

# Applications of high-performance ion chromatography in the mineral processing industry<sup>☆</sup>

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## ABSTRACT

A reversed-phase column, coated with a permanently sorbed ion exchanger ("permanent coating" ion-interaction chromatography), was used for the separation of anions in ground water samples from a hydrometallurgical processing plant. Optimization of the capacity of the anion exchanger and wide linear range calibration curves obtained with these columns permitted the direct determination of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in the presence of large amounts of ammonium and metal ions.

Dynamic ion exchange ("dynamic coating" ion-interaction chromatography) was investigated for the separation of rare earths in samples from an aluminum processing operation. Data is presented to illustrate that with appropriate adjustment of pH of the eluent it is possible to optimize conditions to resolve rare earth metals from interfering metal ions.

The selective sorption of Th(IV) and U(VI) on to reversed phases as their  $\alpha$ -hydroxyisobutyric complexes, formed in situ in the eluent, was used for the analysis of samples from bacterial leaching of uranium ores. By minimizing the baseline noise of the post-column reaction the detection limit for Th(IV) is 5  $\mu\text{g/l}$  and for U(VI) is 15  $\mu\text{g/l}$  ( $3 \times$  baseline noise) for a 100- $\mu\text{l}$  sample injection.

## INTRODUCTION

Canada Centre for Mineral and Energy Technology research activities include increased productivity in mineral processing and development of technologies to reduce the environmental impact of process residues. To analyze the wide range of sample matrices generated by this research, much effort has been focused on the application of high-performance ion chromatography.

In this paper we will discuss some of the ion chromatographic (IC) techniques used and show examples to illustrate the application of these sepa-

ration systems. This will include the separation of anions in ground waters, and the determination of rare earths in metallurgical processing samples by ion-interaction chromatography. This chromatographic technique offers advantages over the use of fixed-site ion-exchangers in that there is a wide range of variables which can be used to manipulate the retention of solutes. For this reason, ion-interaction chromatography is applied in our laboratory to the resolution of difficult sample matrices. Also presented is the separation of thorium and uranium as their  $\alpha$ -hydroxyisobutyric acid complexes by reversed-phase chromatography. In the strict sense, this approach may not be defined accurately as IC, yet it is applicable to the retention of inorganic ions.

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## EXPERIMENTAL

### *Instrumentation*

Several different systems were used in this work. Solvent delivery pumps included Waters M-625 and M-45 (Waters, Milford, MA, USA), Spectra-

Physics 8100 and 8800 (Spectra-Physics, Santa Clara, CA, USA), Dionex 4000i (Dionex, Sunnyvale, CA, USA). Autosamples were Spectra-Physics 8100 and 8200. For absorbance detection, Spectra-Physics 2000, Linear 100 and Kratos 770 variable-wavelength detectors were used. Data handling was done by Spectra-Physics ChromJet integrators and a Spectra Station.

The eluted metal ions were monitored after a post-column reaction with 2,7-bis[(*o*-arsenophenyl)azo]-1,8-dihydroxynaphthalene-3,6-disulphonic acid (Arsenazo III) and the post-column reagent was added to the eluate via a low-volume T-mixer [6] with a modified syringe pump (ISCO M-645, Lincoln, NE, USA), or He-pressurized delivery system.

Analytical columns used were Supelcosil LC-18-DB (5  $\mu\text{m}$ , 150 cm  $\times$  4.6 mm) (Supelco Canada, Oakville, Canada).

### Reagents

All eluents, standard and sample solutions were prepared using water pretreated via ion-exchange and distillation, then passed through a Milli-Q water-purification system (Millipore, Bedford, MA, USA).

**Determination of anions.** A stock solution (5 mM) of the eluent acid, 1,3,5-benzenetricarboxylic, was dissolved in water by adding NaOH to pH of *ca.* 5. Eluents were prepared by diluting the stock solution and adjusting the pH to 6.5 with tris(hydroxymethyl)aminomethane (THAM). Salts of cetyltrimethylammonium bromide (cetrimide) and cetylpyridinium bromide (CTP) were used for coating the columns and these reagents were used as received from the supplier (Sigma, St. Louis, MO, USA).

