



Inorganic Chloride in Refinery Waters

UOP Method 456-19

Scope

This method is for determination of inorganic chloride in various water streams at refineries, containing any of the four major interferences present individually or combined. The lower limit of quantification is 1 mg/kg (mass-ppm). Concentrations greater than 2 mass % can be determined after dilution with deionized water.

References

ASTM Method D1193, "Specification for Reagent Water," www.astm.org

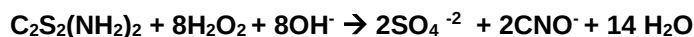
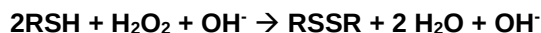
UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is oxidized with hydrogen peroxide in alkaline medium to remove interferences like Sulfides, Cyanide, Rubeanic acid & Mercaptans. It is then titrated with standard silver nitrate solution to a potentiometric endpoint.

Rubeanic acid (Dithiooxamide) is generally formed in refinery water after reaction between dissolved Cyanogen & Hydrogen sulfide gas.

The following reactions takes place with Hydrogen peroxide in alkaline condition



Apparatus

Reference to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1 mg

Beakers, glass, 250-mL, Duran, Sigma Aldrich, Cat No. Z680893

Cylinder, graduated, class A, 50 mL, Sigma Aldrich, Cat No. Z740844

Desiccator, Non-vacuum, ID 170 mm with porcelain plate, Sigma Aldrich, Cat No. SLW1590/02D

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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Electrodes, Combined Ag- ring electrode, Titrode™, Inner filling 1 Mol/Liter KNO₃, Metrohm, Cat No. 6.0450.100.

Flask, Volumetric, Class A, 500 mL, Sigma Aldrich, Cat No. Z306460

Hot plate, Thermo Super-Nuova multi-place digital hotplate, Fisher Scientific, Cat No. 11-475-30Q

Pipets, volumetric transfer, Class A, 1, 2, 10, and 50 mL, Sigma Aldrich, Cat No. Z740920, Z740921, Z740924, and Z740928 respectively

Pipet Filler, Natural rubber, bulb type, Sigma Aldrich, Cat No. Z136468

Pipet, Pasteur plastic 3.5 mL, Sigma Aldrich, Cat No. Z331759

Titration, Potentiometric, recording ± 2000 mv range, 1 mv resolution, capable of reducing the titration rate to a minimum in the vicinity of the end point, with dispenser having a volume readout of 0.00-99.99 ml with 0.0001 of the burette volume resolution, Metrohm Auto titrator Model 905 Titration system with optional sample changer and 20 mL burets, Metrohm USA, Cat. No. 2.905.0010

Titration stand, Metrohm 801 Stirrer, Metrohm USA, Cat. No. 2.801.0040

Reagents

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

Desiccant, Silica gel beads, Indicating, 6 to 18 Mesh, J.T. Baker, Fisher Scientific, Cat No 02-003-900

Hydrogen peroxide, 30%, Emsure, Sigma Aldrich, Cat No. 1072090500

Nitric Acid, trace metal grade, Fisher Scientific, Cat No. A509-P212.

Nitric Acid, 1:1 aqueous solution, prepare by diluting an equal volume of concentrated acid into deionized water

pH strip, 0-14, Sigma Aldrich, Cat No. P4786

Silver nitrate, 0.1 Molar standard ampule, Honeywell Fluka, Fisher Scientific, Cat No. 60-046-732

Silver Nitrate, 0.1 Molar aqueous solution, Tear the ampule and carefully transfer all content of ampule to a 1000 mL standard volumetric flask. Rinse the inside of ampule at least two times to recover all content and transfer to volumetric flask. Make up the volume to the mark with deionized water. Transfer the entire solution to an amber colored bottle.

Silver Nitrate, 0.01 Molar solution, Withdraw 50 ml of 0.1 Molar silver nitrate solution by pipet and transfer to a 500 mL volumetric flask. Make up the volume to the mark with deionized water. Transfer the entire solution to an amber colored bottle.

