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Recent advances in the simultaneous determination of anions and silica in high-purity water

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ABSTRACT

It is possible to determine anions and silica in a single injection. However, there are interactions that occur between the anions and silica that are not completely understood. This work provides the data for the hypothesis that the hydronium ion occurring at a suppressor promotes a catalytic formation of silica complexes. Silica forms halogen complexes and uses sulfur as a bridge to form other compounds thereby reducing the amount of free silica, fluoride, chloride and sulfate. This in turn is reflected in the response at the conductivity and visible detectors. This work also provides the data that even when the system is not coupled there still are anion–silica complexes being formed which inhibit complete detection of either the anions or silica separately. The interactions between silica and the anions occur either precolumn or oncolumn with the possible exception of fluoride which coelutes with silica.

INTRODUCTION

Monitoring water in power plants for anion and silica impurities allows the detection of breakthrough of polishes before changes in conductivity are noticed, thus preventing deposition of these impurities on turbines and steam generators. This deposition “buildup” of impurities can result in decreased heat transfer efficiency and the initiation of stress corrosion cracking in plant equipment. Component failures of this nature will lead to repairs and power plant shutdowns resulting in millions of dollars of repair costs and millions more in loss of generation revenue.

Ion chromatography (IC) as originally designed and reported by Small *et al.* [1] was a technique for the rapid, sensitive determination of multiple inorganic cations or multiple inorganic anions in one injection. This original work revolutionized the determination of inorganic ions, especially the anions, and opened up many new application areas.

IC has been described as a branch of ion exchange chromatography in which two columns are used. The second column is a suppressor which removes from the eluent all non-analyte ions. Having done this a simple conductivity meter can be used for detection. This allows for use of a precise, rapid analytical technique to determine such common anions as fluoride, chloride and sulfate [2]. This technique used in

conjunction with the development of the concentrator (stripping) column now allows for the detection of impurities in the sub-ppb^a range.

Photometrically silica is determined routinely and accurately with the silicomolybdate-heteropolyblue method. Silica in a sample reacts with ammonium molybdate in an acidic medium to form yellow α and β forms of molybdosilicic acid [3]. The molybdosilicic acid is reduced by stannous chloride to the molybdenum blue color, and the absorbance of the solution is measured at 820 nm. Oxalic acid, tartaric acid or citric acid is added to eliminate the interferences caused by any phosphate in the sample reacting to form the blue color [4]. This interference is already eliminated as ion chromatography readily resolves the phosphate and silica.

A logical extension of the work by Small *et al.* is the combination of two different approaches (conductometric and visible detection), producing a technique which performs anion and silica analysis, thus providing greater flexibility and information per injection. Although the coupling of detection systems is not new, the coupling for detection of silica and anions is.

The purpose of this work is to study and define the interactions between silica and anions previously reported [5]. The ion chromatograph coupled system led to the discovery of these interactions. These interactions are important to the power industry to ensure proper quantification of the anions so that cation conductivity and anion-cation balances may be achieved to maintain steam generator integrity.

EXPERIMENTAL

Instrumentation

All chromatography in this study was performed on a Dionex Series 2020i ion chromatograph. The dual-channel ion chromatograph was interfaced with a multichannel data-and-control system consisting of an AI450 (Dionex) interface, Dell System 200 desk-top computer (Dell Computer Corp., Austin, TX, U.S.A.) with a 40-megabyte hard drive and 5.25 in. floppy drive, and an Epson FX850 (Seiko Epson, Japan) printer. This in turn was interfaced with a Dionex reagent delivery module and a Dionex variable-wavelength detector (VDM-II) equipped with a 1500- μ l beaded reaction coil. The software (Dionex) provided data acquisition, data reduction and control of the ion chromatograph.