**Determination of rare earths and thorium.** Standard solutions (1000  $\mu\text{g}/\text{ml}$ ) of the rare earths were prepared from 99.999% pure oxides (Aldrich, Milwaukee, WI, USA). These oxides were ignited to constant weight at 950°C and dissolved in dilute nitric acid. Reagent-grade sodium 1-octanesulphonate and  $\alpha$ -hydroxyisobutyric acid (HIBA) were obtained from Sigma and from Aldrich. Stock solutions of 2 M  $\alpha$ -hydroxyisobutyric acid and of 0.1 M sodium 1-octanesulphonate were purified by passing them through a column packed with a strong cation-exchange resin (AG 50W-X4); resins in the H<sup>+</sup> form were used for HIBA and the Na<sup>+</sup> form for 1-octanesulphonate. Eluents were prepared

by weighing the calculated amounts of stock solution and diluting to approximately 900 ml with water, after which the pH was adjusted to the desired value by addition of 5 M sodium hydroxide, and the solution diluted to 1 l. All vessels used to prepare and store eluents were of polypropylene plastic. A stock solution (0.5 g/l) of Arsenazo III was made 5 M in acetic acid. The post-column reagent solution was prepared by dilution of 100 ml of the Arsenazo III stock solution to 1 l and filtered through a 0.45- $\mu\text{m}$  filter. Acids used for sample dissolution were commercially available high-purity reagents.

### Procedure for coating columns

Solutions containing the coating reagent, CTP or cetrimide, were prepared in water-acetonitrile mixtures (0.5 mM) of reagent with 15–30% of acetonitrile. The solutions were adjusted with THAM to pH 6.5. The analytical column was first washed with a solution of the desired acetonitrile concentration without the reagent, then the reagent containing solution with the same percentage of acetonitrile was pumped through the column. The breakthrough curve was recorded by monitoring the bromide ion with a UV detector at 210 nm. To determine the capacity, a 1.0 mM salicylic acid solution (5% acetonitrile and pH 6.5) was pumped through the column until breakthrough of the salicylic anion was recorded at 290 nm. This was followed by equilibrating the column with the eluent. To remove the sorbed coating reagent a solution of 0.1 M potassium bromide containing 70% acetonitrile was passed through the column for at least for 1 h followed by washing with acetonitrile for 10 min.

### Sample preparation

**Aluminum processing solution.** To a 20-ml sample, 5 ml of HClO<sub>4</sub> and 5 ml of HNO<sub>3</sub> were added and the solution evaporated to near dryness at low hot plate temperature to remove excess HClO<sub>4</sub>. The salts were then dissolved in 10 ml of water and the solution transferred to a 50-ml volumetric flask and diluted to volume with eluent.

## RESULTS AND DISCUSSION

### Separation of anions by "permanent coating" ion-interaction chromatography

Studies have been conducted [1,2] with reversed-

phases that are permanently coated with a large hydrophobic quaternary amine to give a charged surface. Results have shown that such systems can offer several advantages over either dynamically coated or fixed-site ion-exchange columns. These exchangers give greater chromatographic efficiency and greater flexibility with regard to choice of column capacity and eluent for optimum anion separations.

