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Determination of anions and cations in concentrated bases and acids by ion chromatography

Electrolytic sample pretreatment

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ABSTRACT

The development of a high-capacity electrochemical membrane suppressor has resulted in new ion chromatographic methods for the determination of trace ions in concentrated acids and bases. Unlike previous membrane suppressors, the new one does not require chemical regeneration, thus eliminating regenerant leakage across the membranes. The new suppressor electrolyses water to create the acid or base required for neutralization and thus permits contamination-free acid–base neutralizations of concentrated reagents. This makes the new suppressor ideal for sample pretreatment of acids or bases prior to analysis by ion chromatography. This technique has been applied to trace anion determination in concentrated bases (*e.g.* 50% NaOH and concentrated NH_4OH) and trace cation determination in concentrated acids (*e.g.* 48% H_2SO_4, 43% H_3PO_4 and 33% methane sulfonic acid). The detection limits for most ions are 1 to 10 ng/ml.

INTRODUCTION

The determination of trace inorganic constituents in concentrated acids and bases has been important in a variety of chemical and semiconductor processes. Although ion chromatography (IC) has successfully determined trace ionic impurities in a wide range of matrices, it has been limited by matrix concentration [1,2]. Generally, an ionic matrix concentration of more than 10 times the eluent concentration interferes with the analytical separation and detection. Specifically, analyte peaks are obscured by the large interfering peak of the sample matrix. Also, the separation is severely changed because the ionic sample matrix is of such high concentration that it becomes the major eluting ion, temporarily overriding the eluent.

In order to determine trace anions in concentrated bases or trace cations in concentrated acids, the sample is usually diluted to the level at which the sample matrix does not interfere with the analytical separation. Another method commonly used is sample pretreatment with ion-exchange resin to remove the interfering sample matrix ion. Although high-capacity resin can be used to neutralize the concentrated sample matrices, the inherent blank associated with the resin usually contaminates the sample. Moreover, the resin requires periodic regeneration. Other forms of sample pretreatment devices include fiber suppressor [3], MicroMembrane Suppressor (MMS) [4] and dialysis membrane-based devices (see ref. 2 and references therein). The fiber suppressor is comprised of approximately 2 m of Nafion hollow fiber. Because of the need to maintain a relatively thick membrane wall (*e.g.* 0.075 cm) to minimize bursting from down stream backpressure, the fiber suppressor has low suppression capacity and is not useful for sample pretreatment. The MMS uses flat ion-exchange membranes ap-

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proximately 0.005 cm thick and consequently has higher suppression capacity than the fiber suppressor. The dialysis device utilizing a length of ion-exchange hallow fiber bathed in a suitable regenerating solution has also been used for sample neutralization (see ref. 2 and references therein). The only advantage of these devices over packed bed resin is that they do not require periodic regeneration. However, these techniques can only be applied to < 0.2 *M* NaOH samples due to their limited neutralization capacities. Also, they produce a significant blank from the acid anion used for sample neutralization.

Recently, an electrolytic micromembrane suppressor device (Self Regenerating Suppressor, SRS) was introduced for suppressed conductivity detection after ion-exchange analytical separation [5,6]. The SRS takes advantage of the design of the MMS, allowing high suppression capacity with the use of thin ion-exchange membranes and ion-exchange screen filling the chambers, and adds the advantages of electrolysis and electrodialysis. The SRS makes the requisite acid or base required for neutralization electrolytically by splitting water at the electrodes in the regenerant chambers. Fig. 1 shows the internal construction of the SRS for anion determination (ASRS) including cation-exchange membranes and cation-exchange screens. The SRS operates in a constant current mode between 50 mA to 500 mA and in the voltage range of 1 to 7 V, typically 3.5 to 4 V. Fig. 2 indicates the neutralization chemistry in an ASRS. An SRS for cation separations (CSRS) works analogously to the ASRS. For cation determinations the eluent anion is removed and replaced with hydroxide, neutralizing the strong acid eluent. The CSRS is composed of anion-exchange membranes and anion-exchange screens. The SRS device is capable of suppressing the high-conductance acidic or basic eluent to produce very-low-conducting water in a contamination-free neutralization process. This is an ideal sample pretreatment process for reducing the high concentration of acid or base matrices prior to ion analysis by IC.