Reagents and standard solutions

Reagent-grade chemicals were used in the majority of the work with two exceptions. Suprapure sodium hydroxide available from VWR (VWR, Houston, TX, U.S.A.) was used as an eluent, and puriss-grade sodium molybdate from Fluka Chemical (Fluka, New York, NY, U.S.A.) was used as part of the postcolumn reagent. The water used was plant-produced demineralized water passed through a Barnsted Nanopure (Barnsted/Thermolyne, Dubuque, IA, U.S.A.) water system. Stock silica solution was prepared by dissolving 0.473 g sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) in high-purity water and diluting to 100 ml. Two eluents were used in these experiments. The first eluent was 30 mM sodium tetraborate and was prepared by dissolving 22.86 g sodium borate decahydrate in 2 l of high-purity water.

^a Throughout the article, the American billion (10^9) is meant.

The second eluent used was 30 mM sodium hydroxide and was prepared by dissolving 2.40 g of NaOH in 2 l of high-purity water and degassed to eliminate carbonate and sealed under a nitrogen overpressure blanket to prevent the uptake of carbonate. The silica postcolumn reagent was prepared by dissolving 9.68 g of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in 800 ml of high-purity water slowly adding 25.0 ml of concentrated HNO_3 (15.9 M) and mixing thoroughly. To this solution 2.39 g of sodium lauryl sulfate was added and the solution was diluted to a final volume of 1000 ml. The eluent and postcolumn reagent were mixed using a membrane reactor and a 1500- μl beaded reaction coil.

Nalgene plastic labware (Nalge, Rochester, New York, NY, U.S.A.) was used throughout the study to minimize silica contamination. Standard solutions were stored in Teflon fluorinated ethylene propylene (FEP) labware to minimize anion and silica leaching.

Columns

The columns used in this study were a Dionex AS4A analytical column, an AG4A guard column and an AG5 guard column as the concentrator. These columns were packed with a pellicular anion exchange resin. A standard Dionex membrane suppressor (AMMS-I) and a prototype AMMS-II Dionex membrane suppressor were used to lower the eluent background conductivity and enhance sensitivity.

Procedures

Standards and samples were analyzed by ion chromatography under the operating conditions listed in Table I. The calibration standards were prepared from separate stock ppm standard solutions. The precision of the analytical method was

TABLE I
OPERATING CONDITIONS

Item	Condition 1	Condition 2
Eluent	30 mM Tetraborate	30 mM NaOH
Eluent flow-rate	1.5 ml/min	1.5 ml/min
Concentrator	AG5	AG5
Guard column	AG4A	AG4A
Separator column	AS4A	AS4A
Detection		
Anions	Conductivity with AMMS suppressor	Conductivity with AMMS suppressor
Silica	Visible detection at 410 nm	Visible detection at 410 nm
Full-scale sensitivity		
Conductivity	30 μS	30 μS
Visible	0.005 a.u.f.s.	0.005 a.u.f.s.
Suppressor	AMMS-1	AMMS-1
Regenerant	20 mM H_2SO_4	20 mM H_2SO_4
Regenerant flow-rate	10 ml/min	5 ml/min
Postcolumn reagent	40 mM Sodium molybdate 0.4 M Nitric acid 6 mM Sodium lauryl sulfate	40 mM Sodium molybdate 0.4 M Nitric acid 6 mM Sodium lauryl sulfate
Postcolumn flow-rate	0.5 ml/min	0.5 ml/min

determined by replicate analysis of water samples containing varying ratios of F^- , Cl^- , SO_4^{2-} and SiO_3^{2-} .

The determination of silica and anions separately is a well-known process [6,7]. The determination of anions and silica simultaneously has received some attention in the past, but was essentially a method for splitting a process sample into two different analyzers so the separations could run concurrently [8].

Silica can be concentrated as the silicate ion on a strong-base anion-exchange resin and eluted with a base in a more concentrated condition [3]. This is also the method of choice for anions which are water soluble and ionic. Based on this and previous work [7,8] the concentrator selected was a Dionex AG5 due to higher capacity and stronger base form resin as contrasted with the trace anion concentrator (TAC) or AG4A columns. The analytical and guard column selection were also based on previous work [8] and the AS4A and AG4A columns were used.

The eluent described in refs. 7 and 8 (15 mM NaOH–15 mM boric acid) was determined to be satisfactory for the determination of silica, fluoride and chloride; however, this eluent is not strong enough to elute sulfate efficiently. A 30-mM tetraborate eluent is ideal for separation of these species.

