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INTEGRATED SEPARATION SCHEMES IN CHROMATOGRAPHY

SIMULTANEOUS EMPLOYMENT OF ION EXCLUSION AND ION EXCHANGE FOR THE SEPARATION OF BORATE, CHLORIDE, NITRATE AND IODIDE

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SUMMARY

This paper presents the combined use of ion-exclusion and ion-exchange columns to effect the separation of boron as boric acid from the anions chloride, nitrate and iodide. The fully automated system is controlled by a microprocessor housed in one of the system's pumps, flow paths between the columns and detectors are directed by two six-port valves. Detection was by refractive index for boric acid and by conductivity for the anions. The instrumentation was evaluated for performance using a set of solutions over the pH range two to thirteen and was found to give a wide linear dynamic range and reproducibility of less than 1% relative standard deviation.

INTRODUCTION

The analysis of cooling water used in the nuclear power industry requires a rapid and accurate determination of chloride and boron. Cooling water may exhibit dramatic changes in both, ion concentrations and pH during a plant shutdown of during a nulear accident. Thus, any method used for these analyses requires a wide linear range for ion concentrations and stability over a wide pH range.

The instrumentation and method presented in this paper allows the simultaneous analysis of boron (as boric acid) and the anions of analytical interest; chloride, nitrate and iodide, over the wide range required by the nuclear power industry and Nuclear Regulatory Commission (NRC).

Ion-exclusion and ion-exchange columns were utilized for separation, with refractive index and conductivity detection. Sample pretreatment was not required, thus, on-line sampling or injection of batch samples are practical methods of sample introduction.

The sensitive and reliable analysis of anions with pK_a of less than seven has been widely reported[1-3] however, anions with pK_a of greater than seven, such as boric acid pK_a 9.14 (ref. 4) are poorly retained on ion-exchange columns, frequently dis-

playing poor sensitivity with conductivity detection. Sample solutions of high pH present further complications for boric acid analysis with ion-exchange systems, frequently a broad early eluting peak due to the high hydroxide ion concentration will interfere with the separation and detection of the borate ion[5–9].

This paper presents a technique in which the injected sample was first passed through an ion-exclusion column in the presence of a strong acid eluent. The weakly dissociated species, such as boric acid, were well retained by the ion-exclusion column, and thereby were separated from the anionic components of the sample, the boric acid concentration was then determined with direct refractive index detection.

The pH of the anion containing sample band was normalized by mixing with the strongly acidic eluent. This sample band eluted in the "void" volume of the ion-exclusion column and was automatically transferred to the linked ion-exchange system for separation of the anions using an octanesulfonate eluent and quantitation by conductivity detection. In the case of strongly basic samples, the pH of the anion containing sample slug was reduced to well within the range of the ion-exchange system.

The system is described and its performance evaluated for reproducibility and pH stability for boron and chloride in samples encountered in the nuclear power industry.

EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model 410 differential refractometer, Model 430 conductivity detector, Models 510 and 590 solvent delivery systems. Waters automated valve station (WAVS) and Model 840 data station.

Two columns were used in the liquid chromatograph, an ion-exclusion column and a low capacity ion-exchange column. The ion-exclusion column was a "Fast Fruit Juice" 15 cm × 7.8 mm I.D. stainless-steel column packed with 50-Å, 10-μm fully sulphonated resin (Waters Assoc.). The ion-exchange column was a Waters IC Pak A, anion column, 50 × 4.6 mm I.D., packed with 10 μm PMMA resin (quarternary ammonium functional groups) 30 ± 3 mequiv./ml (Waters Assoc.).

Reagents

All reagents were of the highest available purity, standard solutions of the anions were prepared by dissolving weighed amounts of the metal salts in water purified with a Millipore (Bedford, MA, U.S.A.) Milli-Q water purification system. Boron solutions were prepared by dissolving weighed amounts of boric acid in pure water.

