

**ASIAN INSTITUTE OF TECHNOLOGY
SCHOOL OF ENVIRONMENT, RESOURCES AND DEVELOPMENT
Urban Environmental Engineering and Management Program**

Chloride Determination : Argentometric Method

Chlorides occur in all natural waters in widely varying concentration. Chlorides, in the form of chloride (Cl^-) ion, is one of the major inorganic anions in water and wastewater. Human excreta, particularly the urine, contain chloride in an amount about equal to the chlorides consumed from food and water. Thus, sewage effluents add considerable chlorides to receiving streams. A high chloride content exerts a deleterious effect on metallic pipes and structures, as well as on agricultural plants.

Principle:

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

The argentometric method is suitable for use in relatively clear waters when 0.15 to 10 mg Cl^- are present in the portion titrated.

Interference:

Substances in amounts normally found in potable water will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with H_2O_2 . Orthophosphate in excess of 25 mg/L interferes by precipitating as silver phosphate. Iron in excess of 10 mg/L interferes by masking the end point.

Procedure:

50-100 mL **Sample** in 250 ml-flask



Add 1 mL **K_2CrO_4** indicator



Titrate with **0.0141N AgNO_3**



Pinkish yellow at the end point

Note:

- For blank, use distilled water and follow the same procedure.
- If sample is highly colored, add 3 mL **Al(OH)₃**, mix, let settle, and filter.
- If sulfide, sulfite or thiosulfate is present, add 1 mL **H₂O₂** and stir for 1 minute.
- Adjust sample pH to 7-10 with **H₂SO₄** or **NaOH** if it not in this range.

Calculation:

$$\text{Chloride, mg/L} = \frac{(A-B) \times 0.0141 \times 35450}{\text{ML Sample}}$$

Where A = mL titration for sample

B = mL titration for blank

$$\text{NaCl, mg/L} = (\text{mg Cl}^- / \text{L}) \times 1.65$$

Preparation of Reagents**Potassium chromate indicator:**

Dissolve 50 g K₂CrO₄ in a little distilled water. Add AgNO₃ solution until a definite red precipitate is formed. Let stand for 12 h, filter, and dilute to 1 L with distilled water.

0.0141N Silver nitrate titrant:

Dissolve 2.395 g AgNO₃ in distilled water and dilute to 1 L. Standardize against standard NaCl solution as described below. **Store in a brown bottle.**

Standard sodium chloride solution:

Dissolve 824.0 mg NaCl (Dried at 140° C) in distilled water and dilute to 1,000 mL. (1 mL = 500 µg Cl⁻)

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Sulfate Determination : Turbidimetric Method

Sulfate (SO_4^{2-}) is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute large amounts of SO_4^{2-} through pyrite oxidation. Sodium and Magnesium sulfate exert a cathartic action. For this reason the recommended upper limit is 250 mg/L in waters intended for human consumption.

Combustion of fossil fuels in power plants and automobiles leads to the formation of oxides of nitrogen and sulfur, which when mixed with rain, hydrolyze to form sulfuric and nitric acids. The resulting acid rain can lower the pH in poorly buffered lakes, adversely affecting aquatic life, and can increase the amount of chemicals, such as aluminum, leached from soil into surface runoff. For these reasons, control has been placed on the amount of sulfur and nitrogen oxides that can be discharged to the atmosphere through combustion.

Principle:

Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride (BaCl_2) so as to form barium sulfate (BaSO_4) crystals of uniform size. Light absorbance of the BaSO_4 suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

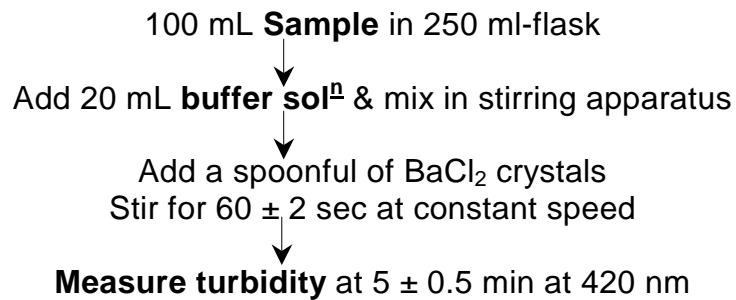
Interference:

Color or suspended matter in large amounts will interfere. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate BaSO_4 satisfactory.

