Trace-level determination of cations in the secondary circuit of a PWR-type nuclear power plant using ion chromatography after inline sample preparation

T. Hartmann, K. H. Viehweger, A. Wille

Metrohm
Ion analysis

Ion Chromatography

Summary

Apart from the target ions, real-life samples often contain interfering substances that complicate quantification and require time-consuming sample preparation steps like filtration, dialysis, SPE, preconcentration, etc.

The presented IC system meets the analytical challenge by applying sample preconcentration. A preconcentration column acts as the interface between the IC system and the MISP – Metrohm Inline Sample Preparation. All preparation steps take place in the low-pressure part of the system, outside the IC system proper. The cations to be analyzed enter the IC system via the preconcentration column. This arrangement is very robust, easy to configure and highly suitable for accurately determining trace levels (ppt) of lithium and sodium in the presence of ppm quantities of ethanolamine. The relative standard deviations are better than 1.5%. Carryover for metal cations is below 0.3%; recovery rates are better than 98.5%.

Introduction

Thermal power plants consume very large amounts of water. Water moderates nuclear fission, works as the heat transfer medium and its expanding vapor drives the turbines to produce electricity. In order to prevent corrosion, the water has to be maintained at a pH above 7. In general, this is achieved by the addition of Lewis bases such as ammonia and ethanolamine. Besides the added chemicals, also corrosive compounds such as sodium, sulfate and chloride can enter the water system of power plants. The presence of these ions indicates intrusions of external cooling water or contamination problems due to condenser tube leaks.

An efficient water chemistry monitoring program controls both the added and the detrimental ions, thus preventing failures and extending the operating lifetimes of components in contact with water.

System Setup

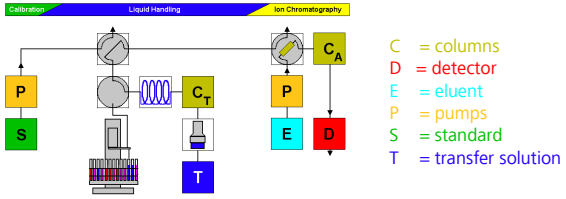
- Professional IC 850 Cation – Prep 2
- Professional Sample Processor 858 – Pump – Injector
- 800 Dosino
- Dosing Unit 10 mL
- Metrosep C PCC 1 HC
- Metrosep C2 – 250
- Metrosep C2 Guard

Inline sample preconcentration

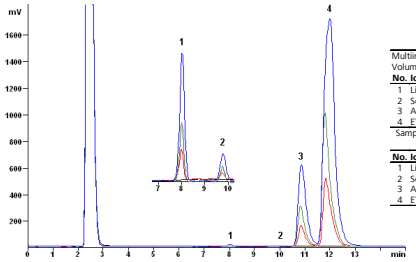
The 800 Dosino transfers any volume of sample accurately to the preconcentration column (PCC). Instead of aspirating the sample into the Dosing Unit it is drawn into the transfer tubing from where it is conveyed to the PCC. After the valve has been switched, multiple sample aliquots can be transferred to the PCC. Afterwards the whole flow path is rinsed with ultrapure water.

Inline calibration

The injection valve of the IC system is equipped with the preconcentration column and the second valve, the calibration valve, with a standard sample loop. The peristaltic pump fills the 10 µL loop with concentrated standard. After this, the injection valve switches to fill and the Dosino starts to pump ultrapure water to transfer the standard to the preconcentration column. After transfer the injection valve is switched and the first value for the calibration is measured. Sequential loop filling and preconcentration steps, controlled by the interplay between the valves and the 800 Dosino, allow to obtain multiple calibration values.



Cation analysis is performed with an isocratic IC system without chemical suppression, allowing for an assessment of amines.



Multiinjection	1 × Level 1	2 × Level 1	5 × Level 1
Volume (µL)	10	20	50
No. Ion	Concentration (µg/L)		
1 Lithium	200	400	1000
2 Sodium	200	400	1000
3 Ammonium	50'000	100'000	250'000
4 ETA	500'000	1'000'000	2'500'000

Sample concentrations corresponding to a preconcentration volume of 5000 µL (= conc. × 10/5000)

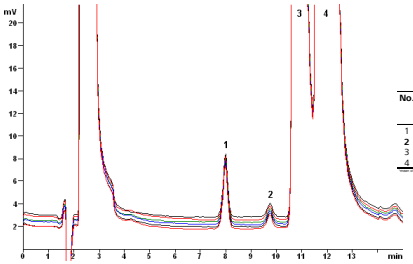
No. Ion	Concentration (µg/L)		
1 Lithium	0.4	0.8	2.0
2 Sodium	0.4	0.8	2.0
3 Ammonium	100	200	500
4 ETA	1000	2000	5000

Column: Metrosep C2 – 250 (6.1010.230)
Eluent: Tartaric acid-dipolinic acid eluent
Sample: Standard level 1, 2 and 3

A single standard in the microgram per liter range can be used to determine **samples** with contents **in the nanogram per liter range**. The resulting correlation coefficients (>0.999) underline the precision of the method, which is superior to that obtained with manual procedures.

Measurement

Standard deviations <1.5% are achieved in the upper ppt range, both for the concentration and the stability of the retention times. The concentration ratio between sodium and ETA is approx. 1:2000.



No. Ion	Concentration (ppb)[1]	RSD (%)	Recovery (%)	$t_{Retention}$ RSD (%)
1 Lithium	0.790	0.60	98.5	0.01
2 **Sodium**	**0.791**	**1.51**	**98.7**	**0.02**
3 Ammonium	199.12	0.41	99.3	0.02
4 ETA	1996.6	0.24	99.9	0.02

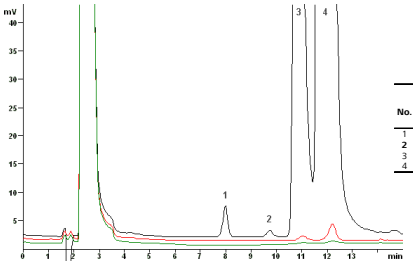
[1] n=6

Column: Metrosep C2 – 250 (6.1010.230)
Eluent: Tartaric acid-dipolinic acid eluent
Sample: From the secondary circuit of a nuclear power plant (n=6)
Concentration: ppb (µg/L)
Preconcentration volume: 5000 µL

The recovery rate of the investigated cations ranged from 98.5 to 99.9%. Interfering adsorption and contamination processes related to the vessel walls are minimized by using very large sample vessels (up to 500 mL). Additionally, time-consuming and error-prone decanting procedures are avoided.

Carryover

Samples, standards, regeneration and transfer solutions partly use the same tubing within the IC system. Carryover is kept negligible by sequential aspiration of a defined volume of air between liquid portions as well as by rinsing the complete flow path and the sample needle with ultrapure water.



No. Ion	Sample Peakarea (mV • s)	First rinsing step Peakarea (mV • s)	(%)	Second rinsing step Peakarea (mV • s)	(%)
1 Lithium	74.98	0	0	0	0
2 **Sodium**	**19.17**	**0**	**0**	**0**	**0**
3 Ammonium	4927.60	13.84	0.28	4.40	0.09
4 ETA	19174.00	54.80	0.29	7.05	0.04

Column: Metrosep C2 – 250 (6.1010.230)
Eluent: Tartaric acid-dipolinic acid eluent
Sample: Sample and 2 rinsing steps with ultrapure water
Concentration: ppb (µg/L)

Metrohm AG, CH-9101 Herisau/Switzerland, ht@metrohm.com, phone +41 71 353 86 47