This paper demonstrates the use of the SRS as sample pretreatment for trace anion determination

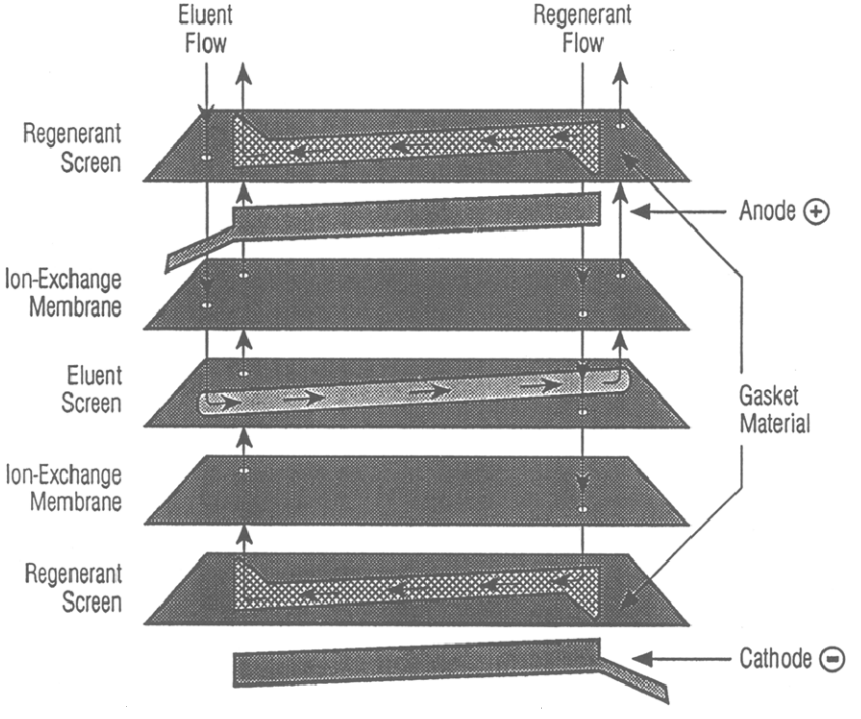

Fig. 1. Internal construction of a Self Regenerating Suppressor (SRS).

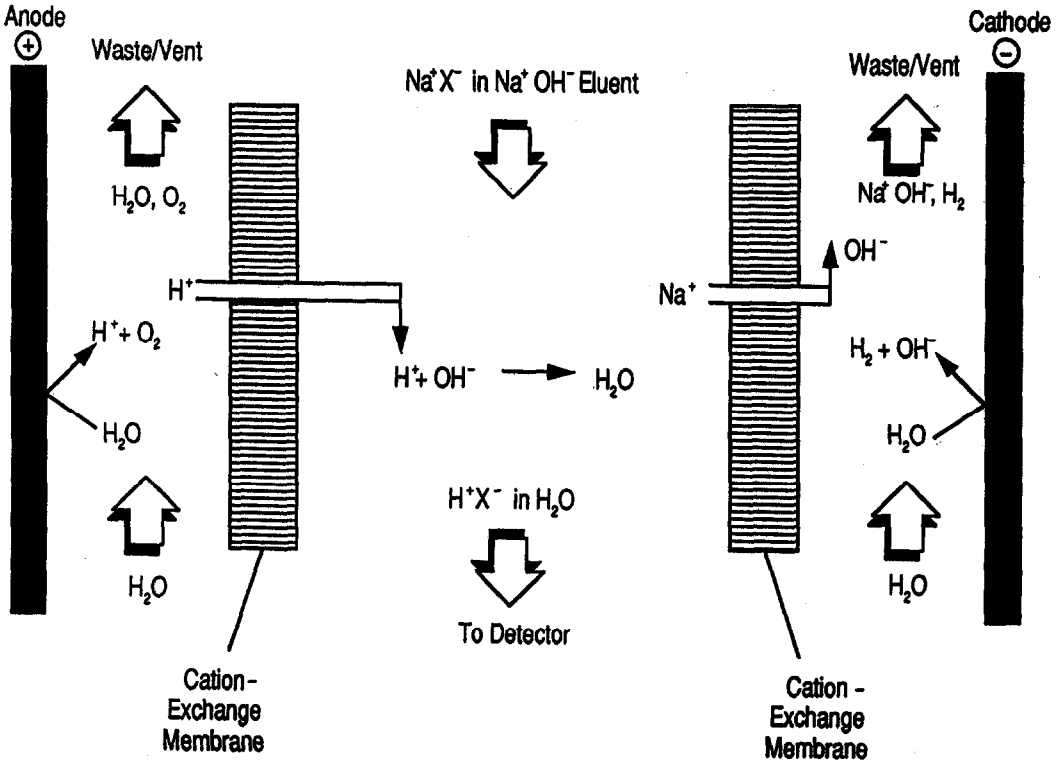

Fig. 2. Suppression chemistry in the Anion Self Regenerating Suppressor (ASRS).

in concentrated bases and trace cation analysis in concentrated acids. The method development, integration of the sample pretreatment to the analytical system, and analytical data are presented.

