

**Zinc sulfate for volumetric analysis** See zinc sulfate heptahydrate.

**Zinc sulfate heptahydrate**  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  [K 8953, Special class]

**Zinc sulfate TS** Dissolve 10 g of zinc sulfate heptahydrate in water to make 100 mL.

**Zirconyl-alizarin red S TS** Dissolve 0.2 g of zirconyl nitrate in 5 mL of dilute hydrochloric acid, add 10 mL of alizarin red S TS, and then add water to make 30 mL.

**Zirconyl-alizarin S TS** See zirconyl-alizarin red S TS.

**Zirconyl nitrate** See zirconyl nitrate dihydrate.

**Zirconyl nitrate dihydrate**  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  [K 8553: 1961, Special class]

### (3) Standard Solutions for Volumetric Analysis

Standard solutions for volumetric analysis are prepared to a specified molar concentration. A 1 molar solution is a solution which contains exactly 1 mole of a specified substance in each 1000 mL of the solution and is designated as 1 mol/L. If necessary, these solutions are diluted to other specified molar concentrations and the diluted solutions are also used as standard solutions. For example, 0.1 mol/L solution is obtained by diluting 1 mol/L solution 10 times by volume.

Unless otherwise directed, standard solutions for volumetric analysis should be stored in colorless or light-resistant, glass-stoppered bottles.

#### Preparation and Standardization

A volumetric standard solution is prepared according to one of the following methods. The degree of difference from a specified concentration  $n$  (mol/L) is expressed as a factor (molar concentration coefficient)  $f$ . Usually, standard solutions are prepared so that the factor is in the range of 0.970 – 1.030. The determination procedure of the factor is called standardization of the standard solution.

(1) Weigh accurately a quantity equivalent to about 1 mole or its multiple or a fractional mole number of the pure substance, and dissolve it in the specified solvent to make exactly 1000 mL to prepare a standard solution having a concentration close to the specified molarity  $n$  (mol/L). In this case, the factor  $f$  of the standard solution is obtained by dividing the mass of the pure substance taken (g) by the molecular mass of the substance (g) and the specified molarity number  $n$ .

When a pure substance is not obtainable, it is permissible to use a highly purified substance whose purity has been exactly determined and certified.

(2) In the case where a pure substance or a highly purified substance is not obtainable, weigh a quantity equivalent to about 1 mole or its multiple or a fractional mole number of the substance specified for each standard solution and dissolve it in the specified solvent to make about 1000 mL to prepare a standard solution having a concentration close to the specified molarity  $n$  (mol/L). The factor  $f$  of this solution is determined by applying the standardization procedure described for the respective standard solu-

tion. The procedure is classified into direct and indirect methods, as follows:

a) Direct method

Weigh accurately a standard reagent or an indicated substance specified for each standard solution, dissolve it in the specified solvent, then titrate with the prepared standard solution to be standardized, and determine the factor  $f$  by applying the following equation.

$$f = \frac{1000m}{VMn}$$

$M$ : Molecular mass equivalent to 1 mole of the standard reagent or the specified substance (g)

$m$ : Mass of the standard reagent or the specified substance taken (g)

$V$ : Volume of the prepared standard solution consumed for the titration (mL)

$n$ : Arithmetical mole number of the specified molar concentration of the standard solution to be standardized (e.g.  $n = 0.02$  for 0.02 mol/L standard solution)

b) Indirect method

When an appropriate standard reagent is not available, titrate a defined volume  $V_2$  (mL) of a standard solution to be standardized with the specified standard solution having a known factor ( $f_1$ ), and calculate the factor ( $f_2$ ) by applying the following equation.

$$f_2 = \frac{V_1 \times f_1}{V_2}$$

$f_1$ : Factor of the titrating standard solution having a known factor

$f_2$ : Factor of the prepared standard solution to be standardized

$V_1$ : Volume of the titrating standard solution consumed (mL)

$V_2$ : Volume of the prepared standard solution taken (mL)

3) Standard solutions may be prepared by diluting exactly an accurately measured volume of a standard solution having a known factor, according to the specified dilution procedure. During this dilution procedure, the original factor of the standard solution is assumed to remain constant.

#### Ammonium Thiocyanate, 0.1 mol/L

1000 mL of this solution contains 7.612 g of ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ : 76.12).