The chromatograph was then set up with a 30-mM tetraborate eluent and 20 mM H_2SO_4 was used as regenerant. This is coupled to a reagent-delivery module (RDM) and a variable-wavelength detector (VDM-II) as shown in Fig. 1. Introduction of the postcolumn reagent was accomplished with a Dionex DQP pump and a membrane reactor. To increase reaction time with the postcolumn reagent before detection a 1500- μ l beaded reaction coil was added between the RDM and VDM-II.

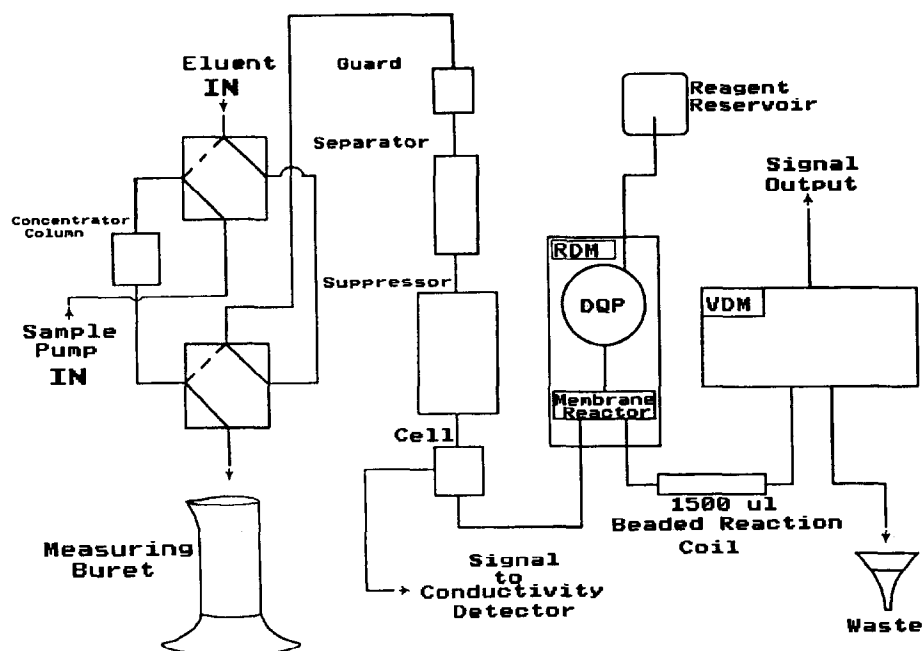


Fig. 1. Scheme of the chromatographic system used in this study.

In all experiments, 18 ml of sample was concentrated for this study. The methodology used was to inject 25 replicates of sample containing known concentrations of F^- , Cl^- , SO_4^{2-} and SiO_3^{2-} to insure reproducibility. The separations containing only 25 ppb of each anion yielded 100% resolution of all peaks in under 6 min with less than 3% relative standard deviation (R.S.D.). This step was then repeated with a 25-ppb standard containing only silica. Again the R.S.D. was less than 3% with silica eluting at 1.9 min. Silica was observed to tail slightly with the tetraborate eluent, but this was considered negligible. It was also observed by measuring the volume between the conductivity cell and the VDM-II and the flow-rate that fluoride and silica were coeluting.

