Development of ion chromatography methods for the determination of trace anions in ultra pure water from power plants

DRAGANA ČIČKARIĆ[1,*,#], IVANA DERŠEK-TIMOTIĆ[2], ANTONIJE ONJIA[3,#] and LJUBINKA RAJAKOVIĆ[1,#]

[1]*Faculty of Technology and Metallurgy, Karnegijeva 4, P. O. Box 494, 11000 Belgrade,* [2]*Hydro-Meteorological Institute of Serbia, Kneza Višeslava 66, 11000 Belgrade and* [3]*The Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia and Montenegro* (e-mail: gaga@tmf.bg.ac.yu)

Abstract: A suppressed ion chromatography (IC) technique, using a carbonate/hydrogen carbonate or a hydroxide eluent, has been evaluated as a monitoring tool for the detection of major anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) in ultra pure water and condensed steam from thermal power plants. An electrical conductivity detector with an anion-exchange column (IonPac AS14), an auto self-regenerating suppressor (ASRS), and an isocratic high-pressure pump system were used for the detection of low concentrations of inorganic anions. It was shown that the suppressed IC technique provides a suitable means for preventing possible damage to generating equipment in power plants. The detection limits of the method for the anions of interest were < 0.3 μg/L.

Keywords: trace analysis, anions, ultra pure water, IC, power plant.

INTRODUCTION

One of the primary concerns in all power plants is to ensure high-purity water which is the basis for the generation of ultra pure steam in the water–steam cycle of a power plant. Anions, cations, transition metals and silica should be monitored in raw water, demineralizer influent/effluent, process steam, boiler feed water, boiler blowdown water, high and low pressure steam condensate and condensate polisher water. The measurement of trace level of ionic impurities throughout the power generation process is critical for the identification and prevention of corrosive conditions in many power plant components. Corrosive ions, such as chloride, should be minimized and continuously monitored. Control of impurities, such as sodium

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* Correpsonding author.

\# Serbian Chemical Society active member.

ions, sulfate ions and other ions (fluoride, phosphate, nitrate, calcium, magnesium) provides valuable information regarding the source of contamination, the likely rates of contaminant build-up, and probable rates of corrosion and timely data during the start-up and shut-down of power plants.[1]

Ion chromatography (IC) has become an important technique for monitoring water quality and for the determination of ionic species with respect to corrosive ions.[2,3] Anions in the mg/L and μg/L levels can be analyzed with the direct injection technique. For the determination of lower levels of ionic impurities (low mg/L or μg/L levels), sample preconcentration is necessary. Typically, the analytes of interest are preconcentrated on a small precolumn in order to "strip" ions from a measured sample volume.[4,5] This preconcentration results in lower detection limits. However, the preconcentration method has several disadvantages compared with the large-volume direct injection technique which is applied in this work.[6–8]

Unlike the non-suppressed detection mode typically used with a single chromatographic column with an eluent which is not chemically modified prior to entering the detector, the suppressed detection mode is characterized by the use of suppression devices which enable chemical conversion of anion salts to their conjugated acids just prior to the conductivity detector. In this way the background conductance of the eluent is lower than the overall conductance of the analyte, resulting in lower detection limits.[9]

Due to this advantages, suppressed IC analysis of anions can provide detection limits up to 10 times lower than non-suppressed systems. This clearly explains why the suppressed IC technique is recommended as the preferred detection mode for the determination of anions. In optimized suppressed IC, the employed working eluents are usually sodium hydroxide or carbonate–hydrogen carbonate buffers. These eluents can be converted into species of low conductance, such as water or H_2CO_3, after the ion exchange of their cations with hydrogen ions by suitable suppression devices, such as packed-bed chemical suppressors, membrane suppressors or self regenerating suppressors. High signal-to-noise ratios are generally achieved by the suppression, extending the linear dynamic concentration range of the analyses from μg/L down to ng/L levels. Such concentration ranges are generally sufficient for any complex IC application where a trace analysis of anions is required.[10]

