

Model Standard Operating Procedures (SOPs) for Cation Analysis using IC

(1) Applicable samples and items

Concentration measurements for NH_4^+ , Na^+ , K^+ , Mg^{++} and Ca^{++} , in precipitation samples, filtrate of dry sampler and field blank samples.

(2) Principles and summary of the measurement method

(3) References

The method is based on the next references

- Guidelines for wet deposition monitoring in East Asia
- Technical Documents for Wet Deposition Monitoring in East Asia
- DX 500 Ion Chromatograph basic operation, Dionex Corporation Japan.
- Peaknet Operation Guide, Dionex Corporation Japan.
- Printer(Canon Laser shot LBP-320)

(4) Analytical method

1) Instruments

- Ion Chromatograph for cation analysis (DIONEX DX500)
- Cation separator column (DIONEX Ion Pac CS12A)
- Guard column (DIONEX Ion Pac CG12A)
- Suppressor (DIONEX CSRS-1 (Recycle mode))
- Auto sampler (DIONEX AS-3500)
- Eluent Generator (EG-40)
- Detector (IC-20 Conductivity Detector)

2) Apparatus

Apparatus used in this procedures are as follows.

- Polyethylene vessels for auto sampler
- Wash bottle for deionized water
- Volumetric flask 1 L
- Volumetric pipet, 1, 2, 6,10,20 ml

3) Reagents

Reagents used in this procedures are as follows.

- Deionized water: more than 18 MΩcm, immediately after purification
- Standard solution:Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺ standard solution
1000 mg/l (Wako Pure Chem. Industry. Co. Ltd. Cat. No.199-10831)

4)Preparation of standard solution

fixed stock standard solution I

- Take 10 ml of each cation standard solutionby volumetric pipet.
- Mix thoroughly.
- Fill to the mark with deionized water and mix thoroughly.
- Transfer the solution to 100 ml of polyethylene bottle, and the solution should be stored in refrigerator at 4°C.

Preparation of mixed anion standard solution

To five volumetric flask add:ca. 50 ml deionized water,
Take 2, 6, 10, 20 ml of standard stock solution by volumetric pipet
Mix thoroughly. Fill to the mark with deionized water and mix
thoroughly.Transfer the solution to 100 ml of polyethylene bottle.
The solution can be stored in refrigerator at 4°C and used for one month.

□ Preparation of a series of calibration solution

- To three volumetric flask add:ca. 50 ml deionized water,
- Take 2, 6, 10 ml of mixed anion standard solution □by fill pipet
- Mix thoroughly.
- Fill to the mark with deionized water and mix thoroughly.
- Transfer the solution to 100 ml of polyethylene bottle.
- The solution can be stored in refrigerator at 4□ and used for a few days.

Table 2 Concentration relationship between mg/l and μmol/l

(mg/L)	0.20	0.60	1.0	2.0	6.0	10	20
Na+(μmol/L)	8.696	26.09	43.48	86.96	260.9	434.8	869.6
NH4+(μmol/L)	11.11	33.34	55.56	111.1	333.4	555.6	1111
K+(μmol/L)	5.116	15.35	25.58	51.16	153.5	255.8	511.6
Mg2+(μmol/L)	8.229	24.69	41.15	82.29	246.9	411.5	822.9
Ca2+ (μmol/L)	5.000	10.00	15.00	20.00	150.0	250.0	500.0

6) Preparation of working standard

Prepare the raw working standard according to the wet deposition monitoring manual(Japan environmental agency, May 1988, pp.23) and keep in a refrigerator at 4□.

Dilute 100 times when it is used (to a 1000 ml volumetric flask add 10 ml of the raw working standard, and fill to the mark with deionized water).

7) Operation procedures

- Check the previous record
- Fill the columns of recording format (name of operator, start time, concentration of eluent, ions to be measured and etc.)

i) Start up of IC for cation analysis

- Dispose all remained deionized water in bottle of eluent generator and in that of washer of auto-sampler. After washing the bottles for 2 times with deionized water, fill the bottles with deionized water.
- Power on the Ion Chromatograph, the detector and the Eluent Generator.

- Power on the auto-sampler and the computer.
- Vacuuming the air There is the possibility that air entered into the flow line of eluent generator. The air should be removed by 50 ml of syringe from the vacuuming mouth of the line. Fix the flow rate of the pump as 1.0 ml/min.
- Fix the current value of the suppressor as 50mA and flew the current on the operation panel icon. Warming up IC more than 30 min.
- Check the base line.
- Wash the syringe of auto-sampler with deionized water.
- Set the data processor as "Auto-Sampler" mode and fix the "Measurement Condition" on the method file screen and prepare the schedule file and select how to make calibration curves. The analysis should be ordered by 7 kind of calibration solution(0.2020 mg/l), deionized water, waking standard and samples. The order of calibration solution should be higher to lower concentration. Waking standard should be analyzed every 20 samples for the sensitivity check.

Table Analytical conditions for cation

Items	Items
Separation column Dionex CG12A	Data taking time 14 min.
Pre-column Dionex CS 12A	Data taking rate 5 Hz.
Eluent 20 m mol Methanesulformic Acid	Initial peak width 10 sec.
Flow rate 1.0 ml/min	Peak threshold value 0.5
Column Temp.. Room Temp..	Minimum peak area 1000
Detector Temp.. 35□	Calibration line approximation secondary curve
Column temp. 40□	Dilution 1
Temp.. Compensation 2.0%/□	Injection volume 50μl

ii) Measurement

Set samples on auto-sampler' tray according to the schedule file and start the measurement. Send a start signal from the computer.

iii) Making calibration curves

Calibration curves are automatically made if the method of calibration curves is set at the setting of method file of measurement condition .

(5) Duplicate analysis

Duplicate sample analyses should be performed on about 5% of routinely analyzed samples.

(7) Analyses of not detected and lowest determination limit