RESULTS AND DISCUSSION

A mixed standard containing 25 ppb of the anions and silica was prepared and 25 injections were made. The resultant chromatograms had a high degree of resolution between all species with less than 5% R.S.D. It is noted that fluoride and silica coelute, but are detected independently by separate detectors. There was also a decrease of approximately 15% in the peak heights of all species when silica was present with the anions. This decrease was not observed when the silica was removed from the samples. To further evaluate this phenomenon, both the peak heights and peak areas were investigated. The evaluation indicated that while peak areas were more stable, the apparent decrease in sensitivity was still present. Injections of steam generator samples at this time indicated fairly good agreement with separate laboratory analysis; however, this might be due to no measurable presence of fluoride or sulfate in the samples. The steam generator values for anions by IC were: $F^- < 1$ ppb, $Cl^- 1.4$ ppb, $SO_4^{2-} < 1$ ppb and silica results by spectrophotometer were 115 ppb. The corresponding values by coupled IC were: $F^- < 1$ ppb, $Cl^- < 1$ ppb, $SO_4^{2-} < 1$ ppb and silica 95 ppb. This lead to the hypothesis that the silica chemistry is interacting at the suppressor and some secondary reactions were occurring. These secondary reactions could interfere with the postcolumn reaction for silica determination. It was also hypothesized that interactions between anions and silica occur oncolumn or precolumn to the suppressor.

Investigation into this behavior revealed that there is a catalytic effect of hydronium ions in the pH range of 0–2 with fluoride ions that affect the state of silica at low pH. It is believed that it converts silica to SiF_4 , SiF_5^- and SiF_6^{2-} [3]. This behavior has been reported in the presence of chloride and other halogens [9]. This information tends to confirm that secondary reactions are occurring at the suppressor and further study was indicated into the suppressor chemistry. Further investigation was called for to explain why the sulfate was affected and it was found that silica may use sulfur as a bridge to form binary compounds [9]. Similar interaction has been reported between silica with cations such as sodium, magnesium and calcium [10–12].

To evaluate the hydronium–silica interactions at the suppressor, a series of experiments was conducted varying the strength of the regenerant to ensure that regenerant strength did not affect the results. A 5-l combined standard at the 25-ppb levels were used to insure uniform standard consistency and were used throughout this experiment. The regenerant flow-rate was maintained at 10 ml/min.

The regenerant varied from 2.5 mM H_2SO_4 and increased in steps of 2.5 mM to

a final concentration of 25 mM. For each concentration of regenerant, 25 injections of the mixed standard were performed. The peak heights and areas remained constant with an overall R.S.D. of 6.4% which indicate the conditions in the suppressor interface are constant, regardless of regenerant strength.

With this information it was decided to check the lower limits of detection. It was determined that by concentrating 18 ml of sample the lowest reliable values (R.S.D. values < 10%) obtained were 5 ppb for fluoride and chloride and 20 ppb for sulfate and silica. It was decided to try sodium hydroxide as an alternate eluent to try and improve sensitivity. The sodium hydroxide was also chosen to study the interactions with a stronger base eluent.

The sodium hydroxide eluent did improve the sensitivity of the ions of interest with no noticeable tailing of the silica peak, as shown in Fig. 2. This is due to changes in selectivity and also the possibility that some of the silica may be inhibited from the formation of SiF_4 , SiF_5^- , SiF_6^{2-} , SiCl_4 and other halogen complexes. This is due to the pH of the eluent being higher and inhibiting the formation of these complexes [10]. The silica reaction may also be increased due to the formation of monomeric silicic acid $[\text{Si}(\text{OH})_4]$ [3,10]. From this point on, all experiments were performed with the NaOH eluent at a flow-rate of 1.5 ml/min and a postcolumn flow-rate of 0.5 ml/min. The linearity response data for these ions is presented in Table II. The lower limit of reliable detection (R.S.D. values < 10%) was then determined to be 1 ppb for fluoride and chloride, 5 ppb for sulfate and 10 ppb for silica. The suppressor experiment previously described using varying strengths of regenerant from 2.5 to 25 mM H_2SO_4 was again performed with the sodium hydroxide eluent. The results for the peak heights and areas also remained constant with an overall R.S.D. of 5.2%. This confirms that conditions in the suppressor interface are constant even with the stronger base sodium hydroxide eluent.