The eluents were made-up using analytical grade reagents and pure water. The anion exchange eluent was 3 mM octanesulfonate containing 0.65 g of sodium octanesulfonate (Sigma, St. Louis, MO, U.S.A.) in 1 l of Milli-Q water, the resulting pH of 5.7 was not adjusted. The ion-exclusion eluent of 1.25 mN sulfuric acid was made by dilution of Ultrex grade sulfuric acid (J. T. Baker, Phillipsburg, NJ, U.S.A.) in Milli-Q water. The mobile phases were passed through 0.45-μm filters (Millipore) and degassed in an ultrasonic bath. Other chromatographic conditions are given in the captions to the figures.

Standard solutions

Three standard solutions were prepared for the evaluation of the system. The first was a solution of 2000 ppm boron as boric acid in pure water. The two remaining solutions were formulated according to NRC[10] regulations, to simulate nuclear reactor cooling water after a nuclear accident. These two solutions contained ions at the levels indicated in Table I, by dissolving potassium iodide, cesium nitrate, barium nitrate, boric acid and lithium hydroxide in pure water. One solution was used at its natural pH (pH 4.7), the second was adjusted to pH 13 by the addition of sodium hydroxide. Sample volume (20 μl) was predetermined by the size of the sample loop connected to valve A (Fig. 1). Samples were injected using 3-cc Plastipak syringes (Becton, Dickinson Co., Rutherford, NJ, U.S.A.).

TABLE I

CONSTITUENT IONS IN NRC SOLUTIONS

See text for details.

Ion	Concentration (ppm)
Iodide	40
Cesium	250
Barium	10
Lanthanum	5
Cerium	5
Chloride	10
Boron	2000
Lithium	2
Nitrate	150
Ammonium	5
Potassium	20

System operation

The basic steps involved in the simultaneous analysis of boric acid and inorganic anions are shown in Table II, the pump microprocessor controls the operation of the high pressure column switching valves in a programmed sequence. Fig. 1 shows a schematic of the system.

In Fig. 2a, the system has flow paths determined by valves A and B. Eluent from pump one passes through valve A (the injector) to the ion-exclusion column, hence, through valve B to the refractive index detector, D. Pump two supplies the eluent for the ion-exchange column through valve B. The ion-exchange column effluent is then directed through the conductivity detector. With the high pressure switching valves in the positions shown in Fig. 2a, the system was allowed to equilibrate. At this stage, the sample loop was filled by a syringe. Alternatively, the sample injection could be carried out from a remote sampling point in the case of an on-line monitoring system.

The next stage is represented in Fig. 2b, the sample loop was switched into the

TABLE II

WATERS M590 PUMP PROGRAM FOR THE SIMULTANEOUS ANALYSIS OF BORIC ACID AND OF CHLORIDE

| Program segment	Segment actuation by M590 keyboard or at a time interval indicated below (min)	Flow-rate (ml/min)	External events (contact closures)				Comments
			Valve A (Fig. 1)	Valve B (Fig. 1)	Integration start, anion system	Integration start, boron system	
1	Keyboard	1.0	On	On	Off	Off	Configuration as in Fig. 2a
2	0.1	1.0	Off	On	On (pulsed)	On (pulsed)	Injects sample at 0.1 min. Fig. 2b
3	2.10	1.0	Off	Off	Off	Off	Cuts excluded anions, Fig. 2c
4	2.40	1.0	On	On	Off	Off	Resumes original position. Fig. 2d. Analysis of anions continues
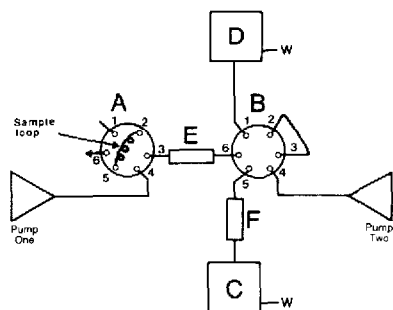
Fig. 1. Details of interconnections used for the simultaneous analysis of boric acid and chloride with ion-exclusion and anion-exchange columns using refractive index and conductivity detection. A, B = Six-port high-pressure switching valves; C = conductivity detector; D = refractive index detector; E = ion-exclusion column; F = ion-exchange column; pump one = ion-exclusion pump; pump two = ion-exchange pump; w = waste.