Of these factors the ability to control the anion-exchange capacity is important. Fig. 1 shows the variation of amount of sorbed CTP and cetrimide on Supelcosil LC-18-DB reversed-phase columns. The amount of sorbed quaternary amine, and therefore the capacity of a column, is a function of the concentration of acetonitrile in the coating solution. As can be seen there was little difference in the number of moles of the two quaternary amines sorbed for a given percentage of acetonitrile. This indicates that the cetyl group, which is common to both compounds, is the main contributor in the hydrophobic interactions with the octadecyl group of the  $C_{18}$  column. The effects of these coated columns on analyte retention were studied using an eluent of 0.5 mM 1,3,5-benzenetricarboxylic acid,

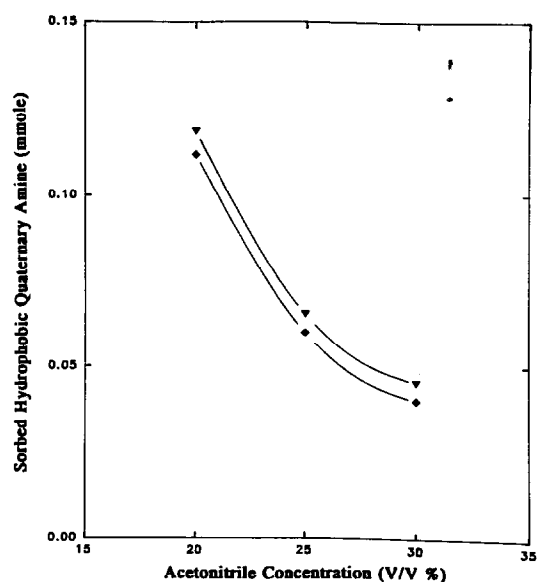


Fig. 1. Variation of amount of sorbed hydrophobic quaternary amine with the concentration of acetonitrile in coating solution. ◆ = Cetyltrimethylammonium; ▼ = cetylpyridinium; column, 5- $\mu$ m Supelcosil LC-18-DB reversed-phase.

neutralized to pH 6.5 with THAM. For both columns, the peak shape and the retention times of the anions  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were similar.

The application of a permanently coated column system is shown in Fig. 2. This chromatogram shows the separation of anions in a sample of ground water from a metallurgical processing plant in Western Canada. Attempts at determining the anions by a non-suppressed column technique were unsuccessful. The high concentrations of ammonium and other cations in the sample eluted near the solvent front and interfered with the separation of chloride. Also the high concentration of sulphate in the injected sample gave a broad and tailing peak which resulted in run times of 30 min to allow for column re-equilibration. Preseparation of the cations and analyzing the sample at different dilutions to solve the problem was unacceptable to the analytical operations in this plant. By adjusting the capacity of a permanently coated column, the retention of the chloride was increased to allow a separation from

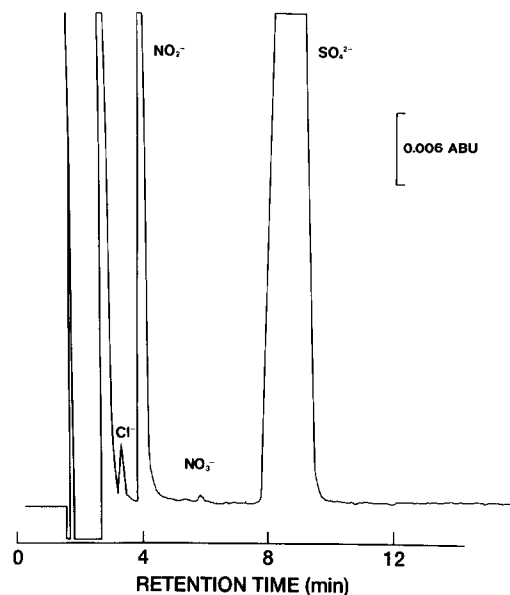


Fig. 2. Separation of anions in ground water sample on a permanent coated anion-exchange column with detection by indirect UV adsorption. Conditions: Supelcosil LC-18-DB column coated with  $5 \cdot 10^{-4}$  M cetyltrimethylammonium ion in 20% acetonitrile; eluent,  $0.5 \cdot 10^{-3}$  M 1,3,5-benzenetricarboxylic acid, neutralized to pH 6.8 with THAM; flow-rate, 1 ml/min; detection by indirect UV at 254 nm (ABU = absorbance units); sample injected, 50  $\mu$ l; sample dilution, 5 ml diluted to 100 ml with eluent.

the early eluting interferences, and good peak shape was obtained for sulphate because of the excellent efficiency of these columns. The eluent used here was 1,3,5-benzenetricarboxylic acid (0.5 mM) neutralized to pH 6.8, and detection was by indirect UV absorbance at 254 nm.