**Preparation**—Dissolve 8 g of ammonium thiocyanate in water to make 1000 mL, and standardize the solution as follows:

**Standardization**—Measure exactly 25 mL of the 0.1 mol/L silver nitrate VS, and add 50 mL of water, 2 mL of nitric acid and 2 mL of ammonium iron (III) sulfate TS. Titrate the solution with the prepared ammonium thiocyanate solution to the first appearance of a persistent red-brown color with shaking. Calculate the molarity factor.

Note: Store protected from light.

#### Ammonium Thiocyanate, 0.02 mol/L

1000 mL of this solution contains 1.5224 g of ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ : 76.12).

**Preparation**—Before use, dilute 0.1 mol/L ammonium thiocyanate VS with water to make exactly 5 times the initial volume.

**Ammonium Iron (III) Sulfate, 0.1 mol/L**

1000 mL of this solution contains 48.22 g of ammonium iron (III) sulfate 12-water  $[\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ : 482.19].

*Preparation*—Dissolve 49 g of ammonium iron (III) sulfate 12-water in a cooled mixture of 6 mL of sulfuric acid and 300 mL of water, add water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 25 mL of the prepared ammonium iron (III) sulfate solution into an iodine flask, add 5 mL of hydrochloric acid, and shake the mixture. Dissolve 2 g of potassium iodide, and stopper the flask. After allowing the mixture to stand for 10 minutes, add 50 mL of water, and titrate the liberated iodine with 0.1 mol/L sodium thiosulfate VS. When the solution assumes a pale yellow color as the end point is approached, add 3 mL of starch TS. Continue the titration, until the blue color disappears. Perform a blank determination. Calculate the molarity factor.

Note: Store protected from light. This solution, if stored for a long period of time, should be restandardized.

**Ammonium Iron (II) Sulfate, 0.1 mol/L**

1000 mL of this solution contains 39.214 g of ammonium iron (II) sulfate hexahydrate  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ : 392.14].

*Preparation*—Dissolve 40 g of ammonium iron (II) sulfate hexahydrate in a cooled mixture of 30 mL of sulfuric acid and 300 mL of water, dilute with water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 25 mL of the prepared ammonium iron (II) sulfate solution, and add 25 mL of water and 5 mL of phosphoric acid. Titrate the solution with 0.02 mol/L potassium permanganate VS. Calculate the molarity factor.

Note: Prepare before use.

**Ammonium Iron (II) Sulfate, 0.02 mol/L**

1000 mL of this solution contains 7.843 g of ammonium iron (II) sulfate hexahydrate  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ : 392.14].

*Preparation*—Before use, dilute 0.1 mol/L ammonium iron (II) sulfate VS with diluted sulfuric acid (3 in 100) to make exactly 5 times the initial volume.

**Barium Chloride, 0.02 mol/L**

1000 mL of this solution contains 4.885 g of barium chloride dihydrate  $(\text{BaCl}_2 \cdot 2\text{H}_2\text{O})$ : 244.26).

*Preparation*—Dissolve 4.9 g of barium chloride dihydrate in water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 100 mL of the prepared barium chloride solution, add 3 mL of hydrochloric acid, and warm the mixture. Add 40 mL of diluted sulfuric acid (1 in 130), warmed previously, heat the mixture on a water bath for 30 minutes, and allow to stand overnight. Filter the mixture, wash the collected precipitate of filter paper with water until the last washing shows no turbidity with silver nitrate TS, transfer the precipitate together with the filter paper to a tared crucible, and then heat strongly to ashes. After cooling, add 2 drops of sulfuric acid, and heat strongly again at about 700°C for 2 hours. After cooling, weigh accurately the residue as barium sulfate  $(\text{BaSO}_4)$ , and calculate the molarity factor.

Each mL of 0.02 mol/L barium chloride VS  
= 4.668 mg of  $\text{BaSO}_4$

**Barium Chloride, 0.01 mol/L**

1000 mL of this solution contains 2.4426 g of barium chloride dihydrate  $(\text{BaCl}_2 \cdot 2\text{H}_2\text{O})$ : 244.26).

*Preparation*—Before use, dilute 0.02 mol/L barium chloride VS with water to make exactly twice the initial volume.