EXPERIMENTAL

Sample recycling method

Although the SRS is capable of continuous neutralization of up to approximately 0.2 *M* acid or base at 1 ml/min, it does not have adequate capacity to neutralize the concentrated acid or base. The required capacity can be improved by recycling the sample through the suppressor several times until it is completely neutralized. This concept is simple, but it requires careful system design. Sample contamination by the system components (*e.g.* pump, injector, valve) must be avoided.

Fig. 3 shows a recycle device consisting of a double stack, 4-way, low-pressure valve, SRS and conductivity cell. The 4-way valve is used to recycle the sample into the SRS by alternating valve ON and OFF. The conductivity cell positioned immediately after the SRS allows monitoring of the sample con-

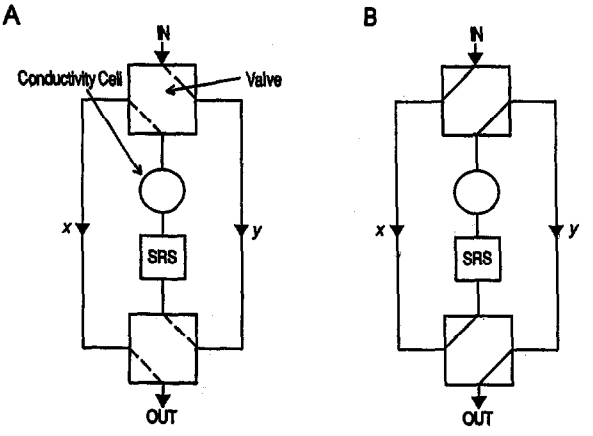

Fig. 3. Sample recycling method. (A) Recycle valve ON, sample flows from *y* to *x*. (B) Recycle valve OFF, sample flows from *x* to *y*.

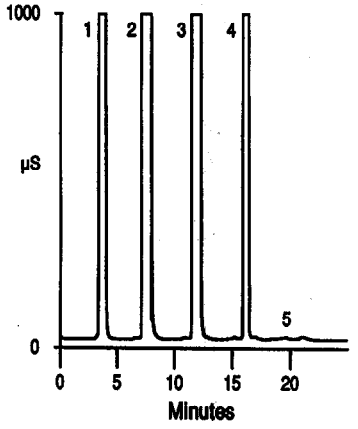

Fig. 4. Monitoring sample conductivity during ASRS sample pretreatment. Sample: 50% NaOH (50 μl), sample flow: 1.0 ml/min, current setting: 100 mA. Cycle 1, 3 and 5 valve B in ON position. Cycle 2 and 4 valve B in OFF position.

ductance to determine when the sample is adequately neutralized. The conductivity signal also serves as a marker for when to actuate the valve. Deionized water delivered by an external pump is used to "push" the sample from the sample loop to the recycle device and the rest of the system. The concentrated acid or base sample never passes through the pump and sample contamination is avoided. A typical sample volume of 5–50 μl is first passed through the SRS when valve is in ON position (Fig. 3A). The sample band passes from the top right of the valve (*y*), SRS and conductivity cell to the left side of the valve. As soon as the sample band has passed through the left side of the valve and before it exits the bottom stack (*x*), the valve is switched to OFF position (Fig. 3B). At this point the sample band passes from the left (*x*), through the SRS and conductivity cell a second time, to the right side of the valve . Before the sample band exits the bottom stack (*y*), the valve is switched back to ON position and the same process as described in Fig. 3A is initiated. When the sample conductivity has been significantly lowered (*e.g.*: less than 20 μS/cm for NaOH) it can be sent from the recycle device to the analytical system. To illustrate the overall process, Fig. 4 shows the recycling of 50% NaOH sample using the recycle valve alternating OFF and ON. The valve switching sequence shown in Fig. 4 is constant as long as the external pump flow-rate is unchanged.

Chomatographic system

The system configuration is shown in Fig. 5. All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-300 system. The anion system consisted of a sample concentration module