Our studies have shown that wide linear range calibration curves are obtained with these permanently coated systems. Standards of sulphate were prepared at the 5, 10, 25, 50, 100, 150 and 200  $\mu\text{g}/\text{ml}$  levels, and the linearity of the calibration curve for sulphate over this range showed a correlation coefficient equal to 0.9998. The peak for sulphate in Fig. 2 is equivalent to 8.25  $\mu\text{g}$  of  $\text{SO}_4^{2-}$  in the injected 50- $\mu\text{l}$  sample. Results obtained for this sample were 28 mg/l  $\text{Cl}^-$ , 214 mg/l  $\text{NO}_2^-$ , 7 mg/l  $\text{NO}_3^-$ , and 3300 mg/l  $\text{SO}_4^{2-}$ .

#### Separation of rare earths by "dynamic coating" ion-interaction chromatography

Dynamic ion-exchange chromatography [3,4] is used in our Laboratory to determine rare earths in a variety of samples. This includes mine tailings, metallurgical processing solutions, sediments, steels, and alloys. In this technique a hydrophobic ion (such as octanesulphonate), which is present in the eluent, is dynamically sorbed onto the hydrophobic surface of a reversed-phase to provide a charged surface that can be used for ion-exchange separations. The eluent also contains a complexing agent such as HIBA to elute the rare earths. The advantages of this approach includes rapid mass transfer characteristics, good reproducibility, and the ability to vary ion-exchange capacity. Changes in capacity along with eluent pH and addition of an organic modifier can be used to adjust the selectivity of the separation. With an on-line post-column reaction, using Arsenazo III and monitored at 658 nm, detection limits are in the low nanogram range.

An example of the application of dynamic ion-exchange chromatography for the direct separation of rare earths is shown in Fig. 3. The sample was a sodium hydroxide leach solution from an aluminium processing operation and contained high concentrations of sodium, iron and aluminium. Due to matrix interference, these solutions could not be accurately analyzed by inductively coupled plasma emission spectroscopy. Fig. 3A shows the chromatogram when the sample was separated by dynamic