**Barium Perchlorate, 0.005 mol/L**

1000 mL of this solution contains 1.6812 g of barium perchlorate  $[\text{Ba}(\text{ClO}_4)_2]$ : 336.23].

*Preparation*—Dissolve 1.7 g of barium perchlorate in 200 mL of water, dilute with 2-propanol to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 20 mL of the prepared barium perchlorate solution, add 55 mL of methanol and 0.15 mL of arsenazo III TS. Titrate the solution with 0.005 mol/L sulfuric acid VS until its purple color changes through red-purple to red. Calculate the molarity factor.

**Bismuth Nitrate, 0.01 mol/L**

1000 mL of this solution contains 4.851 g of bismuth nitrate pentahydrate  $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ : 485.07].

*Preparation*—Dissolve 4.86 g of bismuth nitrate pentahydrate in 60 mL of dilute nitric acid, add water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 25 mL of the prepared bismuth nitrate solution, add 50 mL of water and 1 drop of xylenol orange TS, and titrate the solution with 0.01 mol/L disodium dihydrogen ethylenediamine tetraacetate VS until the red color changes to yellow. Calculate the molarity factor.

**Bromine, 0.05 mol/L**

1000 mL of this solution contains 7.990 g of bromine (Br): 79.90).

*Preparation*—Dissolve 2.8 g of potassium bromate and 15 g of potassium bromide in water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Measure exactly 25 mL of the prepared solution into an iodine flask. Add 120 mL of water, quickly add 5 mL of hydrochloric acid, stopper the flask immediately, and shake it gently. Then add 5 mL of potassium iodide TS, re-stopper immediately, shake the mixture gently, and allow to stand for 5 minutes. Titrate the liberated iodine with 0.1 mol/L sodium thiosulfate VS. When the solution assumes a pale yellow color as the end point is approached, add 3 mL of starch TS. Continue the titration, until the blue color disappears. Perform a blank determination. Calculate the molarity factor.

**Cerium (IV) Tetraammonium Sulfate, 0.1 mol/L**

1000 mL of this solution contains 63.26 g of cerium (IV) tetraammonium sulfate dihydrate  $[\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}]$ : 632.55].

*Preparation*—Dissolve 64 g of cerium (VI) tetraammonium sulfate dihydrate in 0.5 mol/L sulfuric acid VS to make 1000 mL, allow to stand for 24 hours, filter the solution through a glass filter (G3 or G4), if necessary, and standardize the solution as follows:

*Standardization*—Measure exactly 25 mL of the prepared cerium (IV) tetraammonium sulfate solution into an iodine

flask. Add 20 mL of water and 20 mL of dilute sulfuric acid, then dissolve 1 g of potassium iodide in the mixture. Immediately titrate the solution with 0.1 mol/L sodium thiosulfate VS. When the solution assumes a pale yellow color as the end point is approached, add 3 mL of starch TS. Continue the titration, until the blue color disappears. Perform a blank determination. Calculate the molarity factor.

Note: Store protected from light. This solution, if stored for a long period of time, should be restandardized.

**Cerium (IV) Tetraammonium Sulfate, 0.01 mol/L**

1000 mL of this solution contains 6.326 g of cerium (IV) tetraammonium sulfate dihydrate [ $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ : 632.55].

*Preparation*—Before use, dilute 0.1 mol/L cerium (IV) tetraammonium sulfate VS with 0.5 mol/L sulfuric acid VS to make exactly 10 times the initial volume.

**Ceric Ammonium Sulfate, 0.1 mol/L**

See cerium (IV) tetraammonium sulfate, 0.1 mol/L.

**Ceric Ammonium Sulfate, 0.01 mol/L**

See cerium (IV) tetraammonium sulfate, 0.01 mol/L.

**Disodium Dihydrogen Ethylenediamine Tetraacetate, 0.1 mol/L**

1000 mL of this solution contains 37.224 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ : 372.24).

*Preparation*—Dissolve 38 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate in water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Wash zinc (standard reagent) with dilute hydrochloric acid, water and then acetone, dry at 110°C for 5 minutes, and allow to cool in a desiccator (silica gel). Weigh accurately about 1.3 g of this zinc, add 20 mL of dilute hydrochloric acid and 8 drops of bromine TS, and dissolve it by gentle warming. Expel any excess of bromine by boiling, and add water to make exactly 200 mL. Pipet 25 mL of this solution, and neutralize with sodium hydroxide solution (1 in 50). Add 5 mL of ammonia-ammonium chloride buffer solution, pH 10.7, and 0.04 g of eriochrome black T-sodium chloride indicator. Titrate the solution with the prepared disodium dihydrogen ethylenediamine tetraacetate solution until the red-purple color changes to blue-purple. Calculate the molarity factor.

