METHODS OF SAMPLING AND TESTING
MT 530-16
DETERMINATION OF CHLORIDE IN BRIDGE DECK CONCRETE BY ION CHROMATOGRAPHY
(*Montana Method*)

1 Scope

1.1 This method describes the procedure used to determine the concentration of acid-soluble chloride in bridge deck concrete via ion chromatography.

1.2 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM
D1193 Standard Specification for Reagent Water

MT Materials Manual
MT 114 Sampling for Chloride Content of Bridge Deck Concrete

Other
Method Tex-620-J, Determining Chloride and Sulfate Contents in Soil
(http://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/600-J_series/archives/620-0805.pdf)

3 Terminology

3.1 *Chromatography* – the separation and quantitative analysis of ions based on their affinity to the ion exchanger.

3.2 *Eluent* – A solution that transports the sample through the system and contributes to the selectivity of the separation in the ion chromatograph.

4 Summary of Test Method

4.1 The chloride ion is extracted from concrete samples, put into solution, centrifuged, filtered and injected into the Ion Chromatograph (IC). The sodium carbonate/bicarbonate eluent transports the sample through the column which is operating with a suppressed conductivity method. The ion chromatograph detects chloride ions which interface with the column and are read on the instrument's conductivity detector.

5 Significance and Use

5.1 This procedure is used to determine the concentration of the chloride ion in concrete samples collected from bridge decks. The chloride ion concentration is used to evaluate the level of corrosion and determine the maintenance requirement for bridge decks.

6 Apparatus

6.1 *Metrohm Basic Ion Chromatograph Plus 883* equipped with:

6.1.1 Autosampler

6.1.2 Metrosep A Supp 150/4.0 Column

6.1.3 Conductivity Detector

6.1.4 MagIC Net Software

6.2 *Centrifuge*

7 Reagents and Materials

7.1 *Reagent Water* – Purified water that meets ASTM Type II specifications or better (ASTM D1193)

7.2 *Suppressor Regenerant Solution*, 0.1 Molar Sulfuric Acid (H_2SO_4)

7.3 *Suppressor Rinse Solution,* 99.9% MeOH

7.4 *Neutralizing Solution*, 0.5 M Sodium Hydroxide (aqueous)

Add 500mL of reagent water to a 750 or 1000mL glass beaker and slowly add 9.99 g of solid NaOH pellets to the reagent water and mix.

7.5 *Eluent*, 3.2 M Sodium Carbonate, Na_2CO_3/1.0 M Sodium Bicarbonate, $NaHCO_3$ (aqueous); (stock eluent solution, A Supp 5 Eluent 100x, ordered from Metrohm). Shelf life of eluent is 2 days.

7.6 *Nitric Acid (HNO_3),* concentrated Trace Metal Grade, 65-75%

7.7 *Standard Stock Solution*, Dionex Five Anion Standard, chloride concentration of 30 ppm

7.7 *Glassware*: 50 mL beakers, 100mL volumetric flasks for dilution

7.8 *Auto-pipettes*

7.9 *Plastic Syringes*, 30 mL non-sterile

7.10 *Syringe filters* - particle retention of 0.2 µm

7.11 *Dry plastic bottles* that have been stored filled with a dilute HNO_3 acid solution (1 – 5%) prior to use

7.12 *Disposable IC vials*, 11 ml

8 Sampling

8.1 Bridge deck concrete samples are collected in accordance with MT 114 and pulverized in a Bico pulverizer with plates spaced between 1 and 2 mm.

9 Calibration and Standardization

9.1 *IC Instrumentation Settings:*

9.1.1 Flow rate on IC: 0.7 mL/min

9.1.2 Sample Loop: 20 µL

9.1.3 Run time: 20 minutes

9.2 *Calibration Curve Determination*

9.2.1 Prepare standards from a five anion standard. The Dionex Five Anion Standard with a chloride concentration of 30 ppm is commonly used.

9.2.2 Weigh indicated masses from the 5 anion standard bottle into a dry plastic bottle (See Table 1). Record weights to the thousandth decimal place.