eluent stream between pump one and the ion-exclusion column, E. The solvent and anionic components of the sample flowed through the ion-exclusion column essentially unretained, whilst, boric acid was retained for a discrete retention time upon the same column. Having been separated from the boric acid, the anionic components contained in the sample eluted in the void volume of the ion-exclusion column. The anion containing portion of the void volume is transferred to the ion-exchange system
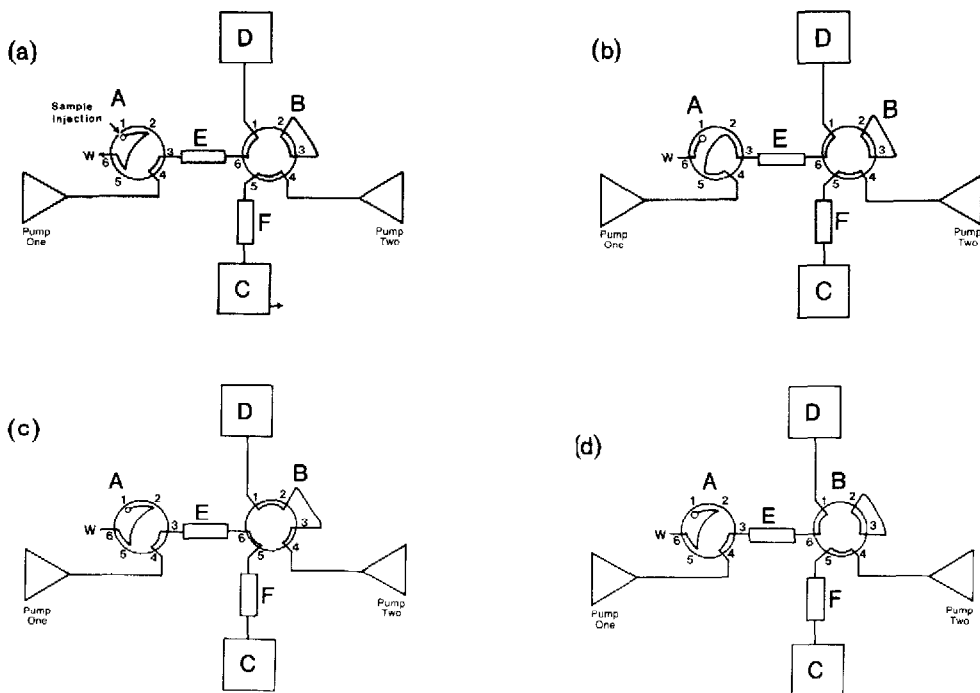

Fig. 2. Flow paths used at various stages of the simultaneous boric acid, chloride analysis. See text for discussion. (a) Injection mode; (b) boric acid capture; (c) transfer of anions to ion-exchange system; (d) simultaneous analysis. See Fig. 1 for abbreviations.

as represented in Fig. 2c. The anion containing band is pumped through valve B toward the anion-exchange column, F. Once the anions had been transferred to the anion-exchange system, the high pressure valves were switched to the positions shown in Fig. 2d, where the independent analysis of boric acid by ion exclusion and anions by anion exchange takes place.

The method described allows considerable flexibility in the choice of eluents in the two systems; ion exchange and ion exclusion, are essentially operated independently throughout the analysis.