Though the suppressed IC technique for separating and detection of inorganic anions has been extensively developed, quantifying anions at low concentration in different types of chemical matrices continues to be an important analytical problem. The development of IC is still a challenge with regard to lowering the detection limits and obtaining better resolution of the ions present in a sample. Bearing this in the mind, a suppressed IC procedure was developed for determining anions in power plant water matrices. The determination of the major inorganic anions (*i.e.*, F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) in ultra pure water samples was the main analytical task in this work, aimed at developing a reliable analytical method for monitoring the chemical impurities in water–steam samples of power plants.

In this investigation the samples were injected using a large-volume direct injection technique (large sample loop volume of 1000 μL). The analyte ions were separated on a selective ion-exchange column using high-purity mobile phases (carbonate/hydrogen carbonate eluents for the determination NO_3^-, PO_4^{3-} and SO_4^{2-}, and sodium hydroxide for the determination of F^- and Cl^- ions) and detected using the suppressed conductivity detection method. The detection limits of the method for most analyte ions in ultra pure water ranged from 0.07 to 0.3 μg/L.

EXPERIMENTAL

Instrumentation

A Dionex DX 100 IC system (Dionex, Sunnyvale, CA, USA) consisting of an IP20 isocratic pump and a CD20 conductivity detector was used. A PeakNet 5.1 chromatography workstation was used for instrument control, data collection and processing. A sample loop with a volume of 1000 μL was made from poly(ether ether ketone) (PEEK) tubing of length of 210 cm and I.D. 0.750 mm. Its volume was verified by measuring the mass difference between the sample loop filled with deionized water and the empty loop. The separations of the target analyte anions were performed on IonPac AS14 (250 mm × 4 mm I.D.) and AG14 (50 mm × 4 mm I.D.) columns. An Anion Self Regenerating Suppressor (ASRS, 4 mm I.D.) operating in the recycle mode was used as the suppressor. Details of the operating conditions of the IC system are presented in Table I.

TABLE I. Operating parameters for anion separation by suppressed IC with an anion-exchange column (IonPac AS14) under isocratic conditions

	Anion chromatography
Column	IonPac AS14 Analytical (4×250 mm)
	IonPac AG14 Guard (4×50 mm)
Eluents	1) Na_2CO_3/$NaHCO_3$ 4.5 mM (3.5:1.0)
	2) NaOH 1.0 mM
Eluent flow rate	1 mL/min
Injection volume	1000 μL
Detection	Suppressed conductivity
Full-scale range	3 μS (for eluent 1); 10 μS (for eluent 2)
Suppression	ASRS recycle mode (4 mm)
Suppressor current	50 mA

Chemical reagents, standard solutions and eluents

All chemicals for the preparation of the IC eluents and standard solutions were of analytical-reagent grade and dissolved in deionized water. Stock standard solutions of anions containing 1000 mg/L, available from Merck (CertiPur), were used in this study. The stock standard solutions were stored at 4 ºC. Standard working solutions of lower analyte concentrations (<100 μg/L) were prepared daily by diluting the stock solutions with deionized water. Fresh working eluents 1 and 2 were prepared daily, filtered through a 0.2 μm pore size membrane filter (Millipore, USA), and degassed prior to use.

Deionized water with a specific resistance of 18.2 MΩ cm was used to prepare all the solutions. Extreme caution was taken to prevent any possible contamination from the environment and the sample handling when preparing all trace-level calibration standard solutions. All calibration

standards and spiked samples were stored in polyethylene containers which had been thoroughly cleaned and presoaked in deionized water for at least 24 h.

Samples

Thermal power water and steam samples were collected *in situ* from different steam pipelines before the steam enters the generation turbines. Two condensed steam samples were additionally collected at the exit of the turbine. All samples were handled carefully to avoid contamination and were analyzed in the chemical laboratory as quickly as possible. The samples were analyzed directly without any pretreatment, except filtering through a syringe membrane filter (0.2 μm) just prior to injection into the suppressed IC system. A 5-ml syringe was used to load the standards and samples into the sample loop.

