34	17.36	17 24 *	* 16 92
t-ratio	NA	10 49*	5 75*	1 68	1.70	NA	7 14*	0 38	0 94	2.03
df = 15										
F-Test of Standard Deviation										
standard deviation	0.19	1 16	0.16	0 51	0 52	3 76	4 16	4 04	3.13	3.08
F-ratio	NA	37.27*	1.41	7 21*	7 49*	NA	1.22	1 15	1.44	1.49
df = 15/15										

* Signifies significant difference between variation in experimental method and standard method ($HgNO_3$)

For both sets of wet candles (tables 2 and 3), the flame emission method provides the closest approximation of those results obtained by the standard mercuric nitrate method. While the correction equations for the FE method that are based on the low (<10mgCl) and high (>10mgCl) ranges may provide a smaller error from the standard method, there is no significant difference in results obtained by using the general equation, mgCl = 1.69·mgNa, for all data ranges.

The average absolute error between the FE results, using the 1.69·mgNa correction equation, and the standard mercuric nitrate method for the wet candles in table 1 is 15.5 percent. Based on the data in tables 2 and 3, the variation of results because of the wet-candle sampling method is 13.1 percent and 18.2 percent, respectively. Hence, the FE analytical method, using the 1.69·mgNa correction equation, introduces no greater variation in chloride measurements than the field sampling method currently used.

Table 8 shows the results of the significance tests on the control data of table 4. No significant differences were found between chloride means for the standard method and FE methods. The standard deviation for the FE method is much less than that for the mercuric nitrate method, therefore causing the significant difference in standard deviations.

The major difference between analyzing control candles and field exposed candles is that control samples do not have interfering ions introduced by the environment, therefore reducing variation in analysis. For the control samples, any of the three analytical methods can be used to obtain equivalent results.

Table 8. Significance Tests on Control Data of Table 4

Significance Tests ($\alpha = 0.05$)	Table 4 Data $HgNO_3$	$mgCl_{SIE}$	$1.54 \cdot mgNa$
t-Test of Means:			
mean	0.61	0.63	0.57
t-ratio	NA	0.24	0.65
df = 15			
F-test of Standard Deviations:			
standard deviation	0.16	0.10	0.07
F-ratio	NA	3.64*	6.23*
df = 11/11			

* Signifies significant difference between standard method ($HgNO_3$).

ECONOMIC ANALYSIS

An economic analysis was completed for this study (see table C-2 for detailed computation) to determine whether the experimental analytical methods of chloride select ion electrode or flame emission spectroscopy were more cost effective than the standard mercuric nitrate method. Based on an economic life of 10 years and a personnel man-hour reduction from 1.325 hours/candle to 0.583 hours/candle for analysis time, a savings to investment ratio of 1.17 will be realized by the Tropic Test Center. This will result in a rate of return on the initial investment of 17 percent per year.

CONCLUSIONS

- The wet-candle sampling method for ambient concentration of chlorides is accurate only to an average of approximately ± 16 percent of the mean chloride content in a salt candle exposed to the tropics of the Canal Zone. The least deviation from chloride measurements made by the mercuric nitrate method was obtained by flame emission spectroscopy for sodium.

- For total chloride measurements less than 10 milligrams,

$$mgCl = 1.67 \cdot mgNa$$

produces the least deviation from the mercuric nitrate standard method.

- For total chloride measurements greater than 10 milligrams,

$$mgCl = 1.72 \cdot mgNa$$

produces the closest approximation of the mercuric nitrate method.

- The chloride to sodium atomic ratios in seawater samples, from both the Atlantic and the Pacific oceans, were nearly equal to the Cl: Na ratio of 1.72. The salt concentration in these candles must be deposited by seawater aerosol and spray impinging on the candle wick.

- For all wet-candle chloride concentration ranges, sodium analysis using the equation,

$$mgCl = 1.69 \cdot mgNa$$

gives the lowest error compared to the standard method, and it is not statistically significant from the standard mercuric nitrate method. The error of analysis is approximately ± 15 percent of the mean chloride content in a wet candle as compared to the ± 16 percent reproducibility of the wet-candle sampling technique.