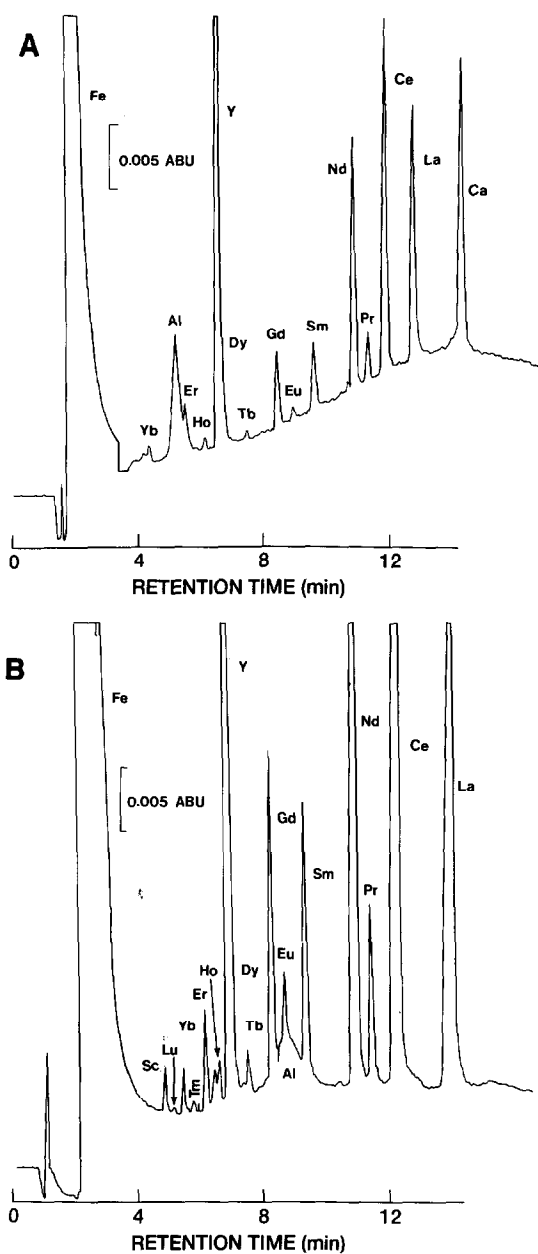


Fig. 3. Direct injection of aluminium processing solution. Conditions: Supelcosil LC-18-DB column; gradient programme at a flow-rate of 1.0 ml/min from 0.05 M HIBA to 0.4 M HIBA over 10 min and held at 0.4 M for 5 min; modifier, 1-octanesulphonate at 0.01 M; (A), eluents at pH 4.5; (B), eluents at pH 3.8; detection at 658 nm after post-column reaction with Arsenazo III; sample injected, 50  $\mu\text{l}$ ; sample dilution, (A) 10 ml to 100 ml, (B) 20 ml to 50 ml.

ion-exchange at an eluent pH of 4.5. The rare earths are well resolved except for Tm and Er which are masked by aluminium. By changing the eluent pH to 3.8 (Fig. 3B) the relative time for aluminium is quite different and appears as a broad peak under Eu and allows the determination of Tm and Eu. With this approach all the rare earths were resolved. In this system iron elutes near the solvent front. The difference in aluminium peak shape between A and B is probably due to its weak complexing properties with HIBA at pH 3.8. The range of results found for rare earths in this sample by dynamic ion-exchange was from  $<0.05$  mg/l for Tm to 10.0 mg/l for Y. A solution simulating the matrix composition and containing 2.0 mg/l of the rare earths was analyzed, and the recoveries of the rare earths were  $2.0 \pm 0.05$  mg/l.

The above results illustrate that the eluent pH can influence retention. The effect of pH on the retention of rare earths and metal complexes of HIBA was tested on a gradient programme from 0.05 M to 0.4 M HIBA for 10 min. Fig. 4 shows data we obtained for the retention of the rare earths, and the results for the metals tested are shown in Fig. 5. By comparison it can be seen that a change in pH can cause significant differences in the relative retention between a rare earth and a transition metal. This parameter can be very useful for optimizing selectivity.

#### Separation of thorium and uranium by reversed-phase

Samples of drainage from uranium tailing deposits and from studies into bacterial leaching of uranium ores are analysed on a regular basis in our laboratory for thorium and uranium. The method used to determine these elements is based on the retention of Th(IV) and U(VI) as their HIBA complexes on a reversed-phase. It has been shown that with only HIBA added to an eluent the rare earths are unretained and the transition metals only weakly sorbed on a reversed-phase, while Th(IV) and U(VI) are strongly retained [4]. Fig. 6 shows the chromatogram obtained for a bacterial leach liquor. Detection was by a post-column reaction with Arsenazo III. This chromatogram illustrates the rapid analysis time and good selectivity obtained with this method. Transition metal ions and the rare earths elute near the solvent front.

