Approaches to sample preparation for ion chromatography Sulfate precipitation on barium-form ion exchangers

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Abstract

Clean-up and matrix elimination of samples are useful for removal of column-fouling substances and interfering ions in many ion chromatography applications. Matrix elimination is especially important in trace analysis, where preconcentration of large sample volumes is often required. Even mid-ppm concentrations of interfering ions can have a detrimental effect on preconcentration efficiency and chromatographic separation. Whereas halides are easily removed from samples by precipitation on silver-form cation exchange resin, sulfate removal on barium-form resin has been problematic. At best, the efficiency of sulfate removal is dependent on the cation content of the sample matrix. In addition, sulfate leakage from the resin bed limits the sample volume that can be applied to a barium-form device.

In this paper we explore the chemical processes that are involved in the precipitation of sulfate with barium, their effects on analyte recovery and the completeness of sulfate removal, and the implications for use of barium-form ion exchange devices for removing sulfate from samples.

Keywords: Sample preparation; Matrix elimination; Sulfate; Barium; Inorganic ions

1. Introduction

The formation of a precipitate with barium is a convenient way to remove sulfate from an aqueous solution, although co-precipitation and entrapment of other species can be a problem. Sulfate precipitation using barium-form resin as the source of Ba^{2+} is often either incomplete or the precipitate appears to re-dissolve under certain circumstances. At best, the efficiency of sulfate removal from the solution is matrix dependent. In addition, sulfate leakage from the resin bed limits the solution volume that can be applied to a barium-form device.

For example, we tried using packed-bed columns containing barium-form resin as precipitation-based suppressors for ion exclusion chromatography many years ago. These suppressors were meant to lower background conductivity for ion exclusion chromatography where the eluent was sulfuric acid. Even though barium sulfate is insoluble in dilute acid, we found considerable leakage of sulfate and barium from the column, such that the background conductivities produced were high and unstable. This result was in contrast with the very low background conductivities produced from silver-based suppressors for ion exclusion chromatography with a hydrochloric acid eluent. We concluded that (a) the sulfate was not completely precipitated with Ba^{2+} and that (b) the barium sulfate was redissolving.

Dissolution of barium sulfate with ion exchange resin has been studied more carefully than requirements for its precipitation using resin. Samuelson [1] first published a method for dissolving slightly soluble salts of divalent cations using H^+-form

cation exchange resin. Brochmann-Hanssen [2] studied dissolving barium sulfate using Dowex 50-X2. Sakurai et al. [3] published data showing that when $BaSO_4$ is in close proximity to acid-form resin, the $BaSO_4$ can re-dissolve and the Ba^{2+} is exchanged onto the resin. Nishino and Won [5] have discussed the dissolution of aluminum phosphate and barium sulfate using ion exchange resin. It seems that this is possible whenever ion exchange sites with counterions of lower selectivity than Ba^{2+} are near the barium sulfate precipitate. The re-exchange of Ba^{2+} onto the resin probably drives the dissolution of the barium sulfate since barium sulfate is insoluble in dilute acid.

When barium sulfate precipitation is to be used in a matrix elimination mode, another difficulty may be encountered. Analyte ions may be lost during precipitation of barium sulfate through co-precipitation, entrapment or ion exchange. One of the most common co-precipitates of barium sulfate is d-Ba-$(CO_3)_{0.90}(SO_4)_{0.10}$, which can form when carbonate is the major precipitable anion present. It seems possible that other oxyanions may also co-precipitate in this way with sulfate. In this paper we specifically examine recoveries of oxyanions and propose a method to improve some of the low recoveries.

The aims of the present work were to (a) identify ways to improve the efficiency of the barium sulfate precipitation in samples with varying matrices, (b) identify ways to minimize barium sulfate re-dissolution, and (c) identify ways to improve analyte recovery.