- The flame emission and selective ion electrode methods both reduce average laboratory analysis time from 8 hours/6 candles (1.3 hours/candle) to 3.6 hours/6 candles (0.6 hours/candle), therefore reducing man-hour requirements and producing a savings/investment ratio of 1.17.

RECOMMENDATIONS

- The presently used standard mercuric nitrate method for measuring water-soluble chlorides in wet candles should be replaced with flame emission spectroscopy for sodium concentration. The correction equation,

$$mgCl = 1.69 \cdot mgNa$$

should be used uniformly for all chloride concentrations to estimate ambient chloride.

No new Test Operations Procedure is recommended because, within the US Army Test and Evaluation Command, this method is used only by the Tropic Test Center.

SECTION III. APPENDICES

APPENDIX A. TEST DIRECTIVE

(COPY)

DEPARTMENT OF THE ARMY
Headquarters, US Army Test and Evaluation Command
Aberdeen Proving Ground, Maryland 21005

Mr. Crowell/dg/870-2775

AMSTE-ME

13 March 1974

SUBJECT: Test Directive, Improved Quantitative Analytical Method for Determination of Atmospheric Chlorides, TECOM Project No. 9 CO 009 000 022

Commander
US Army Tropic Test Center
ATTN: STETC-PD-M
Drawer 942
Ft. Clayton, CZ

1. References:

a. TECOM Regulation 70-12, dated 1 June 1973.

b. Letter, AMSTE-ME, 25 May 1973, subject: FY 74 Methodology Program.

2. This letter and attached Forms 1188 and 1189 (Incl 1) constitute a test directive for the subject investigation under the TECOM Methodology Improvement Program 1U765702D625. Funds will be provided under separate cover. The utilization of funds provided to support the subject investigation is governed by the rules of incremental funding.

3. The Methodology Investigation Proposal at Inclosure 2 and the additional guidance provided at Inclosure 3 are the bases for headquarters approval of the subject investigation. Any deviation from the approved scope, procedures, and authorized cost will require approval from this headquarters prior to execution.

4. Special Instructions:

a. All reporting will be in consonance with paragraph 9, reference 1a. The final report, when applicable, will be submitted to this headquarters by September 1974.

b. Recommendations on new TOPs, or revisions to existing TOPs, will be included as part of the recommendation section of the final report (para 9c, TECR 70-12). Final decision on the scope of the TOP effort will be made by this headquarters as part of the report approval process.

c. This investigation is unclassified.

d. Point of contact at this headquarters is Mr. Albert Crowell, Autovon 870-2775.

FOR THE COMMANDER:

/s/Sidney Wise
/t/SIDNEY WISE
Dir, Methodology Improvement

3 Incl
as

(END COPY)

APPENDIX B. REFERENCES

1. Brierly, W. B., *Bibliography on Atmospheric (Cyclic) Sea-Salts,* US Army Natick Labs, Technical Report No. 70-63-ES, April 1970.

2. Foran, M. R., E. V. Gibbons, and J. R. Wellington, *The Measurement of Atmospheric Sulfur Dioxide and Chlorides,* Chemistry in Canada, Vol 10 (5), p 33–41, May 1958.

3. ASTM-STD, D 2009–65, part 23, *Collection by Filtration and Determination of Mass, Number, and Optical Sizing of Atmospheric Particulates. Recommended Practices for,* pp 854–862, Philadelphia, PA, 1967.

4. Ambler, H. R., and A. A. J. Bain, *Applied Chemistry,* No. 5, p 436, 1955.

5. Intersociety Committee, *Methods of Air Sampling and Analysis, Method 201, Analysis for Chloride Content of the Atmosphere (Manual Method)(12203-01-68T),* p 243, American Public Health Association, Washington, DC, 1972.

6. *Orion Specific Ion Electrodes, Bibliography,* Orion Research Incorporated, Cambridge, MA, 15 January 1970.

7. *Instruction Manual for Model 92-17 Chloride Ion Electrode,* Orion Research Incorporated, Cambridge, MA.

8. National Bureau of Standards, *Experimental Statistics,* Handbook 91, para 3-3.12, 4-2.1, Government Printing Office, Washington, DC, 1963.