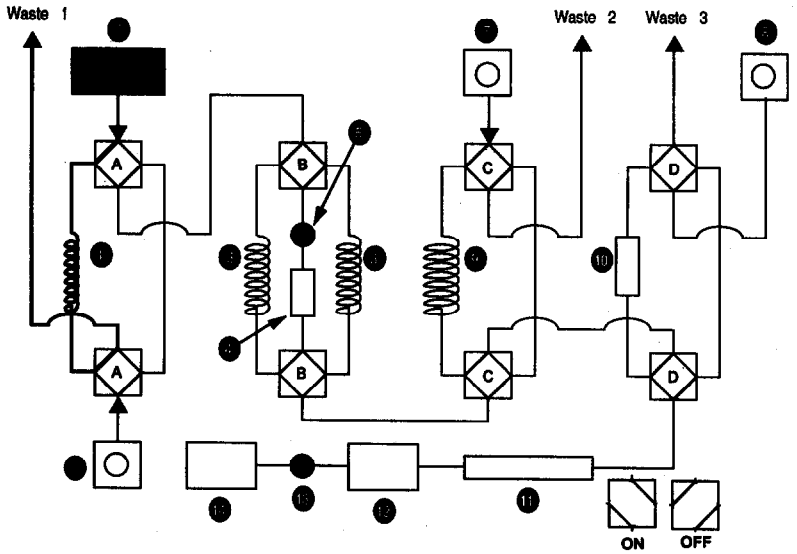

Fig. 5. System configuration. 1 = Sample loop; 2 = autosampler; 3 = recycle loop; 4 = sample pretreatment device; 5 = conductivity cell; 6 = pump 1; 7 = pump 2; 8 = pump 3; 9 = collection loop; 10 = concentrator column; 11 = separator column; 12 = eluent suppressor; 13 = conductivity cell; 14 = data processor.

(SCM), an advanced gradient pump (AGP) and a conductivity detector (CDM-II). The SCM contains two single-piston pumps designated pump 1 and pump 2, three low-pressure, double-stack, 4-way slider valves (valves A, B and C), and one high-pressure, double-stack, 4-way slider valve (valve D). The AGP, pump 3, was used as an analytical pump. The cation system hardware was identical to the anion system except for the columns and the SRSs. The power supply for the CSRS and ASRS was a Dionex SRS Controller capable of supplying constant current power with four settings, 50, 100, 300 and 500 mA and with a voltage range of 1 to 7 V.

Two sets of columns and sample pretreatment devices were used in the anion and cations systems. For the anion system, the Dionex ASRS, a Dionex IonPac AC10 (50 mm × 2 mm) and a Dionex IonPac AS4ASC (250 mm × 2 mm) were used. A Dionex CSRS, a Dionex IonPac TCC-2 (35 mm × 4mm), a Dionex MetPac CC-1 (50 mm × 4 mm) and a Dionex IonPac CS12 (250 × 4 mm) were employed for the cation system. The eluent suppression devices were the Dionex Anion MicroMembrane Suppressor (AMMS-II) and Cation MicroMembrane Suppressor (CMMS-II) for anion and cation systems, respectively. The sulfuric acid and tetrabutyl ammonium hydroxide regenerants were delivered to the AMMS-II and CMMS-II by two Dionex AutoRegen systems. The chromatographic conditions for the anion and cation systems are listed in Table I.

TABLE I

CHROMATOGRAPHIC CONDITIONS

Sample pretreatment	
Pretreatment device	ASRS (anion system) CSRS (cationic system)
Sample loop	50 μl
Recycle loop	3.0 ml
Collection loop	8.0 ml
Pump 1 flow	1.0 ml/min
Pump 2 flow	1.0 ml/min
Analytical system	
Anion system	
Column	IonPac AC10 (2 mm) IonPac AS4A SC (2 mm)
Eluent	1.7 m*M* $NaHCO_3$–1.8 m*M* Na_2CO_3
Flow	0.5 ml/min
Detection	Suppressed conductivity
Cation system	
Column	MetPac CC-1, TCC-2 IonPac CS12
Eluent	22 m*M* Hydrochloric acid
Flow	1.0 ml/min
Detection	Suppressed conductivity

System operation and method development

The valve configuration shown in Fig. 5 was used to automate the overall process. Valves A, B, C and D are designated as injection valve, recycle valve, collection valve and concentration valve, respectively. Valves A, B and C were controlled by valve 5 on the AGP. This single-valve control processed the sample pretreatment steps. Valve D was controlled by valve 6 on the AGP. The sample travels from the left to the right of the diagram. The typical valve sequencing program used for 3-cycle pretreatment is summarized in Table II.

Reagents

The high purity sodium hydroxide, 30% Supra-Pur grade (VWR Scientific) and 50% NaOH (Fisher Scientific) were used as samples for the anion system. For cation analysis, concentrated sulfuric acid (Fisher Scientific), phosphoric acid (Fisher Scientific) and methane sulfonic acid (Aldrich) samples were employed. The sodium bicarbonate–carbonate eluent was prepared from a dilution of Dionex AS4A eluent concentrate solution with 18 Ω cm water. The HCl eluent was prepared from dilution of ultrapure concentrated hydrochloric acid (SeaStar Chemicals) with 18 Ω cm water.

