# METHOD OF TEST FOR DETERMINATION OF TOTAL CHLORIDE ION IN CONCRETE - (ACID SOLUBLE)

### 1. SCOPE

1.1 This method covers procedure for the determination of the total chloride ion content of concrete cores. The method is limited to materials that do not contain sulfides, but the extraction procedure. Section 7 may be used for all such materials.

### 2. RELEVANT DOCUMENTS

2.1 "Standard Methods of Chemical Analysis", Volume III A, 6th Edition, Edited by Frank J. Welcher.

2.2 Clear, K. C., "Evaluation of Portland Cement Concrete for Permanent Bridge Deck Repair", Federal Highway Administration, Report FHWA-RD-74-5, February 1974, National Technical Information Services PB232-604/AS.

### 3. DEFINITION

3.1 The total chloride ion content in concrete is the one determined as described in this method and expressed in percent by mass of the concrete.

### 4. APPARATUS

4.1 CONCRETE SAW.

4.2 CONCRETE PULVERIZER.

4.3 SIEVE: 300 µm.

4.4 ELECTRODE: Solid state or liquid filled chloride-ion or silver/sulfide ion-selective and manufacturer recommended filling solutions.

Note 1: Suggested electrodes are the Orion 96-17 Combination Chloride Electrode or the solid state Orion 96-17A. MTO uses the chloride ion-selective electrode together with a standard calomel electrode filled with saturated Na<sub>2</sub>SO<sub>4</sub> instead of KCI.

4.5 MILLIVOLTMETER: Compatible with the ion electrode.

Note 2: Suggested millivoltmeter is the Orion Model 701A Digital Ph/mV meter or any equivalent with a digital readout.

- 4.6 STIRRER: Teflon-coated magnetic stirring bars.
- 4.7 BURETTE: With 0.05 mL graduations.
- 4.8 BALANCE: Sensitive to 0.0001 g with minimum capacity of 100 g.
- 4.9 HOT PLATE: 250 to 400°C heating surface temperature.

4.10 GLASSWARE: 250 and 400 mL beakers, filter funnels, stirring rods, watch glasses, dropper, mortar and pestle, wash bottles.

4.11 FILTER PAPER: Whatman No. 54 (or equivalent).

### 5. REAGENTS

5.1 DILUTE HNO<sub>3</sub>: (1:16, conc HNO<sub>3</sub>: water by vol.).

5.2 SODIUM CHLORIDE: NaCl, reagent grade (primary standard).

5.3 STANDARD 0.025 N NaCl SOLUTION.

5.3.1 Dry reagent grade NaCl in an oven at 105°C. Cool in a desiccator, weigh out 1.4610 g, dissolve in distilled water, and transfer to a 1-litre volumetric flask. Make up to the one litre mark with distilled water and mix.

5.4 STANDARD 0.025N AgNO3.

5.4.1 Weigh 4.247 g of reagent grade AgNO<sub>3</sub>, dissolve in distilled water filter into a 1-litre brown glass bottle, fill, and mix thoroughly. Standardize against 25.00 mL of the NaCl solution by the titration method described in Section 7.5.

5.5 DISTILLED WATER.

5.6 METHYL ORANGE INDICATOR.

5.7 ETHYL ALCOHOL: Technical grade.

#### 6. SAMPLE PREPARATION

Unless instructed otherwise, each core shall be cut into 10 mm thick (including saw cut) horizontal sections as shown in Figure 1.



### FIGURE 1 LOCATION OF SAW CUTS

6.1 As each section is saw cut, it shall be immediately marked to show its identification number.

6.2 Section 0 - 10 mm, 20-30 mm, 40-50 mm, 60-70 mm and 80-90 mm shall be dried to a constant weight in a 105°C oven, then crushed and pulverized so that the entire section passes the 300 µm sieve. Care shall be taken to avoid loss of material.

6.3 After each section is crushed and pulverized, the sieve and all the pulverizing tools shall be washed with ethyl alcohol or distilled water and shall be dry before use with each separate sample (section).

6.4 As each section has been pulverized, the material shall be placed in a suitable container and the container shall immediately be marked with the section's identification number.

The other sections (10-20 mm, 30-40 mm, 50-60 mm, and 70-80 mm) shall be placed in plastic bags and 6.5 retained for at least six months for contingency tests.

#### 7. PROCEDURE

Weigh, to the nearest milligram, a 5 g powdered sample representative of the material under test. 7.1

Note 3: Running of blank determinations is recommended to allow correction for any extraneous sources of chloride

ion. Such corrections indicate sources of contamination which should be eliminated.

7.2 Transfer the sample quantitatively to a 250 mL beaker; add 120 mL of diluted HNO3, stirring with a glass rod until the sample is thoroughly dispersed.