2. Experimental

2.1. Reagents and materials

Sample preparation devices containing Ba-form, Ag-form and H-form resins were OnGuard brand (Dionex, Sunnyvale, CA, USA). The devices each contain 0.95 g of 16% crosslinked, hydrated resin with an ion exchange capacity of 2.5 mequiv./g. Sodium sulfate, sodium chloride, calcium chloride anhydrous, magnesium chloride hexahydrate and sodium carbonate were analytical reagent grade and were purchased from Aldrich (Milwaukee, WI, USA). Sodium bromate was from EM Science

(Gibbstown, NJ, USA). Sodium tetraborate decahydrate was purchased from Fluka (Ronkonkoma, NY, USA). Sodium hydroxide was from Fisher Scientific (Fair Lawn, NJ, USA). Type 1 reagent grade water with a specific resistance of 17.8 MΩ cm from a NANOpure System (Barnstead/Thermolyne, Dubuque, IA, USA) was used to prepare all solutions.

2.2. Instrumentation

The chromatographic system comprised a GP40 gradient pump, LC30 chromatography module and ED40 conductivity detector (Dionex) and an injection valve (Rheodyne, Berkeley, CA, USA). Data was collected using PeakNet software (Dionex). Sulfate determinations were performed using an IonPac AS4A-SC column (250×4 mm I.D.) using a 3 mM sodium carbonate eluent. Oxyanions were separated with an IonPac AS12A column (250×4 mm I.D.; Dionex) using an eluent consisting of 18 mM sodium hydroxide and 20 mM sodium tetraborate. Chemical suppression was accomplished with an ASRS-1 suppressor (4 mm; Dionex).

Samples were applied to the ion exchange cartridges using a syringe pump (Sage Instruments, Orion Research, Cambridge, MA, USA) mounted in the vertical direction, at the desired flow-rates.

2.3. Experiments

A resin cartridge train was set up in the order disposable syringe, OnGuard-Ba, OnGuard-Ag and OnGuard-H. This train was attached to a Sage pump that was mounted in the vertical direction. This train was washed with 10 ml deionized water and a small air bubble was used to remove most of the wash water. Each sample was applied to an unused cartridge train at a flow-rate of 1 ml/min, using the syringe pump. The first 3 ml of sample was discarded, to eliminate dilution from the wash water. The next 3 ml were collected. If the sample contained carbonate, a 2-min sparge with helium was done.

Samples were spiked with the reagents at the concentrations noted in the tables from stock solutions. The stock solutions were 0.025 M $CaCl_2$,

0.041 M $MgCl_2 \cdot 6H_2O$, and 0.017 M Na_2CO_3. These are 10 000 mg/l in Ca^{2+}, Mg^{2+}, and CO_3^{2-}.

3. Results and discussion

3.1. Cation exchange selectivity

In applying a solution containing sulfate to a barium-form ion exchange cartridge with the purpose of precipitating barium sulfate from the liquid phase, the first main consideration is that of the availability of Ba^{2+}. This consideration is deeply rooted in the subject of cation exhange selectivity, that is, which cations, at what concentration, can displace Ba^{2+} from the resin and make it available for precipitation with sulfate?

Samuelson [4] studied selectivity on cation exchange resins and published several tables of data. In general, a typical selectivity series is

$$Na^+ < K^+ << Mg^{2+} < Ca^{2+} < Ba^{2+} \qquad (1)$$
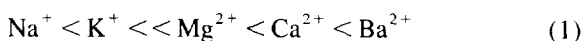
The selectivity coefficient describing the contributions of valency and concentration can be expressed as

$$k = \frac{[A]_r^b [B]^a}{[B]_r^a [A]^b} \qquad (2)$$

where brackets represent concentration, r represents the resin phase, and a and b represent the absolute values of the charges on the ions A and B. This simplified expression assumes that the activity coefficients are unity. For mixed valency exchanges, the selectivity coefficient is also strongly affected by the ionic concentration in the external solution. In general, as the solution becomes more dilute, the higher-valency ion is favored by the resin. Therefore, the displacement of Ba^{2+} by a commonly occurring cation such as Na^+ is influenced by concentration. The exchange of ions with the same charge, i.e. Ca^{2+}, Ba^{2+}, is mostly governed by factors other than concentration, such as hydration and electrostatics.