The parameters used to optimize separation of

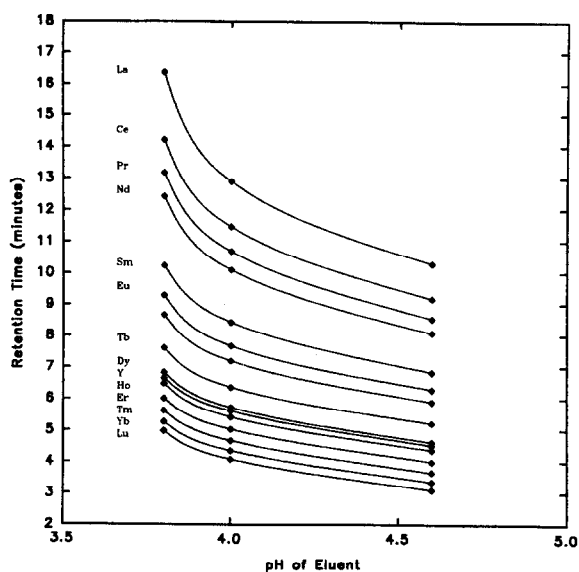


Fig. 4. Effect of pH on the retention time of the rare earths. Conditions: Supelcosil LC-18-DB column; gradient programme at a flow-rate of 1.0 ml/min from 0.05 M HIBA to 0.4 M HIBA over 10 min and held at 0.4 M for 5 min; modifier, 1-octanesulphonate at 0.01 M; detection as in Fig. 3.

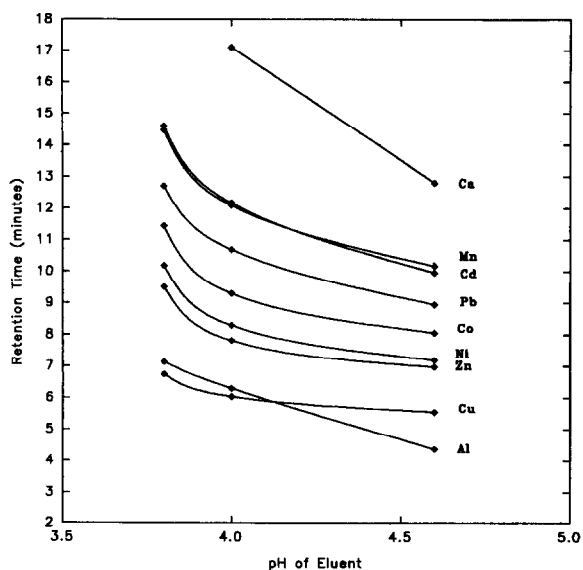


Fig. 5. Effect of pH on the retention time of metal ions. Conditions: Supelcosil LC-18-DB column; gradient programme at a flow-rate of 1.0 ml/min from 0.05 M HIBA to 0.4 M HIBA over 10 min and held at 0.4 M for 5 min; modifier, 1-octanesulphonate at 0.01 M; detection as in Fig. 3.

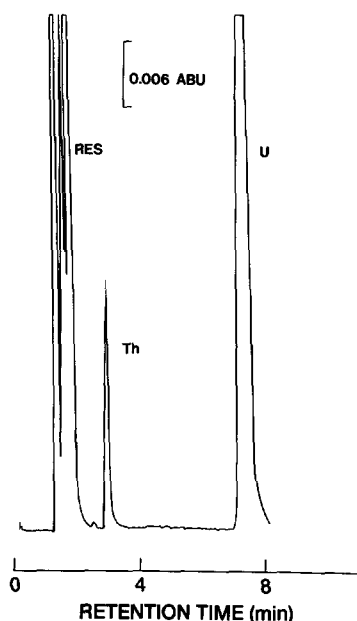


Fig. 6. Separation of thorium and uranium in bacterial leach liquor. Conditions: column, 5- $\mu$ m Supelcosil LC-18-DB; eluent, 0.2 mol/l HIBA at pH 4.2; modifier, 10% (v/v) methanol; flow-rate, 1 ml/min; detection at 658 nm after post-column reaction with Arsenazo III; sample injected, 50  $\mu$ l; sample dilution, 5 ml of leach liquor diluted to 50 ml with eluent.

Th(IV) and U(VI) from transition metals and rare earths were eluent pH, HIBA concentration, and amount of organic modifier in the eluent [5]. Addition of an organic solvent such as methanol or acetonitrile to the HIBA eluent decreased retention times of U(VI) and Th(IV). Increases in the concentration of HIBA had only a slight effect on increasing the retention times, while decreases in pH caused large decreases in retention of U(VI) and Th(IV).

