

CHLORIDE MONITORING

Chloride concentration monitoring of the electrolyte is crucial to the efficiency and success of electrolytic reduction when conserving metal objects recovered from marine environments. Several methods to quantitatively monitor chloride concentration exist. The mercuric nitrate titration method is recommended in this manual due to its simplicity and low cost.

MERCURIC NITRATE METHOD OF CHLORIDE DETERMINATION

The mercuric nitrate test is a quantitative method used to determine Cl^- or NaCl in parts per million in an aqueous solution. It is a quick and simple test to perform and gives accurate and consistent results. The following procedure is a modification of the method outlined by Furman (1962:331-332).

Equipment:

1. One automatic 25 ml burette
2. Two small amber glass bottles with droppers
3. One 500 ml amber glass bottle
4. One 250 ml beaker
5. A magnetic stirrer
6. Teflon-coated stirring bars

Chemicals:

1. Diphenylcarbazone-bromophenol blue indicator
2. 0.02N mercuric nitrate solution.
3. Sulfuric acid

Transfer the blue indicator and the sulfuric acid to the amber dropper bottles. The mercuric nitrate should be stored in the amber glass bottle for refilling the burette.

Procedure:

1. Take a 20 ml sample of electrolyte or solution to be tested, and place it in the glass beaker.
 2. Place the beaker on the magnetic stirrer and put a Teflon stirring bar in the beaker.
 3. Adjust the stirrer until the liquid is in a steady swirl.
 4. Add five drops of diphenylcarbazone-bromophenol blue indicator. This will change the color of the solution to blue.
 5. Add drops of sulfuric acid (usually 18N for sodium hydroxide electrolytes, 9N for sodium carbonate electrolytes, or 4.5N for water solutions) to the solution until an acid end point is reached. The acid end point is indicated by a color change from blue to clear. (The amount of sulfuric acid does not need to be measured as it only acidifies the sample for the next step.)
 6. Titrate 0.02N mercuric nitrate, drop by drop, from the automatic burette into the beaker until the solution reaches a violet end point. The color changes gradually from clear to violet. Near the end point, each drop will show a flash of color. Continue until a single drops swirls into a single even violet color through out the solution. **Note:** the sensitivity of the titration can be increased by using a smaller normality solution or decreased by using a larger normality solution of mercuric nitrate.
 7. Note the amount of mercuric nitrate titrated to reach the end point.

The concentration of chloride or sodium chloride in parts per million is calculated by the following formulas:

$$\frac{T \times N \times 0.03545 \times 1,000,000}{20} = T \times N \times 1772.5 = \text{ppm Cl}^-$$

$$\frac{T \times N \times 0.05846 \times 1,000,000}{20} = T \times N \times 2923 = \text{ppm NaCl}$$

where

T = amount of mercuric nitrate titrated

N = normality of mercuric nitrate

In order to facilitate the calculation of chloride concentrations, a conversion table can be established using the formulas above:

| Amount of Mercuric Nitrate Titrated (ml) | ppm Cl⁻ | ppm NaCl |
|---|---------------------------|-----------------|
| 0.1 | 3.5 | 5.8 |
| 0.2 | 7.0 | 11.7 |
| 0.3 | 10.6 | 17.5 |
| 0.4 | 14.0 | 23.4 |
| 1.0 | 35.0 | 58.5 |
| 10.0 | 350.0 | 585.0 |
| etc. | etc. | etc. |

The mercuric nitrate test gives the total amount of Cl⁻ or NaCl in the electrolyte. Unused electrolyte solution, however, will already contain a certain amount of chlorides. In order to determine the amount of chlorides expelled from the artifact, the amount of chlorides present in an unused sample of the electrolyte must be determined. This provides a 'blank' which is subtracted from the amount of chlorides present in a sample taken from the electrolytic bath. For example, if a sample taken from an active electrolytic bath contains 24.5 ppm of Cl⁻ while an unused sample of the same electrolyte contains 17.5 ppm, the amount of chlorides in the electrolytic bath that have been expelled from the artifact is 7.0 ppm.

Comments on the Mercuric Nitrate Test

Throughout this entire process, the glassware must be kept clean and uncontaminated. To prevent cross contamination, a clean beaker and stirring rod should be used for each electrolyte sample, or these items should be washed thoroughly and rinsed with de-ionized water between each sample. Purple mercuric nitrate stains can be removed from the stirring rods by immersing them in dilute solution of nitric acid.

Two notes should be added with regard to the chloride testing procedure. First, the diphenylcarbazone-bromophenol end point is to some degree subjective, but most individuals are consistent about their end point. Therefore, the most reliable and consistent results are obtained when only one individual is responsible for monitoring the electrolyte. To further assure the consistency of chloride monitoring, the reagents should be tested weekly against a known sodium chloride solution.

All of the chemicals in the concentrations required for the chloride test can be purchased from a chemical supply house. Chemical costs can be considerably decreased, however, if the chemicals are mixed in the lab as follows:

18N Sulfuric Acid, H₂SO₄: Dilute reagent-grade sulfuric acid with an equal volume of distilled or de-ionized water. Slowly add the acid to the water, never the water to the acid. Extreme heat will be generated. Let cool.

0.02N Mercuric Nitrate Solution, Hg(NO₃)₂ · H₂O: Dissolve 3.42 g of reagent-grade mercuric nitrate in 1 liter of distilled or de-ionized water.

Diphenylcarbazone-bromophenol blue indicator: Dissolve 0.5 g of reagent-grade crystalline diphenylcarbazone and 0.05 g of crystalline bromophenol blue in 100 ml of 95 percent ethanol.

1000 ppm Sodium chloride solution (to test reagents): Dissolve 1 g of reagent-grade sodium chloride in 1 liter of distilled or de-ionized water. Dilute in half for 500 ppm NaCl, dilute a second time for 250 ppm, etc.

During electrolytic cleaning, the chloride level should be calculated and recorded at least once a week. These calculations can be used to make a graph that visually depicts at a glance the progress of chloride removal from an artifact. This will save much valuable time and enable the conservator to determine when all detectable soluble chlorides have been removed from the object, as well as when to change a chloride-contaminated electrolyte. Systematic chloride monitoring assures that the artifact will remain in electrolysis for the least amount of time necessary. Chloride monitoring cannot, however, be used to determine the efficiency of the reduction of the iron compounds. This can only be confirmed with analytical tests on samples taken from the artifact before and after treatment.

The graph in [Figure 10A.1](#) presents the progress of a typical iron artifact recovered from a marine environment. It clearly depicts the high initial rise in chlorides released from the artifact and the subsequent decrease as the electrolyte is periodically changed. Drops in the graph to the zero line represent electrolyte changes. The two-week gap in the graph in November indicates when the artifact was taken out of electrolysis in order to mechanically clean the remaining encrustation and loose corrosion products. Occasionally, a drop from a previous high is seen on some chloride graphs, especially when the chloride level is high. This may be caused by chlorides reacting with corrosion products from the anode, chlorate formation, or the actual liberation of chlorine which causes the chlorides to be undetectable by taking them out of solution. Electrolysis is continued until the chloride concentration levels off for several days and does not increase above that present in a 'blank' of the electrolyte.