RESULTS AND DISCUSSION

Boron analysis

The separation of boron as boric acid was achieved using a dilute sulfuric acid eluent with an ion-exclusion column. The low pH of the sulfuric acid eluent ensures that borate anions present in the sample were in the form of boric acid, which was retained in the ion-exclusion column, whilst, strongly ionized ions such as chloride were unretained.

The system was evaluated for linearity and reproducibility for a number of boric acid solutions using refractive index detection.

Reproducibility was evaluated by making ten serial injections of the following solutions: 2000 ppm boron as boric acid, a 2000-ppm boron as boric acid (pH 4.7) solution containing ions according to NRC regulations, detailed in Table II and a solution containing 2000 ppm boron as borate at pH 13 with the NRC ion matrix. Fig. 3 presents a typical chromatogram from this procedure. The results of the reproducibility study are presented in Table III, both retention times and peak heights proved to be unaffected by matrix and sample pH with relative standard deviations (R.S.D.) of less than 1%. Response was shown to be linear over the range of 6 to 6000 ppm boron by injections of solutions which contained 6, 60, 600, 1000, 2000, 3000 and 6000 ppm boron as boric acid in Water. Fig. 4 displays outstanding linearity of the refractive index detection of boric acid.
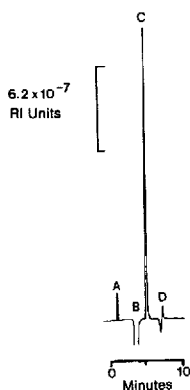

Fig. 3. Chromatogram of boric acid using RI detection with ion exclusion. Column: Waters "Fast Fruit Juice". Eluent: 10 mN sulfuric acid. Flow-rate: 1 ml/min. Sample: 10 μl 2000 ppm boron as boric acid. Detection: Waters M410 refractive index, sensitivity 128, scale factor 10. A = Injection mark; B = solvent peak; C = boric acid; D = system peak.

TABLE III

REPRODUCIBILITY OF PEAK HEIGHTS AND OF RETENTION TIMES (t_R) FOR BORON ANALYSIS BY REFRACTIVE INDEX DETECTION USING CONDITIONS GIVEN IN FIG. 3

	2000 ppm boron as boric acid		2000 ppm boron natural pH, NRC matrix		2000 ppm boron pH 13 NRC matrix	
	t_R (min)	Peak heights (cm)	t_R (min)	Peak heights (cm)	t_R (min)	Peak heights (cm)
	4.01	20.60	4.02	20.60	3.99	20.45
	3.99	20.55	3.98	20.55	3.98	20.50
	4.02	20.55	4.00	20.60	3.99	20.60
	4.01	20.58	4.01	20.65	4.00	20.55
	4.01	20.55	4.02	20.60	4.01	20.60
	4.02	20.60	3.99	20.55	4.00	20.60
	4.01	20.58	4.01	20.60	4.02	20.55
	3.98	20.60	4.02	20.60	4.03	20.60
	3.99	20.55	3.98	20.60	3.98	20.50
	4.01	20.60	3.98	20.60	4.01	20.55
Average	4.01	20.58	4.00	20.60	4.001	20.55
S.D.	0.01	0.02	0.02	0.03	0.02	0.05
R.S.D. (%)	0.34	0.1	0.42	0.14	0.42	0.24

Anion analysis

The suitability of the discussed system for anion analysis was tested by injections of the previously detailed natural and elevated pH, NRC matrix solutions. The performance of ion-exchange systems with conductivity detection has been shown to be effective by numerous workers[1-3]. High pH samples, however, frequently produce baseline perturbations in the section of the chromatogram ascribed to the void volume or lead to troublesome system peaks later in the chromatogram[11]. In our system the sample has passed through a protonated ion-exclusion column and has been mixed with an acid eluent prior to its transfer to the ion-exchange system. In the
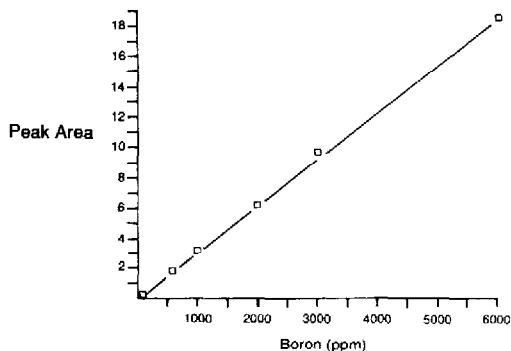