APPENDIX C. DATA

Table C-1. Standard Operating Procedures for Wet Candles

1. Preparation of Wet Candles

▲ Cut a 40-inch length of 2-inch wide No. 2 surgical gauze for each candle.

▲ Boil the gauze in distilled water to remove all chlorides. Check a portion of the wash water for chlorides by adding several drops of a 10 percent silver nitrate solution. If a cloudiness or turbidity develops, repeat the washing operation with fresh distilled water until the silver nitrate tests show the absence of residual chloride on the gauze.

▲ Handle the washed gauze with clean rubber or plastic gloves.

▲ Insert, to the rim, a chemically clean ¾-inch x 5¾-inch test tube in a No. 7 rubber stopper that has two parallel flat sides made by butting the stopper on opposite sides. The test tube should protrude above the top of the stopper.

▲ Using clean gloves, wrap the wet gauze around the test tube, from the stopper to the tube tip and then back to the stopper, so that a double layer of gauze has been applied over all the outside portions of the tube that are not in the rubber stopper. Wrap the gauze smoothly and tightly covering all the exposed surfaces of the tube including the top. Approximately 6-inch lengths of gauze should be available, free, at each end, to serve as wicks.

▲ Unless the candle is to be used immediately, dry in a warm oven at 50°C for about 6 hours.

▲ Store the dry candle in a clean container that can be used for transporting to the site. One-quart plastic containers with well-fitting covers have been found convenient for this purpose, as the containers can also be used later for transporting the solution and exposed candle from the site.

2. Emplacement of Wet Candle at the Site

▲ Re-wet the gauze of the candle with distilled water.

▲ Insert the rubber stopper, of the wet-candle assembly, into a clean 500 ml Erlenmeyer flask containing 300 ml of distilled water. Insert the 6-inch lengths of free gauze into the flask so that the gauze ends enter the flask in the spaces between the flat faces of the stopper and the flask neck. The free ends of the wicks should almost touch the bottom of the flask.

▲ Place the wet-candle assembly about 4 feet above the ground so that it is secure and there is access to air from all sides. Flask holders that are used for shaking machines have been found convenient for holding the assembly.

▲ Protect the wet candle from direct rain and sunlight by a slightly sloping roof, approximately 12 inches x 12 inches, centered over the candle and about 2 inches above the tip of the gauze wrapped tube.

3. Exposure

▲ Allow the wet candle to remain undisturbed for the duration of the exposure period, usually one month.

▲ Be sure the two ends of the wick are always immersed in water in the flask. If, during the exposure period, water evaporates, add distilled water periodically to bring the level back to the 300 ml mark. If, during the exposure, rain enters the flask and raises the water level, remove the excess water and store for later addition to the flask's contents at the end of the exposure period.

4. Removal of Wet Candle from Exposure

▲ At the completion of the exposure period, bring the wet-candle assembly to the laboratory for analysis, suitably protecting the gauze and flask contents. Use plastic gloves to put the stopper and wet candle in a one-quart container, adding to the container the water in the flask plus three rinsings with distilled water. The flask can then be reused at the site and only one container has to be transported.

Table C-1 (cont)

5. Control

▲ Where the atmospheric salt content is low, prepare an extra wet-candle assembly and store in a closed container until the completion of the exposure period. Place the control wet-candle assembly and 300 ml of the distilled water in a container and carry through the analytical procedure the same as the exposed wet candles. Use the determined salt value as a blank to be subtracted from the values determined for the exposed wet candles.

6. Preparation of Sample for Analysis

▲ Using clean plastic or rubber gloves, unwind the gauze from the candle and place in a 600 ml beaker. Pour the water from the transport container (or Erlenmeyer flask) into the beaker. Rinse the container, stopper and test tube with distilled water, and add the rinsings to the beaker.

▲ Boil the water in the beaker, containing the gauze, for ten minutes.

▲ Decant the boiled water into a second beaker.

▲ Pour fresh distilled water over the gauze, bring to a boil, and decant the liquid to the second beaker.