Each mL of 0.1 mol/L disodium dihydrogen ethylenediamine tetraacetate VS  
= 6.539 mg of Zn

Note: Store in polyethylene bottles.

**Disodium Dihydrogen Ethylenediamine Tetraacetate, 0.05 mol/L**

1000 mL of this solution contains 18.612 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ : 372.24).

*Preparation*—Dissolve 19 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate in water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Wash zinc (standard reagent) with dilute hydrochloric acid, water and then acetone, dry at 110°C for 5 minutes, and allow to cool in a desiccator (silica gel). Weigh accurately about 0.8 g of this zinc, add 12 mL of di-

lute hydrochloric acid and 5 drops of bromine TS, and dissolve it by gentle warming. Expel any excess of bromine by boiling, and add water to make exactly 200 mL. Measure exactly 20 mL of this solution, and neutralize with sodium hydroxide solution (1 in 50). Add 5 mL of ammonia-ammonium chloride buffer solution, pH 10.7, and 0.04 g of eriochrome black T-sodium chloride indicator. Titrate the solution with the prepared disodium dihydrogen ethylenediamine tetraacetate solution until the red-purple color changes to blue-purple. Calculate the molarity factor.

Each mL of 0.05 mol/L disodium dihydrogen ethylenediamine tetraacetate VS  
= 3.2695 mg of Zn

Note: Store in polyethylene bottles.

**Disodium Dihydrogen Ethylenediamine Tetraacetate, 0.02 mol/L**

1000 mL of this solution contains 7.445 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ : 372.24).

*Preparation*—Dissolve 7.5 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate in water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Proceed as directed for standardization under 0.05 mol/L disodium dihydrogen ethylenediamine tetraacetate VS, but weigh accurately 0.3 g of zinc (standard reagent), previously washed with dilute hydrochloric acid, with water and with acetone, and cooled after drying in a desiccator (silica gel) at 110°C for 5 minutes, and add 5 mL of dilute hydrochloric acid and 5 drops of bromine TS.

Each mL of 0.02 mol/L disodium dihydrogen ethylenediamine tetraacetate VS  
= 1.3078 mg of Zn

Note: Store in polyethylene bottles.

**Disodium Dihydrogen Ethylenediamine Tetraacetate, 0.01 mol/L**

1000 mL of this solution contains 3.7224 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ : 372.24).

*Preparation*—Before use, dilute 0.02 mol/L disodium dihydrogen ethylenediamine tetraacetate VS with water to make exactly twice the initial volume.

**Disodium Dihydrogen Ethylenediamine Tetraacetate, 0.001 mol/L**

1000 mL of this solution contains 0.37224 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ : 372.24).

*Preparation*—Before use, dilute 0.01 mol/L disodium dihydrogen ethylenediamine tetraacetate VS with water to make exactly 10 times the initial volume.

**Ferric Ammonium Sulfate, 0.1 mol/L**

See Ammonium Iron (III) Sulfate, 0.1 mol/L.

**Ferrous Ammonium Sulfate, 0.1 mol/L**

See Ammonium Iron (II) Sulfate, 0.1 mol/L.

**Ferrous Ammonium Sulfate, 0.02 mol/L**

See Ammonium Iron (II) Sulfate, 0.02 mol/L.

**Hydrochloric Acid, 2 mol/L**

1000 mL of this solution contains 72.92 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Dilute 180 mL of hydrochloric acid with water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Proceed as directed for standardization under 1 mol/L hydrochloric acid VS, but weigh about 1.5 g of sodium carbonate (standard reagent) accurately, and dissolve in 100 mL of water.