To verify that the peak maximum for silica was detected a spectral array detector (Linear Instruments, Reno, NV, U.S.A.) was installed in the place of the VDM-II

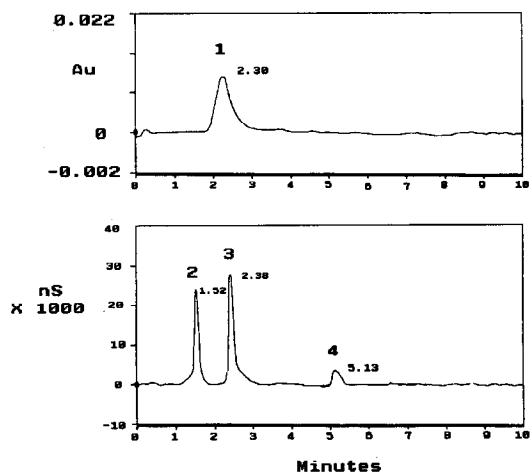


Fig. 2. Separation of anions and silica using NaOH. Peaks: 1 = silica, 10 ppb; 2 = fluoride, 5 ppb; 3 = chloride, 5 ppb; 4 = sulfate, 10 ppb. Au = Absorbance units.

TABLE II
LINEARITY RESPONSE (R^2)

Ion	Range (ppb)	R^2
Fluoride	1-10	0.9996
Chloride	1-10	0.9996
Sulfate	5-25	0.9968
Silica	10-30	0.9994

and five injections performed of the mixed 25-ppb level standard. Scans were performed in both the ultraviolet and visible regions and the peak maximum for silica was observed to be 410 nm (Fig. 3).

After the peak maximum for silica was verified, the system was returned to its original configuration using the VDM-II and another set of experiments was performed to check the suppressor interaction of the hydronium ion and silica in both the AMMS-I and prototype AMMS-II suppressors. The two different suppressors were evaluated at the request of a Dionex research chemist. It was postulated that neutral compounds such as SiF_4 and SiCl_4 may be forming and migrating across the suppressor membrane in the AMMS-I, thereby decreasing the silica and anion response. The theory was that the AMMS-II suppressor had a thicker membrane which would inhibit a migration of neutral compounds across the membrane. This would result in an increase in silica response if this was the case. The experimental conditions are listed in Table III and the results are depicted in Tables IV-VII. As shown in Tables IV-VII, a decreased response is still reported with both the AMMS-I and the prototype AMMS-II suppressor. However, the decrease is not as significant as with the AMMS-I. This provided some evidence for the formation of neutral species, but is not conclusive. Also of interest at this point is that with the system uncoupled there still are interactions occurring between silica and the anions. To further support this hypothesis the AMMS-I was reinstalled and the instrument was recalibrated using peak heights. The anion calibration was carried out in a 3×3 mode at the 5-, 25- and 50-ppb level in silica-free water. Likewise, the silica calibration was performed in a 3×3 calibration mode in anion-free water at the 25-, 50- and 100-ppb level. A 2-l standard containing 25 ppb of F^- , Cl^- and SO_4^{2-} was prepared to insure uniform standard concentration. This standard was split into eight separate 200-ml volu-

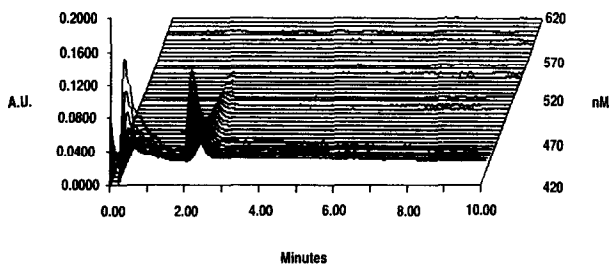


Fig. 3. Visible spectrum of silica. A.U. = absorbance units.

TABLE III
SUPPRESSOR COMPARISON

Experiment	Amount concentrated	100 ppb Standard solution	Conditions
1	18 ml	anions only	AMMS-1, postcolumn on
2	18 ml	anions only	Postcolumn bypassed
3	18 ml	anions only	Prototype suppressor, postcolumn bypassed
4	18 ml	silica only	Prototype suppressor, postcolumn on
5	18 ml	silica only	Suppressor bypassed
6	18 ml	silica only	AMMS-1, postcolumn on
7	18 ml	combined	AMMS-1, postcolumn on
8	18 ml	combined	Prototype suppressor, postcolumn on

TABLE IV
COMPARISON OF ANION RESPONSE WITH AMMS-I VS. AMMS-II^a

All anion concentrations are at the 100-ppb level. Postcolumn system "bypassed" for the study.