The significance here is especially notable in a sample preparation technique where the matrices are usually uncontrolled and often undefined. That is, the percentage of sulfate ions precipitated from a solution will vary with the concentration and valency of the cations from the sample matrix.

3.2. Barium sulfate solubility

The second main consideration is that of the dissolution of the barium sulfate precipitate. Barium sulfate precipitate, as formed from dilute solutions near ion exchange resin, is not easily visible in the cartridge. This observation is compared to the AgCl formed using a silver-form resin. The small particle size probably contributes to the solubility, although the driving force for the dissolution may be the re-exchange of Ba^{2+} onto the resin in areas of the resin bed where the counterions with lower selectivity than Ba^{2+} are present.

3.3. Study of the overall process

We decided that the most meaningful approach to studying the efficiency of sulfate removal from a solution, under conditions that reflect typical use conditions for sample preparation, would be to monitor the amount of sulfate left in solution after flowing through the OnGuard-Ba cartridge. In order to add various displacing cations to the test solutions without adverse effects from the counterions on the chromatography, we decided to set up a 'train' of OnGuard cartridges as previously described and to use the chloride salts of the test displacing cations. In this 'train' the OnGuard-Ag removes the chloride. The OnGuard-H may be used to trap soluble Ag^+ and to acidify the solution so that carbonate could be removed by sparging of the carbon dioxide. The first 3 ml of sample to exit the OnGuard cartridges is discarded in order to avoid dilution effects from wash water left in the cartridges after the initial 10 ml wash required with new cartridges.

Table 1 shows the amount of sulfate left in solutions with various concentrations of Na^+, Ca^{2+}, and Mg^{2+} added. The starting concentration of sulfate was usually 100 mg/l (2.1 mequiv./l) of sulfate. One sample was studied with 400 mg/l sulfate present initially. As expected, solutions with the lowest sulfate concentrations remaining after treatment with barium-form resin were those containing displacing cations with selectivities more similar to Ba^{2+}. Fairly good results can be obtained

Table 1
Sulfate removal using an off-line sample preparation cartridge train

Sample [mg/l (mequiv./l)]				Remaining sulfate (mg/l)
SO_4^{2-} (Na$_2$SO$_4$)	Na$^+$ (NaCl)	Ca^{2+} (CaCl$_2$)	Mg^{2+} (MgCl$_2 \cdot$6H$_2$O)	
100 (2.1)	0	0	0	54
100	50 (2.2)	0	0	38
100	200 (8.7)	0	0	6
100	500 (21.7)	0	0	3
100	0	2.0 (0.1)	0	53
100	0	10 (0.5)	0	47
100	0	50 (2.5)	0	17
100[a]	0	100 (5.0)	0	0.3
400 (8.3)	0	100	0	1
100	0	0	54 (4.4)	5.8
100[b]	0	100	0	100.2

[a]Best results.
[b]This sample through Ag–H resins only.

with Na$^+$ as the only matrix cation if the concentration of Na$^+$ is high enough.

Table 2 shows that when Ca^{2+} is added to the solutions, lower sulfate concentrations are left at larger treated sample volumes. If the barium sulfate is formed in a tight band at the top of the resin bed because the sample matrix contains enough divalent displacing cations, re-dissolution is hampered be-

cause the resin bed does not have regions with mixed, low-selectivity counterions.

Table 3 shows the flow-rate dependence of the overall process. From this table, it is clear that there is an advantage to applying the solution to the cartridge train at 2 ml/min or less. These results may also explain some of the variability in data when samples are applied manually, without flow-rate

Table 2
Dependence of sulfate precipitation on sample volume and sample matrix

Sample volume (ml)	Sample 1: SO_4^{2-} remaining (mg/l)	Sample 2: SO_4^{2-} remaining (mg/l)
6	54	3.8
23	70	1.6
100	97	2.8

Sample 1: 2.0 mequiv./l SO_4^{2-} (100 mg/l), 2.0 mequiv./l Na$^+$; sample 2: 2.0 mequiv./l SO_4^{2-} (100 mg/l), 2.0 mequiv./l Na$^+$, 4.4 mequiv./l Ca^{2+}.