#### Optimizing detection

Minimizing the baseline noise (BLN) level of the post-column reaction is important in achieving low limits of detection in this chromatographic technique. Factors that contribute to detector cell noise are the effectiveness of the post-column reactor system at mixing the column eluent with the colorimetric reagent and stability in the flow-rates of the eluent and reagent solutions. We have found that pump pulsation remained the largest source of BLN in a post-column system. Tests were conducted to evaluate flow pulsations for some eluent pumps and

for both gas-pressurized and syringe delivery of the Arsenazo III reagent. Fig. 7 shows the noise levels observed for systems studied. The newer eluent pumps (the Dionex 4000i and Waters M-625) with more effective pulse dampening and gas-pressurized delivery of the colour reagent, resulted in very low levels of BLN. For the Waters M-625 pump the peak-to-peak BLN level under the conditions was  $3 \cdot 10^{-5}$  ABU. The back-pressure system used with the ISCO M-645 pump was a 7.5 cm  $\times$  4.6 mm column of 10  $\mu$ m styrene-divinylbenzene inserted between the mixing tee and the syringe pump, which gave a back-pressure of *ca.* 400 p.s.i. This system in combination with older eluent pumps was found to be

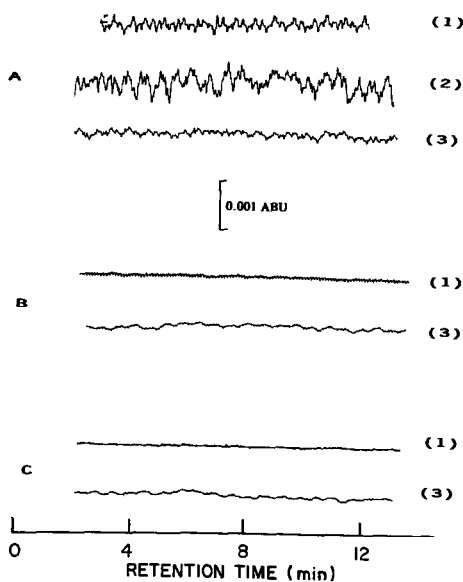


Fig. 7. Comparison of baseline noise for some eluent pumps with gas-pressure and syringe pumping for colour reagent. (A) Spectra-Physics SP8700 eluent pump and colour reagent delivery with (1) He-pressurized, (2) ISCO M314 syringe and (3) ISCO M314 syringe with back-pressure device. (B) Dionex Advanced Gradient eluent pump and colour reagent delivery with (1) He-pressurized and (3) ISCO M314 syringe with back-pressure device. (C) Waters Model M-625 eluent pump and colour reagent delivery with (1) He-pressurized and (3) ISCO M314 syringe with back-pressure device. Back-pressure device used with the ISCO syringe pump is a 7-cm column of 10  $\mu$ m styrene-divinylbenzene (400 p.s.i.). Instrumentation used in these tests: for absorbancy detection, a Spectra-Physics 2000; data handling was done by Spectra-Physics ChromJet integrator, and the post-column reagent was added to the eluent via a low-volume T-mixer [6]. Conditions: column, 5- $\mu$ m Supelcosil LC-18-DB at 32°C; eluent, 0.20 M HIBA at pH 4.6 and flow-rate of 1 ml/min; Arsenazo III,  $1.5 \cdot 10^{-4}$  M at flow-rate of 0.5 ml/min; detection at 658 nm.

more effective in reducing BLN than when a gas-pressurized reagent pump is used. The post-column reactor used was a version of the screen-tee type as used by Cassidy [6]. By minimizing the BLN level of the post-column reaction the detection limit for Th(IV) is 5  $\mu\text{g/l}$  and for U(VI) is 15  $\mu\text{g/l}$  ( $3 \times \text{BLN}$ ) for a 100- $\mu\text{l}$  sample injection.

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