Anion	AMMS-I	AMMS-II	Δ (%)	
Fluoride	height	$1.573 \cdot 10^8$	$1.588 \cdot 10^8$	+ 0.9
	area	$1.065 \cdot 10^9$	$8.203 \cdot 10^8$	-23
Chloride	height	$1.201 \cdot 10^8$	$1.263 \cdot 10^8$	+ 5.0
	area	$9.423 \cdot 10^8$	$7.905 \cdot 10^8$	-16
Sulfate	height	$1.376 \cdot 10^7$	$1.209 \cdot 10^7$	-12
	area	$5.317 \cdot 10^8$	$4.272 \cdot 10^8$	-19.6

^a Prototype—regenerant not optimized for application.

TABLE V
COMPARISON OF ANION RESPONSE WITH AND WITHOUT SILICA PRESENT USING AMMS-I

All anion and silica concentrations were at the 100-ppb level. Postcolumn system "on" for both studies.

Anion	Without silica	With silica	Δ (%)	
Fluoride	height	$1.468 \cdot 10^8$	$1.293 \cdot 10^8$	-11.9
	area	$1.199 \cdot 10^9$	$1.069 \cdot 10^9$	-10.8
Chloride	height	$1.111 \cdot 10^8$	$9.831 \cdot 10^7$	-11.5
	area	$1.010 \cdot 10^9$	$8.915 \cdot 10^8$	-11.2
Sulfate	height	$1.535 \cdot 10^7$	$1.147 \cdot 10^7$	-25.2
	area	$6.298 \cdot 10^8$	$4.850 \cdot 10^8$	-22.9

TABLE VI

COMPARISON OF ANION RESPONSE WITH POSTCOLUMN SYSTEM "ON" VS. POST-COLUMN "BYPASSED" USING AMMS-I

All anion concentrations are at the 100-ppb level. No silica present in samples.

Anion	On	Bypassed	Δ (%)
Fluoride	height	$1.468 \cdot 10^8$	+ 7.1
	area	$1.199 \cdot 10^9$	- 11.1
Chloride	height	$1.111 \cdot 10^8$	+ 8.1
	area	$1.010 \cdot 10^9$	- 6.7
Sulfate	height	$1.535 \cdot 10^7$	- 10.3
	area	$6.298 \cdot 10^8$	- 15.6

metrics to which varying amounts of silica were added. The silica concentration for each sample was as follows: (1) 10 ppb, (2) 20 ppb, (3) 30 ppb, (4) 40 ppb, (5) 50 ppb, (6) 100 ppb, (7) 150 ppb and (8) 200 ppb. For each combined sample, ten injections were performed to ensure reproducibility and the results were averaged. The results obtained are presented in Figs. 4-7, and the R.S.D values for each sample set were: (1) 4.8, (2) 5.4, (3) 6.2, (4) 4.9, (5) 5.4, (6) 3.8, (7) 3.6 and (8) 2.4%.

As the graphs indicate, there is an interaction of the anions with silica due to the formation of silica-halogen and silica-sulfur compounds. This is further documented in that the silica recovery in the presence of the anions is roughly 50% the calibration value as depicted in Fig. 7.

TABLE VII

COMPARISON OF SILICA RESPONSE WITH AND WITHOUT SUPPRESSORS

Silica concentration: 100 ppb. No anions present.