RESULTS AND DISCUSSION

ASRS sample pretreatment: trace anions in concentrated bases

Electrochemical reaction and neutralization. Increasing the current increases the electrolytic reaction. The amount of electrolytic products, hydronium and hydroxide, determine the neutralization capacity. Hence, the number of sample cycles through the SRS can be minimized at high current. The typical sample conductivity response at various ASRS current settings is shown in Fig. 6. The 50% NaOH sample was neutralized as described in the experimental section. The sample conductivity in the recy-

TABLE II

SAMPLE PRETREATMENT STEPS

Time (min)	Event	Valve A, B, C	Valve D	Comments
0.0	Sample loading	Off	On	Sample is injected into the 50-μl loop (valve A)
0.5	Recycling 1	On	On	Sample is flushed from the sample loop (valve A) and passed through valve B for sample neutralization. At the end of this step (time 5.0 min), the sample band is located in the left recycle loop.
0.5	Recycling 2	Off	On	The sample band is passed through the bottom stack of valve B upward through the SRS and the conductivity cell for the second time. At the end of this step (time 8.0 min), the sample band is located in the right recycle loop.
8.0	Recycling 3	On	On	The sample flow path is identical to that of recycle 1. After the sample band has been passed through the SRS for the third time, valve B remains ON for 5 min. The sample band is passed through valve B through valve C. At the end of this step (time 16.0 min), sample band is completely transfered into the collection loop.
16.0	Concentration	Off	Off	Sample band in the collection loop is flushed to the concentrator on valve D. The sample is concentrated on the concentrator column at the end of the step (time 24.0 min).
24.0	Analytical separation	Off	On	Eluent from the AGP removes the concentrated analytes from the concentrator to the analytical system, where they are separated and detected.

cle valve was monitored each time it passed through the ASRS. The sample flow-rate was maintained at 1.0 ml/min. The sample band splitting seen in Fig. 6 is due to the change in sample viscosity and ionic strength during the neutralization process. As the front end of the peak is neutralized, its viscosity is reduced therefore dispersing faster than the rest of the sample band. The peak splitting was not observed when the dilute NaOH sample was injected.

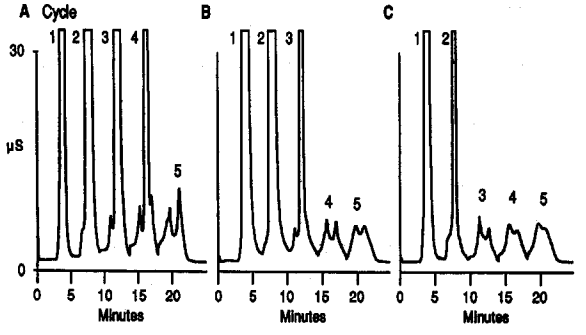

Fig. 6. Increasing the current increases the electrolytic and electrodialytic rates. The ASRS neutralization of 50% NaOH using (A) 100 mA, (B) 300 mA and (C) 500 mA.

It was found that a minimum of 5 cycles was required at 100 mA current setting (Fig. 6A). At higher current settings, 300 mA, 500 mA and 600 mA, the minimum of 4 cycles (Fig. 6B), 3 cycles (Fig. 6C) and 3 cycles (not shown), was observed. The results of these experiments conclude the 3-cycle pretreatment with a current setting of 500 mA is sufficient to reliably neutralize the concentrated NaOH sample.

Coupling to the analytical system. After the sample is completely neutralized, the treated sample composed of acid-form anions in a water matrix can be directly coupled to any standard concentrator column for subsequent analytical separation and detection. Since the SRS maximum operating backpressure is 150 p.s.i. (1 p.s.i. = 6894.76 Pa), a collection loop (Fig. 5) of 8 ml was used to isolate the low-pressure SRS device from the relatively high-pressure concentrator column.

A microbore system, the IonPac AC10 concentrator, and the IonPac AS4ASC analytical column with the AMMS-II (2 mm format), was used for anion separation and detection. Fig. 7 shows the the simultaneous conductivity responses of the 50% NaOH sample during the neutralization and sub-

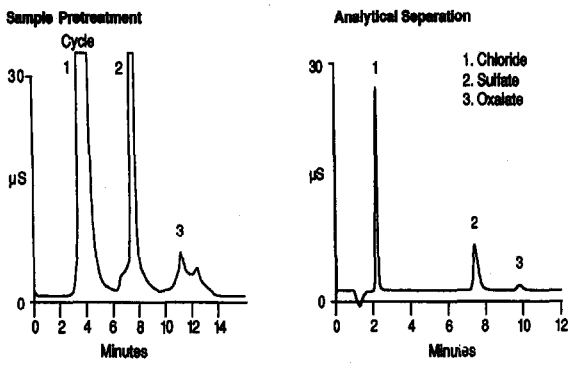

Fig. 7. Trace anions in 50% NaOH.

sequent analytical separation. Pretreatment conductivity monitoring is only necessary as a method development or troubleshooting aid. Once the method is developed, it can be used for several days without any significant changes in the analytical peak response unless the external pump flow-rate changes.