▲ Repeat the addition of water over the gauze, bringing to a boil, and decanting to the second beaker.

▲ Evaporate the liquid to a volume of approximately 400 ml, avoiding spattering.

▲ Filter the liquid to remove any insoluble residue. Rinse the beaker, and filter, and add the filtered washings to the filtrate.

▲ Acidify the sample with 3 drops of 10 percent sulfuric acid solution.

▲ Add 0.5 ml of 5 percent potassium permanganate solution. If the pink color is not retained, continue addition of the permanganate solution until the pink color persists.

▲ Allow the sample to stand at least 30 minutes (sample may stand overnight).

▲ Add 3 ml of 3 percent hydrogen peroxide solution and boil for about 5 minutes.

▲ Filter the sample, rinsing the paper and funnel, and adding to the filtrate. If filtrate is not colorless, add additional peroxide, boil, and refilter.

▲ Evaporate the sample to a volume of about 400 ml.

▲ Transfer the solution to a 500 ml volumetric flask. Rinse the beaker, adding the rinsings to the flask and make up to the mark with distilled water.

7. Titration

▲ Transfer a 100-ml aliquot from the volumetric flask to a titration vessel (flask, beaker, or porcelain casserole).

▲ Add 5 drops of diphenylcarbazone-bromphenol blue indicator.

▲ If a yellow or orange color develops, add 0.25N sodium hydroxide solution, dropwise, until a blue color develops.

▲ To the blue or blue-violet colored sample, add 0.5N nitric acid solution, dropwise, until a yellow or orange color develops.

▲ Add one additional ml of 0.05N nitric acid solution (pH of sample should be 3.2–3.4).

▲ Titrate with 0.025N mercuric nitrate solution to a persistant blue-violet endpoint.

▲ Use the average of three titrations of 100-ml aliquots.

Table C-1 (cont)

8. Calculations

▲ Calculate the chloride trapped by the wet candle in terms of milligrams of chloride per square meter of exposed gauze per day.

$$\text{mgCl/m}^2\text{/day} = \frac{35.46 \cdot f \cdot V \cdot N}{T \cdot A}$$

where f = factor for dilution = 5 for 100-ml aliquot
V = volume, in ml, of mercuric nitrate solution required for titration
N = normality of mercuric nitrate solution
T = exposure time in days
A = exposure area of gauze in square meters—if test tube is used as described above, the exposed area should be 0.01 square meter

For .025N mercuric nitrate solution and a 30-day month,

$$\text{mgCl/m}^2\text{/day} = \frac{35.46 \cdot f \cdot V \cdot N}{T \cdot A} = \frac{(35.46)\ (5)\ (V)\ (.025)}{(30)\ (0.01)} = 14.8V$$

NOTES: If the chloride content is vey low, the titration analysis with mercuric nitrate may be replaced by a spectrophotometer analysis using the mercuric nitrate reagent. See Clarke, F. E., *Analytical Chemistry*, Vol 22, p 553, 1950.

If the chloride content is very high, a less aliquot than 100 ml should be titrated or the sample should be titrated with 0.250 N mercuric nitrate.

9. Reagents

▲ Silver Nitrate

Dissolve 1.6 gm silver nitrate in 100 ml water

▲ Sulfuric Acid Solution (10 percent)

To 90 ml of water add, cautiously, 10 ml concentrated sulfuric acid

▲ Potassium Permanganate Solution (5 percent)

Dissolve 5 gm potassium permanganate in 100 ml of water

▲ Hydrogen Peroxide (3 percent)

Use commercially available solution

▲ Sodium Hydroxide (0.025N)

Dilute 2.5 ml 1 N sodium hydroxide to 100 ml. Prepare 1 N sodium hydroxide by dissolving 42 grams sodium hydroxide sticks or pellets in water and dilute to 1 liter.