RESULTS AND DISCUSSION

Separation of anions

The use of an IonPac AS14 column with an eluent mixture of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ and a suppression device operated in the continuous self-regeneration mode has been shown to be a well-established IC setup for separating anions. All the anions are eluted in less than 15 min (Fig. 1). Despite the relatively short analysis time exhibited in these runs, all five anion peaks of interest were well separated at these low concentrations. The analysis time can be reduced by modifying the eluent composition, the eluent flow-rate, the stationary phase composition or the column temperature.[11] Shorter retention times can also be obtained due to a loss of column efficiency, which is unfavorable because the peak resolution worsens.[12] In this work, the optimum IC conditions, as presented in Table I, were determined by trial-and-error. No further reduction in the analysis time was made in order to enable sufficient resolution between adjacent peaks for samples in which a large difference in the concentrations of the anions exists.
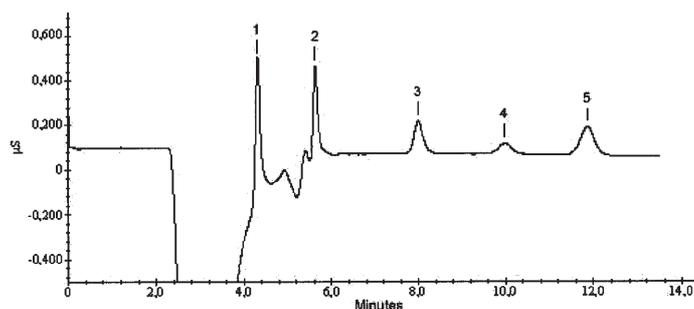

Fig. 1. Separation of inorganic anions of a standard mixture (40 μg/L). Peaks: 1–fluoride, 2–chloride, 3–nitrate, 4–phosphate, 5–sulfate. The operating conditions are given in Table I (Eluent 1)

Precision and calibration tests

Reproducibility tests based on five injections of an anions standards consisting of F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were performed. Reproducibility data for retention times and peak areas and peak heights, obtained using the operation parameters described in Table I, were statistically evaluated from the relative stan-

dard deviation (*RSD*) and are presented in Tables II and III. The *RSD* values for the retention times and peak areas were less than 0.8 and 9 %, respectively.

TABLE II. Reproducibility data (*RSD*) of retention times of the target analyte anions ($n = 5$). Operating conditions were the same as in Table I (Eluent: 4.5 mM Na_2CO_3/$NaHCO_3$)

	Concentration / µg L^{-1}								
Anion	0.1	0.4	0.7	1.0	5.0	10	40	70	100
	τ / min								
Fluoride	0.43	0.64	0.21	0.41	0.59	0.42	0.33	0.55	0.62
Chloride	0.40	0.61	0.29	0.54	0.33	0.31	0.60	0.53	0.78
Nitrate	0.26	0.55	0.45	0.49	0.28	0.38	0.31	0.43	0.26
Phos-phate	n.d.	n.d.	0.46	0.31	0.54	0.33	0.53	0.21	0.39
Sulfate	0.58	0.33	0.21	0.15	0.35	0.29	0.26	0.18	0.35

n.d. – Not detectable

TABLE III. Reproducibility data of the method (*RSD*) for target analyte anions ($n = 5$). Operating conditions were the same as in Table I (Eluent: 4.5 mM Na_2CO_3/$NaHCO_3$)