7.3 Cover with a watch glass, keeping the stirring rod in the beaker, and boil the slurry for 5 minutes on a hot plate. Remove the beaker from the hot plate and filter the slurry through Whatman No. 54 filter paper into a 400 mL beaker, first decanting the clear supernatant liquid, then washing over the residue using hot distilled water. Wash the stirring rod and the inside of the beaker into the filter. Repeat until all residue has been transferred. Wash the filter paper with hot distilled water 6 times until free of chlorides. Lift the filter paper carefully from the funnel, and wash the outside of the paper with hot distilled water. Set aside the paper, and wash the interior of the funnel and its tip with hot distilled water a minimum of three times.

7.4 Cool the filtrate to  $23 \pm 2^{\circ}$ C, immersing the beaker in an ice bath if necessary. Add 1 to 2 drops of methyl orange indicator to the 400 mL beaker; then, if necessary, add concentrated HNO<sub>3</sub> drop wise with continuous stirring until a permanent pink to red colour is obtained. Add distilled water to bring the volume up to 250 mL.

7.5 Prepare the CI electrode as recommended by the manufacturer and plug it into the millivoltmeter. Determine the approximate equivalence point by immersing the electrode in a beaker of distilled water and noting the approximate millivoltmeter reading (which may be unsteady in water). Remove the beaker of distilled water from the electrode, wipe the electrode with absorbent paper, and immerse the electrode in the sample solution. Place the entire beaker-electrode assembly on a magnetic stirrer and begin gentle stirring. If the millivoltmeter reading is 40 mV or more below the approximate equivalence point determined with distilled water, proceed as directed in 7.7. If the reading is less than 40 mV below the equivalence point, proceed as directed in 7.6.

7.6 Pipette 5.00 mL of 0.025 N NaCl into the sample and mix thoroughly. Remove the beaker of distilled water, wipe the electrode and immerse it in the sample solution. Place the entire beaker/electrode assembly on a magnetic stirrer and begin stirring. Using a calibrated burette, add gradually and record the amount of standard 0.025 N AgNO<sub>3</sub> solution necessary to bring the millivoltmeter reading to -40 mV of the equivalence point determined in distilled water. Then continue titrating as outlined in 7.7.

7.7 Add standard 0.025 N AgNO<sub>3</sub> solution in 0.25 mL increments recording the millivoltmeter reading after each addition. As the equivalence point is approached, the equal additions of AgNO<sub>3</sub> solution will cause larger and larger changes in the millivoltmeter reading. Past the equivalence point, the changes per unit volume will again decrease. Continue the titration until the millivoltmeter reading is at least 40 mV past the approximate equivalence point.

The end point of the titration usually is near the approximate equivalence point in distilled water. It shall be determined by following the method listed in "Standard Methods of Chemical Analysis" (Volume III A, 6th Edition, edited by Frank J. Welcher). Following this method, the titration end point is computed as the volume of AgNO<sub>3</sub> solution added up to the point where  ${}^{2}E/V^{2}$  becomes zero.

An illustration is given in Table 17-1 of page 288 of the above mentioned "Standard Methods of Chemical Analysis". A slightly modified version is as follows:

Vol. in mL	E in mV	E/ V in mV/0.25 mL	<sup>2</sup> E/ V <sup>2</sup>
10.00	620		
		5	_
10.25	625		+7

		12	
10.50	637	32	+20
10.75	669	32	+74
11.00	775	106	-36
11.25	845	70	-20
11.50	895	50	

V (at 
$${}^{2}\text{E}/{}^{2}\text{E} = 0$$
) = 10.75 + 0.25  $\frac{74}{74 + 36}$  mL

## 8. CALCULATIONS

8.1 Determine the end point of the titration as described in Section 7.7. Calculate the percent of chloride ion from the equation.

% CГ = 
$$3.5453 \quad \frac{V_1 \quad N_1 - V_2 \quad N_2}{W}$$
  
where:  $V_1$  = end point in mL  
 $V_2$  = Volume of NaCl solution added in mL  
 $N_1$  = Normality of AgNO<sub>3</sub>  
 $N_2$  = Normality of NaCl solution  
 $W$  = mass of original concrete sample in g

8.2 The percent chloride may be converted to kilograms of Cl<sup>-</sup> per cubic metre of concrete as follows: kg Cl<sup>-</sup>/m<sup>3</sup> =  $\frac{(\% Cl^{-})(UW)}{100}$ 

where: UW = Density of concrete in  $kg/m^3$ 

Note 4: A density of 2375 kg/m<sup>3</sup> is often assumed for normal structural mass concrete when the actual density is unknown.