Dynamic range of sample pretreatment and spike/recovery. The linearity of anions detected in varying concentrations of the same NaOH sample reflects the dynamic range of the sample pretreatment. Varying the matrix concentration not only identifies the degree of matrix interference, if there is any, it also indicates the limitation of the sample pretreatment process. The spike/recovery experiment of varying analyte concentrations in a fixed matrix concentration alone does not isolate the degree of matrix interference from dynamic range of the method. In many instances, similar methods fail when applied to the real samples of varying matrix concentrations without matrix matching (identical matrix concentration used in standard calibration). To validate any method for highly complex matrices, the linearity study of analytes as a function of matrix concentration experiment is performed, followed by an evaluation of the spike/recovery of analytes in matrix concentration within the linear range.

To determine the linearity of anions in various NaOH concentrations, the 50% NaOH was spiked with anions to make a 49.9% spiked NaOH sample. This sample was then diluted with deionized water to make up 6.08, 12.2, 24.4 and 48.4% NaOH samples. To avoid the density differences in various NaOH concentrations the sample was prepared volumetrically instead of gravimetrically. Since various amounts of water were used for sample dilution, the water was analyzed for trace ion contamination and the result was used for blank correction. The five samples containing 6 to 49.9% NaOH were analyzed; typical chromatograms are shown in Fig. 8. The corresponding linearity of Cl^-, NO_2^-, HPO_4^{2-}, SO_4^{2-}, Br^-, NO_3^- and oxalate as a function of

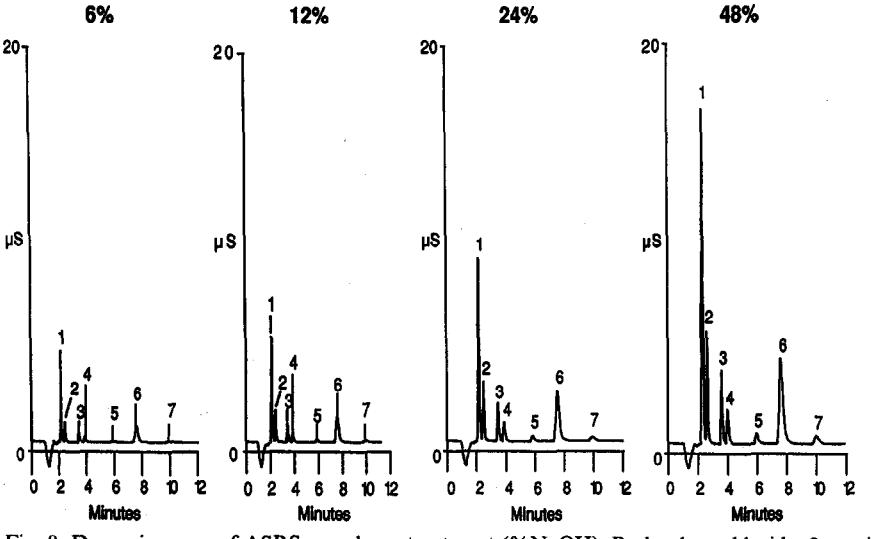

Fig. 8. Dynamic range of ASRS sample pretreatment (%NaOH). Peaks: 1 = chloride; 2 = nitrite; 3 = bromide; 4 = nitrate; 5 = phosphate; 6 = sulfate; 7 = oxalate.

NaOH matrix concentration is 0.9999, 0.9996, 0.9955, 0.9995, 0.9994, 0.9997 and 0.9995, respectively.

The spike/recovery study was performed using ultrapure 30% NaOH, which was found to contain 0.2 μg/ml chloride and 0.3 μg/ml sulfate. The results shown in Table III are blank corrected for these chloride and sulfate concentrations. Good recovery was observed for all anions studied. Recovery of fluoride was not studied because it partially coelutes with an unknown peak in the 30% NaOH sample. The ASRS sample pretreatment is limited to strong anions. For weak acid analytes with pK_a greater than about 3 (such as fluoride, formate and acetate) the non-ionized weak acids pass through the membrane resulting in low recoveries. This observation perhaps also explains the high R.S.D. for phosphate shown in Table III.

Although ASRS sample pretreatment is virtually a contamination-free neutralization process, it was determined that some of the blank was due to the device. The high-capacity sulfonated membranes release sulfate, especially in a newly installed ASRS. It was found that the level of sulfate blank declined to a constant level after 10 to 15 h of operation. The sulfate blank does not effect the quantification of the sulfate analyte since it is consistent; however, it does decrease the calculated detection limit of this method for sulfate.