9.2.3 Dilute with reagent water for a target total mass of 50 g (± 0.001)

Table 1: Standard calibration solutions and masses of components

Concentration, ppm	Mass of 5 anion standard, g	Mass of solution, g
0.5	0.834	50.000
1.0	1.667	50.000
2.0	3.334	50.000
4.0	6.667	50.000
5.0	8.334	50.000
10.0	16.668	50.000

Note 1 - The masses in Table 1 above have been developed for the Dionex Five Anion Standard which has a chloride concentration of 30 ppm, if another standard is used the weights in the table are not applicable

9.2.4 Determine concentration of each standard and enter into the IC software.

10 Procedure

10.1 *Preparation of Controls*

10.1.1 For each sequence to be analyzed on the IC, prepare and analyze a quality control (QC) sample. Use a QC sample with a concentration which is mid-range of the calibration curve. For example, chloride standard preparations range from 0.5 ppm to 10 ppm. A QC sample with a target of approximately 3 ppm is sufficient. Using a Portland cement with a qualified standard of 0.127% is an acceptable QC sample. Determine percent recovery per Section 11.5 below. Analysis is considered acceptable with a percent recovery on the quality control sample of ±10%.

10.2 *Sample Preparation and Analysis*

10.2.1 Weigh 0.25 g of sample into a 50 – 60 mL beaker using a balance with an accuracy of ± 0.0001 g. Record the sample weight to be used in final calculation (W_s). Add 1 mL of reagent water to the beaker to liquefy the cement sample.

10.2.2 In a fume hood, Add 100 µL of concentrated HNO_3 to the cement paste and and swirl gently to mix well. CO_2 gas liberates from the reaction between the cement constituents and nitric acid. Wait roughly 10 minutes for the extraction to occur.

10.2.3 Neutralize the solution by adding approximately 1.5 mL of 0.5 M NaOH (2-4 mL may be needed). Test with litmus paper strips to make sure the solution is neutral.

10.2.4 Transfer the neutral solution into a 100 mL volumetric flask (V), rinsing the beaker to transfer the solids from the beaker to the flask. Dilute to the fill line with reagent water.

10.2.5 Pour approximately 10 mL of the solution into a plastic syringe equipped with a 0.2 µm nylon filter tip. Filter the solution into a plastic ion chromatography test tube.

Note 2 – If the turbidity of the sample is such that light cannot pass through it, then centrifuge the sample at 500 rpm for roughly 15 minutes in a plastic nunc tube prior to pouring the sample into the IC vial centrifuge.

10.6 Analyze the sample and the QC sample simultaneously on the IC to determine the chloride concentration. Shelf life of the sample is one week.

11 Calculation or Interpretation of Results

11.1 *Dilution Factor*

$$DF = \frac{Vf}{Vi}$$

Where:
DF = Dilution factor
Vf = Final volume (diluent and aliquot)
Vi = initial volume

11.1.1 Dilution Factor for Concrete Sample

The dilution factor (DF) for the concrete sample is the volume of the volumetric flask used in Section 10.2.4 (i.e., 100 mL).

11.2 *Chloride Concentration in Concrete*

$$Ccl = \frac{(Cic * DF)}{Ws}$$

Where:
C_{cl} = Concentration of the chloride in the original concrete, ppm
C_{ic} = Concentration of the chloride as determined by the IC, ppm
DF = Dilution factor
W_s = Weight of the sample, g

11.2.1 *Example*: C_{ic} = 2.78 mg/L (*or ppm)*
DF = 100
W_s= *0.2529 g*

C_{cl}= *(*2.78*100)/0.2529 = 1099 ppm

11.3 *Percent Chloride in Concrete*

$$\%Cl = \frac{Ccl}{10{,}000}$$

11.3.1 *Example:* C_{cl} *= 1099 ppm (from above)*

%Cl = 1099/10,000 = 0.1099%

11.4 *Pounds of Chloride per cubic yard of Concrete*

$$Pc = \frac{(Ccl * Dc)}{1{,}000{,}000}$$

Where:
P_c = Pounds of chloride per cubic yard of concrete
C_{cl} = Concentration of chloride ions in the original concrete sample, ppm
D_c = Density of concrete (4,000 lb/cy)

11.5 *Percent Recovery of Quality Control Sample*

$$\% \text{ Recovery} = [C_{IC(QC)} * DF / W_{QC} / 10{,}000 / C_{QC}] * 100\%$$

Where:
$C_{IC(QC)}$ = Concentration of the Quality Control Sample as determined by the IC, ppm
C_{QC} = Known value of the quality control sample
DF = Dilution factor
W_{QC} = Weight of the Quality Control Sample, g

11.5.1 Example: $C_{IC(QC)} = 3.15$ *ppm*
DF = 100
$W_{QC} = 0.2529$*g*
$C_{QC} = 0.127\%$

*% Recovery = [3.15*100/0.2529/10,000/0.127]*100 = 98.07%*

12 Report

12.1 Enter chloride analysis results in the following location:
X:\CHEMISTRY\LAB\Bridge Chlorides 20XX.xlsx