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

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Metrohm
Ion analysis

Ion Chromatography

Summary

The analysis of ultratraces of anions in the primary circuit of a nuclear power plant is especially challenging as requirements of the hot zone as well as the high amount of boric acid (typically 2.5 g/L boron) in the sample and the presence of transition metals have to be taken into account. This is achieved by Metrohm inline sample preparation with matrix elimination to remove the boric acid, cation exchange to exclude interfering cations, inline calibration, preconcentration and chemical suppression. Even though the system involves several sample preparation steps, it yields extremely precise results for widely varying sample volumes.

Besides the standard anions chloride, nitrate and sulfate, also important organic degradation products such as glycolate, formate and acetate can be determined with high precision in one isocratic run.

Introduction

Thermal power plants consume very large amounts of water. In pressurized water reactors (PWR), water is the heat transfer medium and its expanding vapor drives the turbines to produce electricity. Moreover, aqueous solutions of boric acid are used as a moderator to slow down neutrons and thus control the nuclear reaction.

Monitoring the water quality and the addition of chemicals used to treat the water is of crucial importance for the security of power plants. Even trace amounts of chloride, nitrate and sulfate can lead to corrosion in the materials that are in contact with water and/or water vapor. Additionally, the concentration of short-chain organic acids in the water provide important information regarding the condition of the ion exchangers used in the nuclear power plant.

A highly efficient water chemistry monitoring program is needed to determine anionic trace level contaminations in highly borated waters.

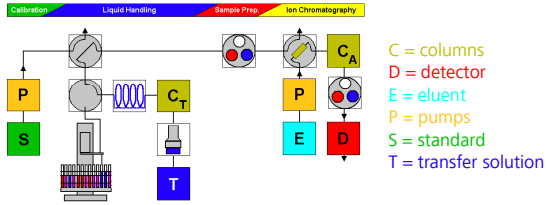
System setup

- Professional IC 850 Anion – MCS – Prep 2
- Professional Sample Processor 858 – Pump – Injector
- 833 Advanced IC Liquid Handling Sample Preparation Unit (not shown)
- Dosing Unit 10 mL
- 800 Dosino
- Metrosep A PCC 1HC
- Metrosep A Supp 7 – 250
- Metrosep RP Guard

Inline sample preparation

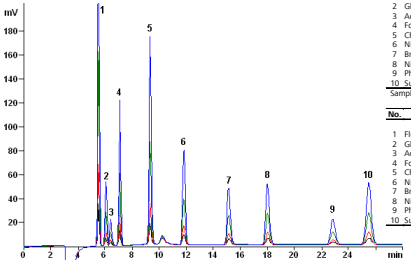
Ultratrace analysis of anions in the water of the primary cooling circuit of PWRs is complicated by the presence of interfering cations and high levels of boron. While the first problem can be solved by an inline cation exchange, the presence of boric acid requires inline matrix elimination: After transferring the sample to the preconcentration column (PCC) and prior to chromatographic separation, the rinsing with ultrapure water removes the boric acid from the PCC.

The excellent system performance is based on the «intactness» of the IC system itself. All sample preparation steps are performed outside the central IC system. As a result, they influence neither the separation itself nor the detection of the anions.



Inline calibration

System handling is optimized in a way that only one standard solution of higher concentration is used. Sequential loop filling and preconcentration steps allow to inject multiple calibration values, derived from a single concentrated standard solution.



Multiinjection	1 × Level 1	2 × Level 1	5 × Level 1	10 × Level 1
Volume (µL)	10	20	50	100
No. Ion	Concentration (µg/L)			
1 Fluoride				
2 Glycolate				
3 Acetate				
4 Formate				
5 Chloride	500	1000	2500	5000
6 Nitrite				
7 Bromide				
8 Nitrate				
9 Phosphate				
10 Sulfate				

Sample concentrations corresponding to a preconcentration volume of 2000 µL (= conc. × 10/2000)

No. Ion	Concentration (µg/L)			
1 Fluoride				
2 Glycolate				
3 Acetate				
4 Formate				
5 Chloride	2.5	5.0	12.5	25.0
6 Nitrite				
7 Bromide				
8 Nitrate				
9 Phosphate				
10 Sulfate				

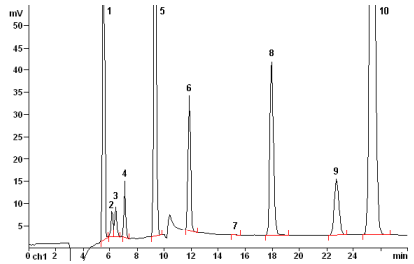
Column: Metrosep A Supp 7 – 250 (6.1006.630)
Eluent: Sodium carbonate eluent
Sample: Standard level 1, 2, 3 and 4
Concentration: ppb (µg/L)

Calibration values are selected so that the whole of the expected concentration range is covered. The obtained linearity of the inline calibration is excellent. The coefficients of correlations for all anions are better than 0.9999.

Measurement

The preconcentration volume depends on the expected concentrations and the matrix. For determinations in the lower ppt range, larger sample volumes can be preconcentrated.

For the following chromatogram a 2000 µL sample was used.



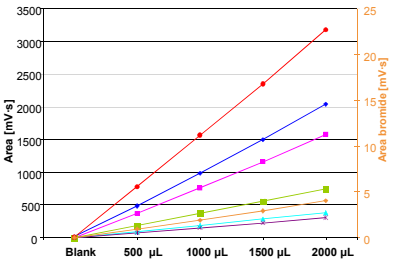
No.	Ion	Concentration (ppb)[1]	RSD (%)
1	Fluoride	20.17	0.29
2	Glycolate	3.63	0.07
3	Acetate	9.68	0.99
4	Formate	3.1	0.89
5	Chloride	25.54	0.33
6	Nitrite	10.82	0.80
-	Carbonate	-	-
7	Bromide	0.2	n.d.
8	Nitrate	22.35	0.18
9	Phosphate	17.75	0.24
10	Sulfate	69.71	0.15

Column: Metrosep A Supp 7 – 250 (6.1006.630)
Eluent: Sodium carbonate eluent
Sample: From the primary circuit of a nuclear power plant
Concentration: ppb (µg/L)
Preconcentration volume: 2000 µL

The Metrosep A Supp 7 – 250 column separates the rapidly eluting anions glycolate, acetate and formate in a single isocratic run. The relative standard deviation is better than 1%.

Linearity

Four different volumes – 500, 1000, 1500 and 2000 µL – were preconcentrated and a three-fold determination carried out on each.



No.	Ion	Concentration RSD (%)	Correlation coefficient r	Coefficient of determination r^2
1	Fluoride	0.29	0.99984	0.99969
2	Glycolate	0.07	n.d.	n.d.
3	Acetate	0.99	n.d.	n.d.
4	Formate	0.89	n.d.	n.d.
5	Chloride	0.33	0.99987	0.99974
6	Nitrite	0.80	0.99982	0.99964
7	Bromide	0.98	0.99930	0.99860
8	Nitrate	0.18	0.99995	0.99989
9	Phosphate	0.24	0.99993	0.99985
10	Sulfate	0.15	0.99992	0.99984

The fixed sample loop, the use of only one concentrated standard solution and the extraordinary precision of the 800 Dosino provide excellent results; both under normal laboratory conditions and under rough conditions prevailing in the power plant turbine room.

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