Minimum detectable concentration:

Approximately 1 mg SO_4^{2-} /L

Procedure:



Calculation :

$$\text{Sulfate, mg/L} = \frac{\text{mg SO}_4^{2-} \times 1000}{\text{ML Sample}}$$

Preparation of Reagents

Buffer solution A:

Dissolve 30 g magnesium chloride, MgCl₂·6H₂O, 5 g sodium acetate, CH₃COONa·3H₂O, 1.0 g potassium nitrate, KNO₃, and 20 mL acetic acid, CH₃COOH (99%), in 500 mL distilled water and make up to 1000 mL.

Barium chloride:

BaCl₂, crystals, 20 - 30 mesh. In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

Standard sulfate solution:

Prepare a standard sulfate solution as described in 1) or 2) below; 1.00 mL = 100 µg SO₄.

- 1) Dilute 10.4 mL standard 0.0200 N H₂SO₄ to 100 mL with distilled water
- 2) Dissolve 0.1479 g anhydrous Na₂SO₄ in distilled water and dilute to 1000 mL.

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Metals Determination by Atomic Absorption Spectrophotometer

The effects of metals in water and wastewater range from beneficial through troublesome to dangerous toxic. Some metals are essential, others may adversely affect water consumers, wastewater treatment systems, and receiving waters. Some metals may be either beneficial or toxic, depending on concentration.

Because requirements for determining metals by atomic absorption spectrometry vary with metals and/or concentration to be determined. The determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc can be done by direct aspiration into an air-acetylene flame.

Principle of Flame Atomic Absorption Spectrometry:

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over limited concentration range. Most atomic absorption instrument also equipped for operation in an emission mode.

TABLE 3111:1. ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wave length nm	Flame Gases*	Instrument Detection Limit mg/L	Sensitivity mg/L	Optimum Concentration Range mg/L
Ag	328.1	A-Ac	0.01	0.06	0.1-4
Al	309.3	N-Ac	0.1	1	5-100
Au	242.8	A-Ac	0.01	0.25	0.5-20
Ba	553.6	N-Ac	0.03	0.4	1-20
Be	234.9	N-Ac	0.005	0.03	0.05-2
Bi	223.1	A-Ac	0.06	0.4	1-50
Ca	422.7	A-Ac	0.003	0_08	0.2-20
Cd	228.8	A-Ac	0.002	0.025	0.05-2
Co	240.7	A-Ac	0.03	0.2	0.5-10
Cr	357.9	A-Ac	0.02	0.1	0.2-10
Cs	852.1	A-Ac	0.02	0.3	0.5--15
Cu	324.7	A-Ac	0.01	0.1	0.2-10
Fe	248.3	A-Ac	0.02	0.12	0.3-10
Ir	264.0	A-Ac	0.6	8	-
K	766.5	A-Ac	0.005	0.04	0.1-2
Li	670.8	A-Ac	0.002	0.04	0.1-2
Mg	285_2	A-Ac	0.0005	0.007	0.02-2
Mn	279.5	A-Ac	0.01	0.05	0.1-10
Mo	313.3	N-Ac	0.1	0.5	1-20
Na	589.0	A-Ac	0.002	0.015	0.03-1
Ni	232.0	A-Ac	0.02	0.15	0.3-10
Os	290.9	N-Ac	0.08	1	-
Pb ⁺	283.3	A-Ac	0.05	0.5	1-20
Pt	265.9	A-Ac	0.1	2	5-75
Rh	343.5	A-Ac	0.5	0.3	-
Ru	349.9	A-Ac	0.07	0.5	-
Sb	217.6	A-Ac	0.07	0.5	1-40
Si	251.6	N-Ac	0.3	2	5-150
Sn	224.6	A-Ac	0.8	4	10-200
Sr	460.7	A-Ac	0.03	0.15	0.3-5
Ti	365.3	N-Ac	0.3	2	5-100
V	318.4	N-Ac	0.2	1.5	2-100
Zn	213.9	A-Ac	0.005	0.02	0.05-2

*A-Ac = air-acetylene; N-Ac = nitrous oxide-acetylene..