Sodium hydroxide bead, 500 g, Sigma Aldrich, Cat No. S5881-500G,

Sodium Hydroxide Solution, 1 Molar, 250 mL, Pour 80-100 mL Deionized water in a 250ml beaker. Carefully weigh 10 gm of Sodium Hydroxide beads in watch glass and transfer to beaker. Dissolve the beads by stirring with glass rod. Using funnel, transfer this solution to a 250 mL volumetric flask. Rinse the beaker with approx. 50 mL of Deionized water and transfer to the 250 mL volumetric flask. Then make up the volume to the mark with Deionized water. Transfer and store the entire solution in

a plastic bottle- OR- Prepare from Honeywell Fluka, Fisher scientific Sodium Hydroxide Concentrate, for 1 Liter ,1 Molar solution, Cat No. 60-014-63. Tear the ampule and carefully transfer all content of ampule to a 1000 mL standard volumetric flask. Rinse the inside of ampule at least two times to recover all content and transfer to volumetric flask. Make up the volume to the mark with deionized water. Transfer and store the entire solution in a plastic bottle

Sodium Chloride salt, 500 gm, Sigma-Aldrich, Cat No. S5886-500G

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory practice, technique of potentiometric titration and equipment being used. Inorganic chloride are abundant in a wet lab. The most common source of contamination is tap water. Care must be taken during washing of beakers, pipette & stirrer before starting activity. It is always advisable to wash all glassware thoroughly by deionized water before this analysis.

Silver–Silver Chloride Electrode Preparation and Reconditioning

Proper electrode preparation is essential to obtain reproducible and noise-free titration curves having good endpoints. An electrode should be dedicated to chloride analysis. Prepare and recondition the silver-silver chloride electrode as follows:

1. Clean the silver surface with a Scotch-Brite pad. Rinse with distilled water.
2. Weigh approximately 0.1 g of Sodium chloride and place in a beaker. Using a graduated cylinder, add 20 mL of 20% sulfuric acid and 80 mL of distilled water to the beaker. Immerse the electrode and titrate to the endpoint with 0.1N silver nitrate.
3. Remove the electrode from the solution and rinse with distilled water.
4. Wipe the excess silver chloride from the electrode with a wiper.
 - The electrode should be cleaned after each titration by rinsing with distilled water.

The freshly coated silver-silver chloride electrode may be stored in distilled water or carefully dried using tissues and stored for future use. It is necessary to repeat the electrode preparation when the AgCl begins to peel from the surface.

Standardization of Silver Nitrate solution

1. Assemble and operate the titrator & electrodes according to the manufacture's instruction.
2. Fill the dispenser reservoir of the titrator with 0.01 M or 0.1 M Silver nitrate solution. It is better to have dedicated dispenser reservoirs for different concentrations of silver nitrate to avoid contamination.
3. Transfer Sodium Chloride to a weighing bottle and dry it at 120°C in air oven for 2 hours.
4. Remove weighing bottle containing Sodium Chloride and place it inside desiccator, cover it and allow to cool to room temperature.
5. Weigh accurately 0.05-0.06 g of dried Sodium Chloride, to the nearest 0.1 mg, in a 250-mL glass beaker and record the mass of Sodium Chloride taken.
6. Pour 100 mL of Chloride free deionized water into the beaker and dissolve the Sodium Chloride completely.

7. Place a stirring bar in 250 mL beaker. Place beaker on titration stand, immerse electrode & dispenser tip in such a way that they are well apart from each other. The electrode tip should be adequately immersed inside solution being titrated but should not be too close to the stirring magnet bar, which may damage electrode.
 - Adjust the stirring speed to create a vortex inside standard solution such that bubbles do not develop and accumulate over the electrode surface.
8. The titration using an auto titrator is to be carried out in Dynamic Equivalence Point titration ('DET') mode. This ensures that initial dosing rate will be higher and it will slow down as titration approaches the end point
9. For each titration, calculate molarity of Silver nitrate solution to three significant figures, using Equation 1.

$$M = \frac{A10^3}{58.44B} \quad (1)$$

where:

M = Molarity of Silver nitrate, Moles/ L
10³ = Factor to convert Moles / mL to Moles / L
A = Mass of Sodium Chloride weighed in beaker, g
B = Volume of silver nitrate consumed to reach endpoint, mL
58.45 = Molar mass of Sodium Chloride, g/ Mol.

10. Calculate the average of three determinations to three significant figures.
 - Results of three successive values should not deviate more than 0.001 M. If results deviate more than this, check reagent preparation and also check settings of instrument.
 - It is better to standardize silver nitrate solution once per week and the solution should be kept in an amber color bottle.

Titration of Sample

Chlorides are one of the most available sources of contamination in wet chemistry labs. The easy route of contamination is from glassware like beakers, pipettes, reagent bottles, etc. The analyst must make sure that all glassware are properly cleaned with Deionized water.