	RSD / %					
Anions	Nitrate		Phosphate		Sulfate	
Concentration/µg L^{-1}	Peak area	Peak height	Peak area	Peak height	Peak area	Peak height
0.1	6.0	3.0	n.d.	n.d.	7.6	2.9
0.4	4.8	5.3	n.d.	n.d.	3.0	8.5
0.7	2.7	6.3	8.3	8.0	2.9	6.7
1.0	0.1	1.5	7.4	8.8	2.1	2.6
4.0	5.4	8.5	6.3	6.1	7.7	2.4
7.0	4.6	7.1	5.3	4.7	1.8	1.7
10	1.3	1.9	2.9	3.4	1.5	2.8
40	2.0	0.2	5.4	5.4	3.7	2.0
70	3.4	3.5	3.3	1.2	2.7	1.3
100	2.2	2.4	3.1	2.8	2.1	1.9

Fluoruide and chloride were determined using the hydroxide eluent (eluent 2). To increase the detector response to the analytes, the large-volume direct inject technique was used to inject 1000 µL of sample in this method. Since the IonPac AS14 column has sufficient ion-exchange capacity, no noticeable band broadening of the analyte peaks was observed due to the loading of such a large sample vol-

ume. The use of the large-volume direct injection technique eliminates the neces-
sity for sample pre-concentration, which typically involves the use of a concentra-
tor column and is so more cumbersome and time-consuming.

A representative chromatogram obtained for standards solutions of the target
anions is shown in Figure 2. The analyte concentrations in the standards ranged
from 0.1 μg/L to 100.0 μg/L for fluoride and chloride.

The relative standard deviations (*RSD*) of the peak areas and peak height were less
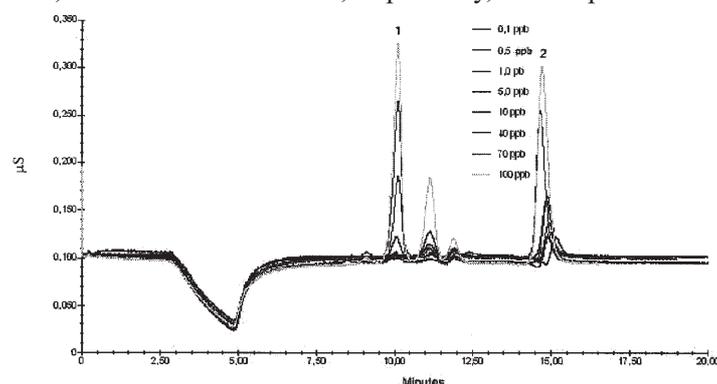than 5 and 3 %, for fluoride and chloride, respectively, and are presented in Table IV.

Fig. 2. Representative chromatograms of inorganic anions of standard mixtures (0.1 – 100.0
μg/L). Peaks: 1–fluoride, 2–chloride. The operating conditions are given in Table I (Eluent 2).

TABLE IV. Reproducibility data (*RSD*) of the IC method for fluoride and chloride using an aqueous
NaOH solution as the eluent (*n* = 5)

Concentration/μg L^{-1}	*RSD* / %							
	0.1	0.5	1.0	5.0	10	40	70	100
Anion	Peak area							
Fluoride	3.2	2.8	3.5	2.0	1.1	1.2	0.6	1.3
Chloride	4.3	1.6	2.2	2.2	0.8	3.5	2.2	0.7
Anion	Peak height							
Fluoride	2.5	3.2	2.1	1.9	2.9	1.8	1.2	1.7
Chloride	2.6	2.2	2.5	0.7	0.4	1.1	1.2	0.8

The method detection limits (MDL)

The *MDL* for all the chromatographic analyses were calculated using the
well-known "3σ method".[1,13] This statistical method can determine a *MDL* based
on a trace-level standard. To determine the precision, five replicates of the anions
standards were injected. The standard deviation of these replicates was divided by
the slope of the calibration curve to estimate the standard deviation (*SD*) value in
concentration units. This *SD* was finally multiplied by the corresponding Student's

t-value (for a 99 % confidence level) to calculate the *MDL* of the anion. The *MDL* value obtained in these IC experimental runs are given in Table V. Although the *MDL* values achieved with the present IC instrument were higher than expected, they were generally suitable for most of the analyzed samples.