Table 3
Effect of flow-rate on the efficiency of sulfate removal by barium-form cartridges

Flow-rate (ml/min)	Matrix 1: remaining SO_4^{2-} (mg/l)	Matrix 2: remaining SO_4^{2-} (mg/l)
0.1	0.3	19
1.0	1.0	33
2.0	1.3	54[a]
5.0	2.9	57
10.0	4.7	62

Matrix 1: 100 mg/l SO_4^{2-}, 23.9 mg/l Na$^+$, 100 mg/l Ca^{2+}; matrix 2: 100 mg/l SO_4^{2-}, 23.9 mg/l Na$^+$.
[a]Rec. max. flow-rate.

Table 4
Effect of pH on the efficiency of sulfate removal by barium-form cartridges

pH	Matrix 1: remaining SO_4^{2-} (mg/l)
1	4.8
3	4.8
7	1.0
11	2.2

Flow-rate: 1 ml/min. Matrix 1: 100 mg/l SO_4^{2-}, 23.9 mg/l Na^+, 100 mg/l Ca^{2+}.

control. Table 4 shows a minor effect from pH, although the optimum results are obtained at neutrality.

3.4. Recovery of other anions

Table 5 deals with the recovery of oxyanions after treatment using the cartridge train. The four matrices shown contain combinations of SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, and CO_3^{2-}. Matrix 1 does not contain sulfate, and the results with this matrix show that when sulfate is not present recoveries for the listed analytes are always higher than when sulfate is present. Matrix 2 contains both sulfate and Ca^{2+} at a level

found to be useful from Table 1. Recoveries are lower than with matrix 1. The lack of a phosphate recovery reflects the precipitation of calcium phosphate. Matrix 3 shows that when carbonate is added to the solutions, most recoveries are improved significantly. These data suggest that co-precipitates of the oxyanions, Ba^{2+} and SO_4^{2-} may be responsible for the low recoveries. When carbonate is present, it competes with the oxyanions. Since barium carbonate has low solubility relative to the listed oxyanions, it may compete very successfully for the barium.

Another possibility considers the mixed salt, d-$BaCO_3$, which is $Ba(CO_3)_{0.90}(SO_4)_{0.10}$. Some of these oxyanions, such as nitrate, which is isoelectronic with carbonate, may fit into a similar structure with Ba^{2+} and SO_4^{2-}. When carbonate is present it is preferred in the structure, essentially excluding nitrate until the carbonate is depleted.

3.5. The sample preparation method

With the understanding of the ion exchange selectivity of monovalent and divalent cations, the effect of mixed valency counterions on the resin and barium sulfate solubility, and the effect of carbonate

Table 5
Recovery of oxyanions from Ba^{2+}-form resin

	Sample matrix composition (mequiv./l)			
	1	2	3	4
SO_4^{2-}	0	1.0	1.0	4.2
Cl^-	1.0	5.0	5.0	5.0
Na^+	1.0	2.1	5.4	11.7
Ca^{2+}	0	5.0	5.0	5.0
CO_3^{2-}	0	0	3.3	3.3

Analytes	Sample matrix composition							
	1		2		3		4	
	added (ng)	recovered (%)	added (ng)	recovered (%)	added (ng)	recovered (%)	added (ng)	recovered (%)
NO_3^-	10	98	10	46	10	90	10	93
BrO_3^-	10	97	10	37	10	100	10	98
SeO_3^-	20	97	20	7	20	18	–	–
ClO_3^-	–	–	15	75	15	98	–	–
SeO_4^{2-}	–	–	25	89	25	97	–	–
AsO_4^{3-}	–	–	10	94	10	96	–	–
PO_4^{3-} [a]	20	87	20	0	20	0	20	0

[a] Samples in a matrix of 1 mM Na_2SO_4 (without Ca^{2+}) show a 42% recovery of phosphate.

on recovery of oxanions, we constructed a strategy for sulfate elimination from sample matrices. We used the cartridge train described previously and spiked samples with 0.005 M Ca^{2+} and 0.00167 M CO_3^{2-}.