+The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

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W A T E R Q U A L I T Y S T A N D A R D S

1) Industrial Effluent Standards for Industrial Plants and Industrial Estates

Item	Unit	Standard Values
1. pH Value	-	5.5-9.0
2. Total Dissolved Solids (TDS).	mg/l	2.1) not more than 3,000 mg/l depending on receiving water or type of industry under consideration of Pollution Control Committee (PCC) but not exceed 5,000 mg/l 2.2) not more than 5,000 mg/l exceed TDS of receiving water having salinity of more than 2,000 mg/l or TDS of sea if discharge to sea
3. -Suspended Solids (SS)	mg/l	not more than 50 mg/l depending on receiving water or type of industry or type of waste water treatment system under consideration of PCC but not exceed 150 mg/l
4. Temperature	°C	not more than 40
5. Color and Odor	-	not objectionable
6. Sulfide (as H ₂ S)	mg/l	not more than 1
7. Cyanide (as HCN),	mg/l	no t more than, 0.2
8. Heavy Metals		
8.1 Zinc	mg/l	maximum permitted value is 5
8.2 Chromium (Hexavalent)	mg/l	maximum permitted value is 0.25
8.3 Chromium (Trivalent)	mg/l	maximum permitted value is 0.75
8.4 Arsenic	mg/l	maximum permitted value is 0.25
8.5 Copper	mg/l	maximum permitted value is 2.0
8.6 Mercury	mg/l	maximum permitted value is 0.005
8.7 Cadmium	mg/l	maximum permitted value: is 0.03
8.8 Barium	mg/l	maximum permitted value is 1.0
8.9 Selenium	mg/l	maximum permitted vale is 0.02
8.10 Lead	mg/l	maximum permitted value is 0.2
8.11 Nickel	mg/l	maximum permitted value is 1.0
8.12 Manganese	mg/l	maximum permitted value is 5.0
9. Fat Oil and Crease (FOG)	mg/l	not more than 5 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 15 mg/l
10. Formaldehyde	mg/l	not more than 1
11. Phenols	mg/l	not more than 1

Items	Unit	Standard Values
12. Free Chlorine	mg/l	not more than 1
13. Pesticide	mg/l	none
14. Biochemical Oxygen Demand (BOD) *	mg/l	not more than 20 mg/l unless the specific type of industry or different level of capacity of receiving water can be permitted more than 20 mg/l by PCC consideration but maximum allowance figure should not more than 60: mg/l
15. Total Kjeldahl Nitrogen (TKN)**	mg/l	not more than 100 mg/l unless the specific type of industry or different level of capacity of receiving water can be permitted more than 100 mg/l by PCC consideration but maximum allowance figure should not more than 200 mg/l
16. Chemical Oxygen Demand (COD)***	mg/l	not more than 120 mg/l depending on receiving water or type of industry under' consideration of PCC but not exceed 400 mg/l

Note : * 10 Types of industries which has been accepted by PCC to discharge the Effluent BOD up to 60 mg/l are

- | | |
|--------------------------------|-------------------------------|
| 1) animal food industries | 6) cold storage industries |
| 2) starch industries | 7) chemical industries |
| 3) food from starch industries | 8) textile industries |
| 4) pulp and paper industries | 9) pharmaceutical industries |
| 5) tanning industries | 10) slaughterhouse industries |

** Effective after 1 year of announcement for other industries except after 2 years for food finishing and animal finished food industries.

*** 5 Types of industries which has been considered and accepted by PCC to discharge the Effluent COD up to 400 mg/l are

- 1) pulp and paper industries
- 2) textile industries
- 3) tanning industries
- 4) finished food industries
- 5) animal finished food industries

Remark : 1) mg/l means milligram per liter.

2) Factory means factories according to the Factory Law.

3) Industrial Estate means industrial estates according to the Industrial Estate Law or any industrial projects that discharge waste water into public water sources or into the environment.

Source : Notification of Ministry of Science, Technology and Environment No.3, B.E. 2539 (1996), dated January 3, B.E. 2539 (1996), published in the Royal Government Gazette, Vol. 113, Part 13 D, dated February 13, B.E. 2539 (1996)

: Notification of Ministry of Industry, No.2, B.E. 2539 (1996), issued under Factory Act B.E. 2535 (1992), dated June 14, B.E. 2539 (1996), published in the Royal Government Gazette, Vol. 113, Part 52 D, dated June 27, B.E. 2539 (1996).