TABLE V. Method detection limits obtained for the five studied analyte anions (*n* = 5)

Anion	MDL^b/μg L^{-1}	Correlation coefficient *r*
Fluoride	0.07	0.9999
Chloride	0.08	0.9903
Nitrate	0.18	0.9975
Phosphate	0.23	0.9993
Sulfate	0.20	0.9989

[b]$MDL = (S.D.) \times (t_s)_{99 \%}$, for *n* = 5

Application: determination of anion impurities in condensed steam samples

The proposed suppressed IC procedure was applied as a monitoring analytical tool for the analysis of the inorganic anion composition of steam samples collected from thermal power plants. Most of these samples were strategically selected in order to collect steam before it goes through the turbines. However, two condensed steam samples were additionally collected at the exit of the turbines. Such samples were selected for evaluating the background anion composition of steam in the entire power generation cycle. Examples of the application of the IC procedure using an IonPac AS14 column for measuring the major anions in power plant ultra pure water and steam samples are presented in Fig. 3 and Fig. 4, respectively. These Figures present typical expanded chromatograms showing the efficient separation of all of the investigated anions for their detection at trace levels.[14]
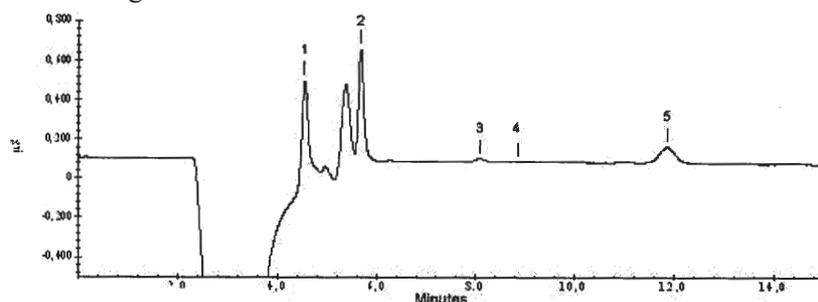

Fig. 3. Representative chromatogram of anions corresponding to suppressed IC analysis of a condensed steam sample. Peaks: 1–fluride, 2–chloride, 3–nitrate, 4–phosphate, 5–sulfate. The operating conditions are given in Table I (Eluent 1).

The NO_3^- and PO_4^{3-} peaks were near the background noise levels and were therefore reported as being below the *MDL* (see Table V). An interesting monitoring case was found when the steam samples collected at the entrance of the turbine
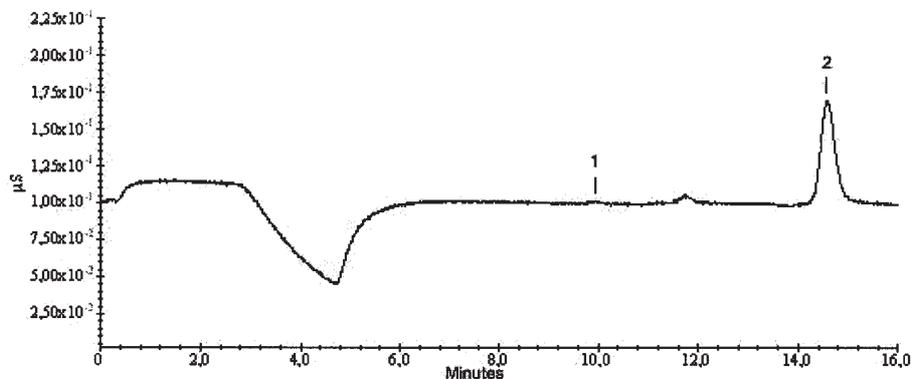
Fig. 4. Representative chromatogram obtained for a condensate sample. Peaks: 1–fluride, 2–chloride. The operating conditions are presented in Table I (Eluent 2).

and at its exit were analyzed separately. An increase in the Cl^- and SO_4^{2-} concentrations was observed in these samples. Such small increases could probably be attributed to the effect of steam separation in the condenser section of the thermal power plant. This separation process tends to slightly concentrate the resulting condensed steam phase at that sampling site.