Each mL of 2 mol/L hydrochloric acid VS  
= 105.99 mg of Na<sub>2</sub>CO<sub>3</sub>

**Hydrochloric Acid, 1 mol/L**

1000 mL of this solution contains 36.461 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Dilute 90 mL of hydrochloric acid with water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Weigh accurately about 0.8 g of sodium carbonate (standard reagent), previously heated between 500°C and 650°C for 40 to 50 minutes and allowed to cool in a desiccator (silica gel). Dissolve it in 50 mL of water, and titrate with the prepared hydrochloric acid to calculate the molarity factor (Indicator method: 3 drops of methyl red TS; or potentiometric titration). In the indicator method, when the end-point is approached, boil the content carefully, stopper the flask loosely, allow to cool, and continue the titration until the color of the solution changes to persistent orange to orange-red. In the potentiometric titration, titrate with vigorous stirring, without boiling.

Each mL of 1 mol/L hydrochloric acid VS  
= 52.99 mg of Na<sub>2</sub>CO<sub>3</sub>

**Hydrochloric Acid, 0.5 mol/L**

1000 mL of this solution contains 18.230 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Dilute 45 mL of hydrochloric acid with water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Proceed as directed for standardization under 1 mol/L hydrochloric acid VS, but weigh accurately about 0.4 g of sodium carbonate (standard reagent), and dissolve in 50 mL of water.

Each mL of 0.5 mol/L hydrochloric acid VS  
= 26.497 mg of Na<sub>2</sub>CO<sub>3</sub>

**Hydrochloric Acid, 0.2 mol/L**

1000 mL of this solution contains 7.292 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Dilute 18 mL of hydrochloric acid with water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Proceed as directed for standardization under 1 mol/L hydrochloric acid VS, but weigh accurately about 0.15 g of sodium carbonate (standard reagent), and dissolve in 30 mL of water.

Each mL of 0.2 mol/L hydrochloric acid VS  
= 10.599 mg of Na<sub>2</sub>CO<sub>3</sub>

**Hydrochloric Acid, 0.1 mol/L**

1000 mL of this solution contains 3.6461 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Before use, dilute 0.2 mol/L hydrochloric acid VS with water to make exactly twice the initial volume.

**Hydrochloric Acid, 0.05 mol/L**

1000 mL of this solution contains 1.8230 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Before use, dilute 0.2 mol/L hydrochloric acid VS with water to make exactly 4 times the initial volume.

**Hydrochloric Acid, 0.02 mol/L**

1000 mL of this solution contains 0.7292 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Before use, dilute 0.2 mol/L hydrochloric acid VS with water to make exactly 10 times the initial volume.

**Hydrochloric Acid, 0.01 mol/L**

1000 mL of this solution contains 0.36461 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Before use, dilute 0.2 mol/L hydrochloric acid VS with water to make exactly 20 times the initial volume.

**Hydrochloric Acid, 0.001 mol/L**

1000 mL of this solution contains 0.036461 g of hydrochloric acid (HCl: 36.461).

*Preparation*—Before use, dilute 0.2 mol/L hydrochloric acid VS with water to make exactly 200 times the initial volume.

**Iodine, 0.05 mol/L**

1000 mL of this solution contains 12.690 g of iodine (I: 126.90).

*Preparation*—Dissolve 13 g of iodine in 100 mL of a solution of potassium iodide (2 in 5), add 1 mL of dilute hydrochloric acid and water to make 1000 mL, and standardize the solution as follows:

*Standardization*—Weigh accurately about 0.08 g of arsenic trioxide (standard reagent), previously powdered and dried at 105°C for 3 to 4 hours and allowed to cool in a desiccator (silica gel), and dissolve it in 20 mL of a solution of sodium hydroxide (1 in 25) by warming, if necessary. Add 40 mL of water, 2 drops of methyl orange TS and then dilute hydrochloric acid until the solution acquires a pale red color, and add subsequently 2 g of sodium bicarbonate. Titrate slowly with the prepared iodine solution to calculate the molarity factor (Indicator method: 3 mL of starch TS; or potentiometric titration: platinum electrode). In indicator method, titrate until the solution acquires a persistent blue color.

Each mL of 0.05 mol/L iodine VS = 4.946 mg of As<sub>2</sub>O<sub>3</sub>

Note: Store protected from light. This solution, if stored for a long period, should be restandardized before use.

**Iodine, 0.01 mol/L**

1000 mL of this solution contains 2.5381 g of iodine (I: 126.90).

*Preparation*—Before use, dilute 0.05 mol/L iodine VS with water to make exactly 5 times the initial volume.