▲ Nitric Acid (0.05N)

Dilute 3.2 ml nitric acid (sp gr 1.42) to 1 liter

▲ Diphenylcanbazone-bromphenol blue mixed indicator

0.5 gm diphenylcanbazone, C. P. crystal
0.05 gm bromphenol blue, C. P. crystal
Dissolve in 95 percent ethanol, or absolute methanol
Dilute with alcohol to 100 ml

▲ Standard, Potassium Chloride (1 gm chloride per liter)

Dissolve 2.103 gm potassium chloride (C. P.) in 500 ml distilled water
Dilute to 1 liter

▲ Mercuric Nitrate (0.025N)

Dissolve 4.17 gm mercuric nitrate ($Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$, C. P.) in about 50 ml of distilled water to which the equivalent of 0.35 ml concentrated nitric acid had been added. Dilute to 1 liter with distilled water. Standardize by titration against potassium chloride solution containing 0.01 gm chloride prepared by taking a 10-ml aliquot of the potassium chloride stock solution. Add 100 ml distilled water. Adjust pH to 3.2 to 3.4 with 0.05N nitric acid. Titrate with mercuric nitrate solution using the diphenylcanbazone-bromphenol blue indicator.

$$\text{Normality of mercuric chloride} = \frac{\text{grams chloride}}{0.03546 \times \text{ml mercuric nitrate solution}}$$

If 10 ml of stock solution is used:

$$\text{Normality} = \frac{0.01}{0.03546 \times \text{ml}} \doteq \frac{.282}{\text{ml}}$$

Table C-2. Economic Analysis/Program Evaluation Summary of Costs for Format A-1

Submitting DOD Component: US Army Tropic Test Center

Economic Analysis of Three Analytical Procedures for Chloride
[$HgNO_3$ Titration – Flame Emission (FE) – Select Ion Electrode (SIE)]

Objective: To determine the most cost effective method for processing wet candles without sacrificing accuracy.

Present Alternative: $HgNO_3$ titration method requiring a large amount of reagents, supplies, laboratory space and handling. Economic Life: 10 years

Proposed Alternative: FE or SIE method Economic Life: 10 years

	(Operations) Costs				
Project Year	Present Alternative	Proposed Alternative	Differential Cost	Discount Factor	Discounted Differential Cost
1976	$3811	$1677	$2134		
1977	3811	1677	2134		
1978	3811	1677	2134		
1979	3811	1677	2134		
1980	3811	1677	2134		
1981	3811	1677	2134		
1982	3811	1677	2134		
1983	3811	1677	2134		
1984	3811	1677	2134		
1985	3811	1677	2134		
TOTALS				6.447	$13,758

Present Value of New Investment:	
Land and buildings	None
Equipment	None
Other—Man-hour cost for chemical research required to develop the new method	$11,800
Working capital (change—plus or minus)	
Total Present Value of New Investment:	$11,800
Plus: Value of existing assets to be employed on the project	None
Less: Value of existing assets replaced	None
Less: Discounted Terminal Value of new investment	None
Total New Present Value of New Investment:	$11,800
Present Value of Cost Avoidance:	$13,758
Plus: Present value of the cost of refurnishment or modification eliminated	None
Total Present Value of Cost Avoidance:	$13,758

Savings/Investment Ratio: $13,758 ÷ $11,800 = 1.17

Rate of Return on Investment: 17 percent

Source/Derivation of Cost Estimates:

Investment Costs—

Changes in working capital—total cost of the investigation was $11,800
Net terminal value—NA

Recurring Costs (Operations)—

Personnel—assuming 22 wet candles will be processed each month, the following estimates are presented—

$HgNO_3$ Method	FE or SIE Method
Twenty-two candles per month times 12 months times 1.325 hours/candle times $10.89 per man-hour equals $3,809 per year.	Twenty-two candles per month times 12 months times 0.5833 hours/candle times $10.89 per man-hour equals $1,677 per year.

Operating—operating costs are nominal and approximately equal and therefore not considered.

Overhead Costs—these costs do not change as a result of the investigation and therefore were not considered.

J. C. Bryan, Operations Research Analyst 2 June 1975

APPENDIX D. SYMBOLS AND ABBREVIATIONS

Cl = Chloride ion
Cl:Na = Chloride to sodium atomic ratio
$HgNO_3$ = Mercuric nitrate
Na = Sodium ion
ppm = Parts-per-million = micrograms/milliliter of solution
SIE = Chloride select ion electrode