Interferences

The shifting observed for the Cl^- peaks in all sample chromatograms may be associated with matrix effects, the origin of which should be studied in the future.

In the case of the separation of fluoride and chloride using hydroxide eluent, the nitrate, phosphate and sulfate which were present in the injected samples did not interfer; their retention times being more than 15 min.

CONCLUSION

A simple suppressed IC procedure for the efficient separation and quantification of anions under isocratic conditions was evaluated. This method was used for the chemical analysis of inorganic anions at concentations ranging from 0.1 to 100 μg/L. The use of anion-exchange chromatography with an IonPac AS14 separation column, a working eluent containing 3.5 mM $Na_2CO_3^-$ 1.0 mM $NaHCO_3$, or 1 mM NaOH and suppressed conductivity detection provided a simple, cost-effective, fast, accurate, and highly sensitive technique for the determination of F^-, Cl^-, and SO_4^{2-} (NO_3^- and PO_4^{3-} were usually below their *MDL*) in thermal power condensed steam samples. The method was linear ($r > 0.99$) over the working concentration range. The detection limits were found to be 0.080, 0.160, 0.180, 0.230 and 0.200 μg/L for F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}, respectively, with the carbonate eluent and 0.077 and 0.082 μg/L for F^- and Cl^-, respectively, with the hydroxide eluent. With this suppressed IC technique, it was possible to measure inorganic anions at trace level in condensed steam samples from thermal power plants.

The present method, therefore, may be taken as an appropriate analytical tool for monitoring the chemical impurities of steam in thermal power plants. Such monitoring should be considered essential for extending the life-time of power generation equipment in the thermal power industry.

ИЗВОД

РАЗВОЈ МЕТОДА ЈОНСКЕ ХРОМАТОГРАФИЈЕ ЗА ОДРЕЂИВАЊЕ ТРАГОВА АНЈОНА У УЛТРА ЧИСТИМ ВОДАМА ИЗ ТЕРМОЕЛЕКТРАНА

ДРАГАНА З. ЧИЧКАРИЋ[1], ИВАНА ДЕРШЕК-ТИМОТИЋ[2], АНТОНИЈЕ ОЊИА[3] и ЉУБИНКА РАЈАКОВИЋ[1]

[1]Технолошко-металурш͘ки факулш͘еш͘, Карнеīијева 4, ͠. ͠р. 494, 11000 Беоīрад, [2]Реͥублички хидромеш͘еоролошки завод Србије, Кнеза Вишеслава 66, 11000 Беоīрад и [3]Инсш͘иш͘уш͘ за нуклеарне науке "Винча", ͠. ͠р. 522, 11001 Беоīрад

Техника супресивне јонске хроматографије (IC) развијена је за анализу трагова анјона (F⁻, Cl⁻, NO_3^-, PO_4^{3-} и SO_4^{2-}) у узорцима ултра чисте воде. Детектор електричне проводљивости са колоном за јонску измену (IonPac AS14), саморегенеришући анјонски супресор (ASRS) и изократична IC пумпа високог притиска успешно су примењени за откривање ниских концентрација неорганских анјона. Развијене су две IC методе, једна са карбонатним (за анализу NO_3^-, PO_4^{3-} и SO_4^{2-}-јона), а друга са хидроксидним елуентом (за анализу F⁻ и Cl⁻-јона). Границе детекције примењених метода биле су: < 0,3 µg/L (метода са карбонатним елунтом) и < 0,1 µg/L (метода са хидроксидним елуентом). На овај начин развијене су две IC методе које се могу применити за контролу трагова анјона у систему вода-пара у термоелектранама.

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