	AMMS-I	AMMS-II	No suppressor	Δ (%)
Silica	height	1026	1236	+ 20.5
	area	14 087	15 114	+ 7.29
Silica	height	1026	1698	+ 65.5
	area	14 087	18 383	+ 30.5
Silica	height		1698	+ 37.4
	area		18 383	+ 21.6

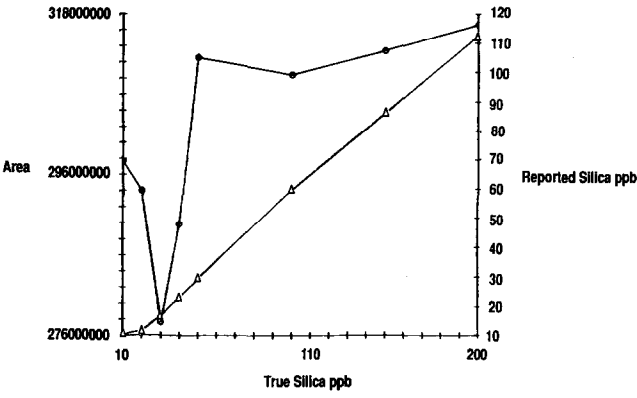


Fig. 4. Peak-height areas of fluoride *versus* silica. ○ = Fluoride; △ = silica.

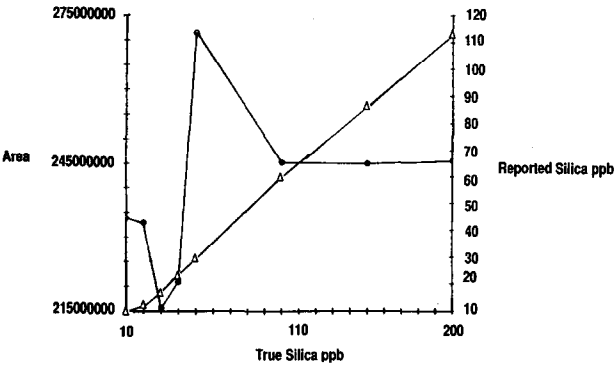


Fig. 5. Peak-height areas of chloride *versus* silica. ○ = Chloride; △ = silica.

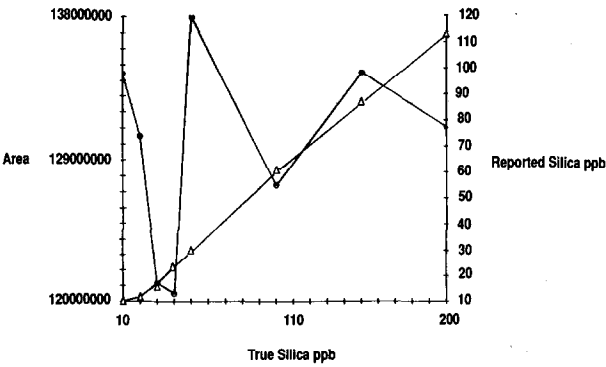


Fig. 6. Peak-height areas of sulfate *versus* silica. ○ = Sulfate; △ = silica.

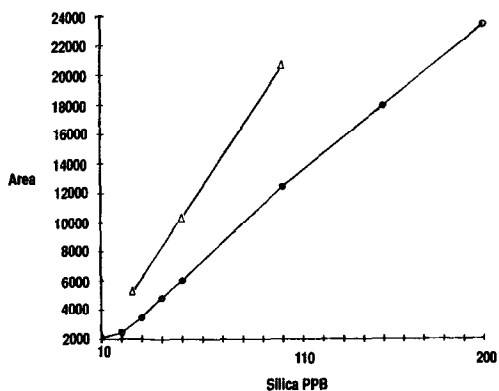


Fig. 7. Silica response with and without anions present. \circ = With anions present; \triangle = without anions present.

CONCLUSIONS

It is possible to determine anions and silica simultaneously using a single chromatograph with dual detectors. However, much work still needs to be done to verify that the reactions for silica are occurring at the suppressor and to verify the chemistry involved. It becomes necessary to determine where in the system (precolumn or oncolumn) the interactions between the anions and silica occur. The verification of complexes that are being formed between the anions and silica still needs to be performed. Models will have to be developed to explain the interaction between anions and silica. This will provide information for improved quantification of anions and silica in power-plant waters. This study is also useful in that it helps explain why we in the power industry are not able to achieve a cation conductivity balance with the reported anions in the system. The versatility of IC has been demonstrated in this study and holds promise for future developments in the area of coupled detection. Further work on this separation will be forthcoming, including the use of a single-column chromatography.

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