1. It is advisable that withdrawing of sample, addition of reagents and sample digestion is carried out under a laboratory fume hood. Some refinery water may contain dissolved Hydrogen sulfide gas, and those sample bottles must be handled under fume hood.
2. Pipette out a suitable volume of aliquot (see table 1) in to a 250-mL graduated beaker. Considering the sample contain lower level of chloride, add 30 mL of deionized water to it. Add approximately 1 mL of 1 M sodium hydroxide using a plastic Pasteur pipette. Carefully stir the solution with glass rod. Use a color indicator pH strip to make sure that pH is above 12.
3. Add carefully 20 mL of 30% hydrogen peroxide with constant stirring by glass rod.
 - In case of sample containing around 1% Hydrogen sulfide, a vigorous reaction takes place during addition of Hydrogen peroxide. This reaction is exothermic. In this case and in every case, add Hydrogen peroxide portion wise and stir with glass rod until the reaction subsides.
4. Adjust the volume of solution to 100 mL by adding deionized water from a graduated cylinder.
5. Gently boil the content over a hot plate. Keep the glass rod inside beaker to stir the solution intermittently.
 - Keep eye on digital display of hot plate, at no time should the hot plate surface temperature exceed 145°C. Thermal decomposition of Hydrogen peroxide accelerates at 150°C, which may produce potential explosive conditions.

6. Repeat steps 2 – 5 for each additional sample and also for a reagent blank using 80 mL of deionized water.
7. Gently boil until the volume is reduced to 50 mL, indicated by mark of graduated beaker. Cool to room temperature.
8. Adjust the volume of solution to 100 mL. Acidify the solution by adding 1:1 Nitric acid using a plastic Pasteur pipette and color indicator pH paper strip to approximately pH 2.
9. Wash the glass rod and inner wall of glass beaker with deionized water to collect the last trace of chloride.
10. Add a stirring bar and Place the beaker on the titration stand. Immerse the electrode and start titration. Note the endpoint at end of potentiometric titration and calculate chloride concentration manually or using a formula created in the auto titrator software.
 - Adjust the stirring speed to a create vortex inside solution such that bubbles do not develop and accumulate over the electrode surface.
 - The dispenser tip and electrode should be positioned far enough apart to get a noise free titration and a perfect inflection point.
 - Depending on chloride concentration, the starting potential difference (in millivolt) generally lies on negative side. Higher negative value indicates higher chloride concentration in sample.
11. Titrate the reagent blank using the same procedure as the samples. This ensures exclusion of the trace amount of chloride contamination which may come from the reagents.
 - In general, the blank value may vary from 0.05 to 0.1 mL, depending on sensitivity of electrode, during titration with 0.01 M Silver nitrate.
 - A proper blank value may not be detected during titration with 0.1 M silver nitrate. In that case, the blank value may be excluded.

Table 1
Recommended sample size and Titrant Molarity

<u>Sample Size, ml</u>	<u>Silver Nitrate Molarity</u>	<u>Chloride content, mass-ppm</u>
50	0.01	1-100
10	0.01	100-1000
2	0.01	1000-8000
1	0.1	8000 & above

Calculations

Determine the amount of Chloride in the sample using Equation 2

$$\text{Chloride, mg/kg} = \frac{35450 (A - B)M}{DV} \quad (2)$$

where:

A = volume of silver nitrate used in titration for sample, mL

B = volume of silver nitrate used in titration for blank, mL

M = molarity of silver nitrate used

D = density of sample (usually unity), g/mL

V = volume of sample, mL.

35450 = Molar mass of Chloride multiplied by 1000, to convert g to mg.

Potentiometric Curve

See Figures 1 & 2 for examples of typical titration curves for Chloride determination in aqueous medium by Silver nitrate as titrant under DET (Dynamic Equivalence Point Titration) mode, using Metrohm Autotitrator.

Precision

Precision statements were determined using UOP Method 999, from precision data obtained using a Metrohm Autotitrator Model 905

Repeatability and Intermediate Precision

A nested design was carried for determining Chloride in four samples of different concentration levels with two analysts in one laboratory with each-analyst performing two analyses on two separate days on each level chloride concentration, resulting eight analyses for each chloride concentration. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable differences shown in Table 2 with 95% confidence.

Table 2
Repeatability and Intermediate Precision, mass -ppm

	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Chloride, ppm	8	0.3	1	0.4	2
Chloride, ppm	247	1.6	6	1.9	7
Chloride, %	0.15	0.001	0.01	0.001	0.01
Chloride, %	1.19	0.006	0.02	0.008	0.03

The data in Table 2 represents short term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 1.2 hours. The labor requirement is 0.7 man-hour.