Fig. 4. Peak areas (arbitrary units) obtained for various boric acid concentrations expressed as ppm boron. Sample concentrations as indicated. Conditions as in Fig. 3.

process, sample pH is adjusted toward a lower pH by the acidic eluent, so that the otherwise troublesome broad solvent beak is avoided.

Fig. 5 displays two chromatograms obtained from the injection of the pH 4.7 and pH 13 NRC standard solutions. The ions chloride, nitrate and iodide were all well resolved and exhibited good peak shapes. Whilst, the sample band was inevitably broadened by mixing with the acid eluent in the ion-exclusion column, on contact with the ion-exchange column the band was concentrated to a narrow band prior to elution, termed the relaunch effect[12], thus, efficiencies and resolutions for the anion peaks were commensurate with an independently operated system. The ion-exchange column was not overloaded by the sulfate ion resulting from the mixing with the acid eluent, as can be seen in Fig. 5 the system quickly returns to baseline. By employing the technique discussed in this article, the analysis of the anions chloride, nitrate and iodide in high pH solutions can thus be effectively conducted using the same chromatographic conditions as for neutral pH solutions, as shown in Fig. 5.
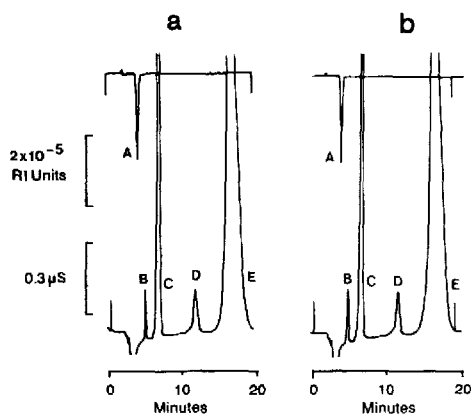

Fig. 5. Chromatograms for boric acid and anions by simultaneous ion-exclusions and ion-exchange analysis. Columns: as described in text. Eluents: 1.25 mN sulfuric acid (ion exclusion) 1.0 ml/min, 3 mM sodium octane sulfonate (ion exchange) 1 ml/min. Samples: (a) 20 μl 2000 ppm boron, NRC matrix pH 4.7; (b) 20 μl sample (a) adjusted to pH 13. Detection: Waters M430 (conductivity) 2.5 μSFS; Waters M410 (refractive index) sensitivity 16, scale factor 2. Peak identities: A = boric acid (2000 ppm); B = chloride (3.8 ppm); C = nitrate (138 ppm); D = iodide (40 ppm); E = sulfate.

CONCLUSIONS

The simultaneous analysis of boron as boric acid and of the anions chloride, nitrate and iodide in a wide range of sample pH values may be successfully achieved by using linked ion-exclusion and ion-exchange columns with refractive index and conductivity detection. The wide linear range of refractive index detection is particularly appropriate to the analysis of boron in nuclear reactor cooling water. The system has been shown to give fast, highly reproducible results for the ions of interest, with freedom from interferences caused by variations in sample pH. Although the method and apparatus presented here have been used for weakly and strongly ionized inorganic anions, our current work has shown that with minor modifications, the same

apparatus is suitable for the analysis of alkaline or alkaline earth cations in the presence of strongly ionized anions, and for inorganic ions in the presence of concentrated organic acids. By the use of automated switching valves to control columns of differing selectivity, separations of widely varying sample matrixes can be effectively conducted.

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