TABLE III

SPIKE/RECOVERY OF TRACE ANIONS IN 30% SODIUM HYDROXIDE

The results are blank corrected. Measured chloride and sulfate concentrations in unspiked 30% NaOH are 0.24 μg/ml and 0.32 μg/ml, respectively.

Anion	Spike (μg/ml)	Recovery (μg/ml)	R.S.D. (%) (n = 7)
Chloride	0.06	0.07	3.2
Nitrite	0.50	0.58	1.1
Bromide	0.50	0.55	2.3
Nitrate	0.30	0.27	1.2
Phosphate	0.45	0.51	12
Sulfate	0.45	0.55	3.3

CSRS sample pretreatment: trace cations in concentrated acids

Electrochemical reaction and neutralization. The study of acid neutralization as a function of the CSRS current setting was performed identically to that of the ASRS neutralization. The acid concentration used was a 1:1 dilution of the concentrated acids. Three acids were studied: methanesulfonic acid sulfuric acid, and phosphoric acid representing mono-, di- and trivalent acid samples, respectively. The heat generated by mixing the 1:1 diluted acid sample with water during recycling made it difficult to monitor sample conductivity due to baseline shift. Method development for valve sequencing was accomplished using 1:4 dilution acid sample or calcium or sodium salts of the acid. It was determined that three cycles of a 1:1 dilution of the acid being studied and 500 mA current, was sufficient for neutralization of all three acids studied.

Coupling to the analytical system. After the sample is completely neutralized, the treated sample composed of hydroxide-form cations in a water matrix can be directly concentrated onto any standard concentrator column for subsequent analytical separation and detection. In this case, the combination of the MetPac CC-1 and the TCC-2 was used to concentrate mono- and divalent cations prior to analytical separation on the IonPac CS12. The unique combination of chelating resin and cation-exchange allows the use of dilute acid eluent without any complexing agents making the method compatible with the CS12 analytical column. The sample flows through the MetPac CC-1 where the divalent cations are retained, then through the TCC-2 where the monovalent cations are concentrated. The acid eluent flow was in reverse direction so that the monovalent cations were removed first, followed by the divalent cations.

Dynamic range of sample pretreatment and spike recovery. To determine the linearity of cations in various sulfuric acid concentrations, the 1:1 sulfuric acid was spiked with cations to make a 48% spiked sulfuric acid. The sample of 6, 12, 24, 36 and 48% sulfuric acid were prepared in a similar manner to that of NaOH samples. These samples were analyzed and the chromatograms are shown in Fig. 9. The corresponding linearity of Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} as a function of sulfuric acid matrix concentration is 0.9995, 0.9997, 0.9986, 0.9998, 0.9998 and 0.9986, respectively.

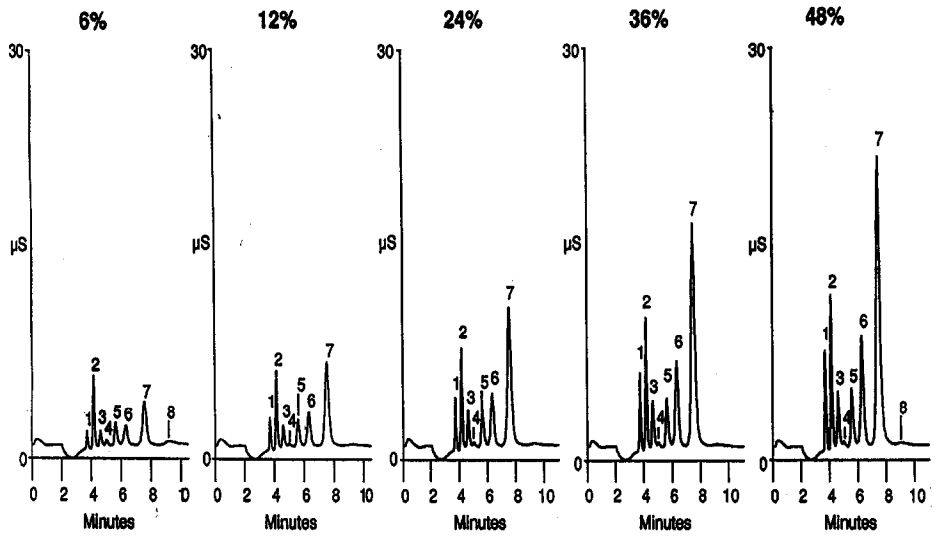

Fig. 9. Dynamic range of CSRS sample pretreatment (%H_2SO_4). Peaks: 1 = lithium; 2 = sodium; 3 = ammonium; 4 = unknown; 5 = potassium; 6 = magnesium; 7 = calcium; 8 = unknown.