Suggested Supplier

Metrohm USA 9250 Camden Field Parkway, Riverview, FL 33578, USA, www.metrohm.com

Sigma Aldrich, Customer Support, PO Box 14508, St. Louis, MO 63178, USA, (800-325-3010)
www.sigmaaldrich.com

Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300) www.fishersci.com

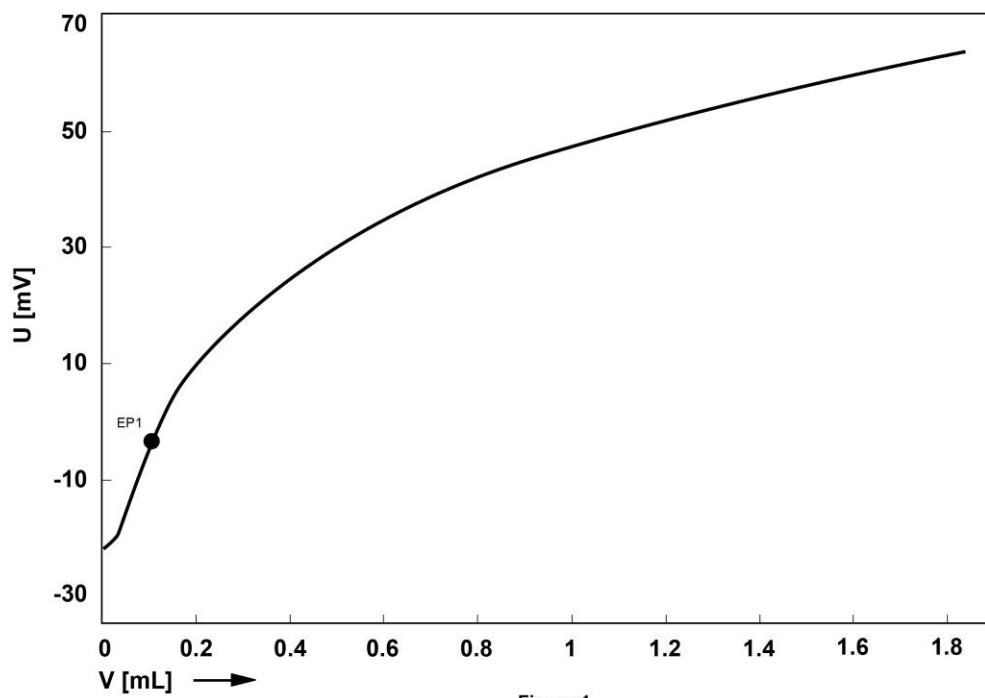


Figure 1
A typical curve of blank titration

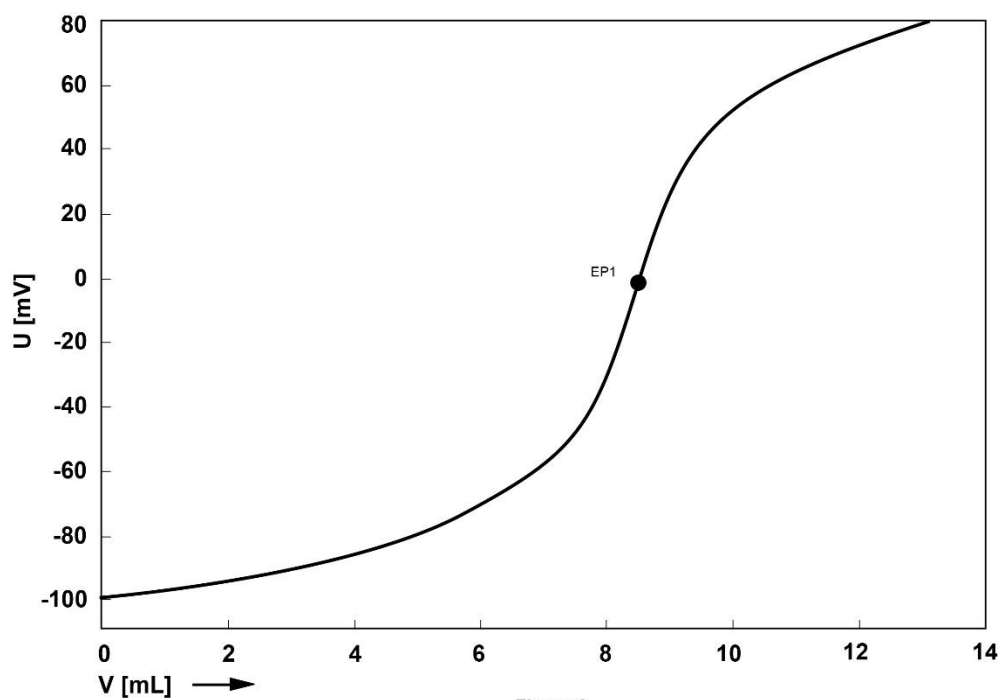


Figure 2
A typical curve of sample titration