AOAC Official Method 936.15
Standard Solution of Hydrochloric Acid

First Action 1936
Final Action

A. Preparation of Standard Solutions

Table **936.15** gives approximate volumes of 36.5–38% HCl required to make 10 L standard solutions.

B. Standard Sodium Hydroxide Method

Titrate 40 mL against standard alkali solution, 936.16C–E (*see* A.1.12), of ca same concentration as acid being standardized in 300 mL flask that has been swept free from CO_2, using CO_2-free H_2O and 3 drops phenolphthalein.

$$\text{Molarity} = \frac{\text{mL standard alkali} \quad \text{molarity of alkali}}{\text{mL HCl}}$$

If more concentrated than desired, dilute solution to required molarity value by following formula:

$$V_1 = V_2 \quad M_2/M_1$$

where M_2 and V_2 represent molarity and volume of stock solution, respectively, and V_1 = volume to which stock solution should be diluted to obtain desired molarity, M_1.

Check exact concentration of final solution by titration as above. Molarity will be exact only if same indicator is used in determination as in standardization. Restandardize if indicators other than phenolphthalein are used.

References: *JAOAC* **19**, 107, 194(1936); **49**, 250(1966).
Kolthoff & Stenger, "Volumetric Analysis," **II**, 52(1947).

B. Constant Boiling Method

Dilute 822 mL HCl (36.5–38% HCl) with 750 mL H_2O. Check specific gravity with spindle and adjust to 1.10. Place 1.5 L in 2 L flat-bottom distilling flask, add ca 10 SiC grains (ca "20 mesh"), and connect to long, straight inner-tube condenser. Heat on electric hot plate and distil at 5–10 mL/min, keeping end of condenser open to air. When 1125 mL has distilled, change receivers and catch next 225 mL, which is constant boiling HCl, in Erlenmeyer with end of condenser inserted into flask, but above surface of liquid. Read barometer to nearest mm at beginning and end of collection of 225 mL portion and note barometer temperature. Average readings.

Calculate air weight in g (G) of this constant boiling HCl required to give one equivalent weight of HCl from one of following equations:

For P_0 = 540–669 mm Hg:

$$G = 162.255 + 0.02415\ P_0$$

For P_0 = 670–780 mm Hg:

$$G = 164.673 + 0.02039\ P_0$$

where P_0 = barometric pressure in mm Hg corrected to 0°C for expansion of Hg and of barometer scale. For brass scale barometer, following correction is accurate enough:

$$P_0 = P_t(1 - 0.000162t)$$

Table 936.15. Volumes of concentrated HCl required to prepare solutions of different molarities

Approximate molarity	mL HCl to be diluted to 10 L
0.01	8.6
0.02	17.2
0.10	86.0
0.50	430.1
1.0	860.1

where t = barometer temperature in C.

Weigh required amount of constant boiling HCl in tared, stoppered flask to at least 1 part in 10 000. Dilute immediately, and finally dilute to volume with CO_2-free H_2O at desired temperature.

References: *JAOAC* **25**, 653(1942); **36**, 96, 354(1953); **37**, 122, 462(1954).

Standard Borax Method

C. Reagents

(**a**) *Methyl red indicator.*—Dissolve 100 mg methyl red in 60 mL alcohol and dilute with H_2O to 100 mL.

(**b**) *Reference solution.*—Prepare reference solution of H_3BO_3, NaCl, and indicator corresponding to composition and volume of solution at equivalence point. For use in determination of end point of titration with 0.1M HCl, reference solution should be 0.1M in H_3BO_3 and 0.05M in NaCl.

(**c**) *Standard borax.*—Saturate 300 mL H_2O at 55 C (not higher) with $Na_2B_4O_7{\cdot}10H_2O$ (ACS) (ca 45 g). Filter at this temperature through folded paper into 500 mL Erlenmeyer. Cool filtrate to ca 10 C, with continuous agitation during crystallization. Decant supernate, rinse precipitate once with 25 mL cold water, and dissolve crystals in just enough water at 55 C to ensure complete solution (ca 200 mL). Recrystallize by cooling to ca 10 C, agitating flask during crystallization.

Filter crystals onto small Büchner with suction, wash precipitate once with 25 mL ice-cold water, and dry crystals by washing with two 20 mL portions alcohol, drying after each washing with suction. Follow with two 20 mL portions ether. (Just before use, free alcohol and ether from any possible reacting acids by vigorously shaking each with 2–3 g of the pure, dry $Na_2B_4O_7{\cdot}10H_2O$ and then filtering.) Spread crystals on watch glass, immediately place dried $Na_2B_4O_7{\cdot}10H_2O$ in closed container over solution saturated with respect to both sucrose and NaCl, and let it remain ≥24 h before using. Then transfer the pure $Na_2B_4O_7{\cdot}10H_2O$ to glass-stoppered container and store in closed container over solution saturated with respect to both sucrose and NaCl (stable under these conditions 1 year).

D. Standardization

Accurately weigh enough standard $Na_2B_4O_7{\cdot}10H_2O$ to titrate ca 40 mL and transfer to 300 mL flask. Add 40 mL CO_2-free H_2O, 936.16B(**a**) (*see* A.1.12), and stopper flask. Swirl gently until sample dissolves. Add 4 drops methyl red and titrate with solution that is being standardized to equivalence point as indicated by reference solution.

$$\text{Molarity (mol/L)} = \text{g } Na_2B_4O_7{\cdot}10H_2O \quad 1000/\text{mL acid} \quad 190.69$$

Reference: *JAOAC* **22**, 102, 563(1939).

Standard Sodium Carbonate Method

E. Reagents

(**a**) *Methyl orange indicator.*—0.1% in H_2O.

(**b**) *Reference solution*.—80 mL CO_2-free H_2O containing 3 or 4 drops methyl orange.

(**c**) *Anhydrous sodium carbonate*.—Heat 250 mL H_2O to 80 C and add $NaHCO_3$ (ACS), stirring until no more dissolves. Filter solution through folded paper (use of hot water funnel is desirable) into Erlenmeyer. Cool filtrate to ca 10 C, swirling constantly during crystallization. Fine crystals of trona that separate out have approximate composition: $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. Decant supernate, drain crystals by suction, and wash once with cold water.

Transfer precipitate, being careful not to include any paper fibers, to large flat-bottom Pt dish. Heat 1 h at 290 C in electric oven or furnace with pyrometer control. Stir contents occasionally with Pt wire. Cool in desiccator. Place the anhydrous Na_2CO_3 in glass-stoppered container and store in desiccator containing efficient desiccant. Dry at 120 C and cool just before weighing.

References: Kolthoff & Stenger, "Volumetric Analysis," **II**, 80(1947).
Ind. Eng. Chem., *Anal. Ed*. **9**, 141(1937).
JAOAC **22**, 563(1939).

F. Standardization

Accurately weigh enough anhydrous Na_2CO_3, **E**(**c**), to titrate ca 40 mL, transfer to 300 mL Erlenmeyer, and dissolve in 40 mL H_2O. Add 3 drops methyl orange and titrate until color begins to deviate from H_2O tint (reference solution). (Equivalence point has not been reached.) Boil solution gently 2 min and cool. Titrate until color is barely different from H_2O tint of indicator.

$$\text{Molarity HCl, moles/L} = \frac{\text{g } Na_2CO_3 \quad 1000/\text{mL HCl}}{(105.988/2)}$$

Reference: *JAOAC* **22**, 102, 563(1939).

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