The spike/recovery studies were performed using 48% sulfuric acid, 43% phosphoric acid, and 33% methane sulfonic acid (MSA). The spike/recovery data for those matrices are shown in Table IV. Good recovery was observed for all strong-base cations studied. The CSRS sample pretreatment is limited to relatively strong-base analyte cations (pK_a > 10). For weak-base analytes, such as ammonium and amines, the non-ionized weak base formed during matrix neutralization passes through the membrane and out of the sample stream, resulting in low recoveries. This observation explains the low recovery of ammonium as shown in Table IV.

Although the CSRS pretreatment is essentially a contamination-free neutralization process, some of the inherent blank released from the device was observed. The high-capacity aminated materials release alkylamines, especially in a newly installed CSRS. The example of this blank is shown in Fig. 9, peaks 4 and 8. It was found that the level of these blanks declined over time to a constant level after 10 to 15 h of operation. The amine blanks do not

TABLE IV

SPIKE/RECOVERY OF TRACE CATIONS IN CONCENTRATED ACIDS

Cation	48% Sulfuric acid		43% Phosphoric acid		33% Methanesulfonic acid	
	Expected (μg/ml)	Found (μg/ml)[a]	Expected (μg/ml)	Found (μg/ml)[a]	Expected (μg/ml)	Found (μg/ml)[b]
Li^+	0.064	0.063 ± 0.001	0.063	0.066 ± 0.001	0.064	0.064 ± 0.001
Na^+	0.401	0.42 ± 0.04	0.499	0.445 ± 0.006	0.261	0.229 ± 0.005
NH_4^+	0.610	0.314 ± 0.006	0.729	0.570 ± 0.001	0.494	0.383 ± 0.009
K^+	0.276	0.256 ± 0.005	0.358	0.340 ± 0.006	0.191	0.202 ± 0.005
Mg^{2+}	0.299	0.30 ± 0.02	0.332	0.35 ± 0.02	0.190	0.194 ± 0.006
Ca^{2+}	1.415	1.51 ± 0.06	1.846	2.14 ± 0.05	1.01	1.00 ± 0.09

[a] $n = 8$.
[b] $n = 6$.

TABLE V

DETECTION LIMITS BY SRS SAMPLE PRETREATMENT COUPLED IC FOR CONCENTRATED REAGENTS

Anion	Detection limit (ng/ml)	Cation	Detection limit (ng/ml)
Chloride	3.0	Lithium	0.1
Nitrite	8.0	Sodium	0.8
Bromide	8.0	Ammonium	5.0
Nitrate	6.0	Potassium	0.8
Phosphate	30	Magnesium	0.6
Sulfate	20	Calcium	1.0

affect the quantification of cations since they are consistent and separated from the rest of the cations studied.

Concentrated hydrochloric and concentrated nitric acid matrices were also evaluated, and it was found that even with a three-fold dilution of these concentrated acids the process of neutralization eventually damaged the ion-exchange components of the SRS. In the case of concentrated HCl, this is probably due to the electrochemical formation of hypochlorite at the anode, followed by concentration of the hypochlorite in the adjacent anion-exchange screens and membranes, which caused oxidative decomposition of the ion-exchange media by the concentrated hypochlorite. Concentrated nitric acid is probably also oxidatively decomposing the ion-exchange media since molar concentrations of nitric acid are present in the anode chamber during neutralization of this matrix. Therefore, this technique is not applicable with matrices that are strong oxidizers. We are currently studying if larger dilutions (1:10 to 1:100) of the matrix, followed by sample re-concentration of a larger volume (5 to 50 ml) will provide an acceptable life for the SRS with these matrices.

Detection limits by SRS sample pretreatment coupled IC

Table V summarizes the detection limits obtained by the anion and cation system for base and acid samples, respectively. The detection limits are based on three times signal to noise. The reported detection limits are comparable to those obtained by direct injection of ions in H_2O matrix. Since the sample volume injected into the pretreatment system is comparable to sample volumes used for direct injection, this indicates that the pretreatment process is relatively efficient and that sample dispersion is minimized.

CONCLUSIONS

New methods for trace anions in concentrated bases and trace cations in concentrated acids have been developed. The methods use the electrolytic sample pretreatment devices to neutralize acid and base matrices to produce water. The recycling method has been introduced to overcome the limited capacity of the electrolytic ion-exchange membrane devices. These methods have been applied to trace anion determination in 50% sodium hydroxide and trace cation analysis in several concentrated acids. The detection limits obtained by this technique are comparable to those obtained by analysis for the same analyte is deionized water, using direct injection.

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