3.5.1. Choice of divalent displacing cation

Results from Table 1 show that the preferred divalent displacing cations are Ca^{2+} or Mg^{2+}. The Ca^{2+} concentration is most effective in the range of 4-7 mequiv./l in the sample. Mg^{2+}, which has somewhat lower selectivity on the cation exchange resin than Ca^{2+}, is most effective in the range of 18-20 mequiv./l. Ca^{2+} is the displacing cation of choice except when high concentrations of carbonate or precipitatable anions such as phosphate are present. In these cases, Mg^{2+} is used. Organic divalent cations such as ethylenediamine are also good possibilities as long as they are available at high purity. Ethylenediamine has the advantage of availability at high concentration as well as high purity without the presence of a chloride counterion, although we have not tested its application in this project.

The chloride salts of calcium or magnesium can be used if it is necessary to minimize the anionic content of the sample. The chloride can be removed by passing the sample through silver-form cation exchange resin such as OnGuard-Ag cartridges. The silver-form resin also precipitates bromide, iodide, phosphate, arsenate, chromate, cyanide, molybdate, selenate, and any other ions with suitably low solubility products, i.e., generally $k_{sp} < 1 \times 10^{-8}$.

Lowering the chloride concentration becomes important in methods that require preconcentration. As with high concentrations of any matrix anion, chloride can overload the anion exchange sites of the preconcentrator column so that concentration efficiency of the anionic analytes is low.

3.5.2. Use of carbonate

Sodium carbonate is spiked into the sample in order to improve the recovery of many oxanions. Carbonate is most effective when present in the sample in the range of 50-100 mg/l. Calcium carbonate will begin to precipitate at approximately 100 mg/l. This does not seem to affect analyte recovery and the slight precipitate is collected onto the OnGuard cartridge train. Magnesium carbonate is

about 100 times more soluble than calcium carbonate.

Carbonate can be removed from the sample matrix as carbon dioxide by acidifying the sample through OnGuard-H and sparging with helium for 3-5 min. As carbonate is usually a fairly low efficiency peak, this step is often needed.

4. Summary

The interest in removing sulfate from ion chromatography sample matrices centers around the chromatographic problems that may be caused by the high concentration of a matrix ion. These problems are exacerbated when a method requires preconcentration of large sample volumes. Sample pretreatment to lower the concentration of sulfate in a sample is indicated in the analysis of anions when the sulfate peak is large and (1) the analyte peak is obscured by the large sulfate peak, (2) the retention times of the analytes are not reproducible, (3) the recoveries of analytes, especially when preconcentrating, are low and not reproducible, and/or (4) precision is low for quantitation of analytes that elute near sulfate.

Several points can be made about the methodology required to obtain efficient removal of sulfate from ion chromatography samples by precipitation on barium-form ion exchange resin, while also achieving high recoveries of the analytes of interest. First, Ba^{2+} must be available in solution for a precipitation reaction with SO_4^{2-} to occur. This is best accomplished by addition to the sample of a low concentration of a divalent cation capable of displacing the Ba^{2+} by ion exchange. The counterion of this cation should be removable as well. Chloride is removable by precipitation on Ag-form resin. Halide salts such as calcium chloride or magnesium chloride were found to be very effective at promoting the efficient precipitation of sulfate. Secondly, sample pH and flow-rate through the sample pretreatment cartridges also affect the efficiency of barium sulfate precipitation.

Lastly, recoveries of certain oxanions such as bromate and nitrate are significantly improved when carbonate is present in the sample. In order to normalize recoveries for samples with various matrix

compositions, we spike carbonate into samples prior to applying to the Ba-form cation exchange device.

In this paper we present a method[1] that overcomes much of the uncertainty in the use of barium-form devices for sulfate removal by dealing with these points. In this technique, as in any other for sample pretreatment, the recovery for the analytes of interest should be determined for each sample type.

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[1] Patent pending.