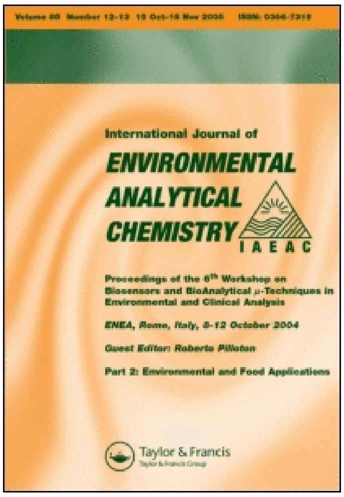

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A Multicolumn Ion Chromatographic Determination of Nitrate and Sulfate in Waters Containing Humic Substances

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A three-column ion chromatographic system for the removal of humic substances from natural waters, and subsequent on-line concentration and determination of nitrate and sulfate using non-suppressed ion chromatography is presented. Humic substances are removed using disposable adsorption columns packed with chemically bonded amine silica material. The sample is directly transfered to an ion exchange column where the anions are concentrated ca 10 times. After reversing the flow, the ions are transferred to a third column where they are separated and quantified. The detection limit is less than $1\,\mathrm{mg\,L^{-1}}$ of nitrate or sulfate in water containing $45\,\mathrm{mg\,L^{-1}}$ of humic acid.

KEY WORDS: Humic substances, natural waters, three-column ion chromatographic system, nitrate, sulphate.

INTRODUCTION

The analysis of nitrate and sulfate in natural waters is of great biological and environmental significance. A large variety of traditional techniques has been used for their determination.[1] All these techniques are influenced by the presence of humic substances in the samples and there is a continous need for selective methods.

In recent years, the technique of non-suppressed ion chromatography (IC) has become a sensitive and efficient method for anion analysis. Sensitivity enhancement is possible by the use of preconcentrator columns and large injection volumes.[2–4] Also ion chromatographic determinations are severely disturbed by interference from humics since those substances adsorb irreversibly to the quaternary amine groups in the separation column and destroy the column performance.

Several applications of IC for the determination of nitrate and sulfate in soil[5–8] and waters[6, 8–13] have been published. Usually, the samples are cleaned by extraction[6, 7, 11] or injected directly in the IC system. The separation column is in some cases protected by a guard column.[14]

Recently, we investigated different kinds of chemically bonded liquid chromatography phases for the selective adsorption of humics prior to ion chromatographic determination of anions.[12] The chemically bonded amine material was found to be superior. Also, a clean-up method using commercially available solid phase extraction columns of similar type was developed.[15]

This paper presents an on-line multicolumn system for sample clean-up, concentration and non-suppressed ion chromatographic separation of nitrate and sulfate in waters containing humic substances.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade unless otherwise stated. Stock solutions of nitrate, sulfate and phthalate were prepared from the corresponding potassium salts. The pH of the phthalate solution was adjusted with NaOH (Suprapur quality). The water was purified with a Milli-Q/RO-4 unit (Millipore, Bedford, MA). Reference solutions were prepared from humic acid (Fluka A. G., Buchs, Switzerland) with a molecular weight of 600–1,000 Daltons and an ash content of 10–15%. The solution was stirred at 60°C for 20 h and filtered through a 0.65μm membrane filter (Millipore). After evaporation to dryness, an elemental analysis of an aliquot of the reference humic solution gave the following results: C, 43.5%; H, 3.0%; N, 0.95%. The content of dry matter was 45 mg L^{-1}. Thus, the content of dissolved organic carbon (DOC) was 20 mg carbon per L.

Apparatus

The chromatographic system (Figure 1) consisted of two high pressure pumps (Model 2150, LKB Bromma, Sweden and Milton Roy miniPump, LDC, Riviera Beach, FL), two injector valves (Model 7125, Rheodyne, Cotati, CA), and three columns (see below). A conductometric detector ("Conductomonitor", LDC) was connected to a reporting integrator (Model CI-10, LDC). The conductometric detector was used in the "absolute" mode (10 uMHo full scale deflection) and the conductance of the eluent was electronically off-set.

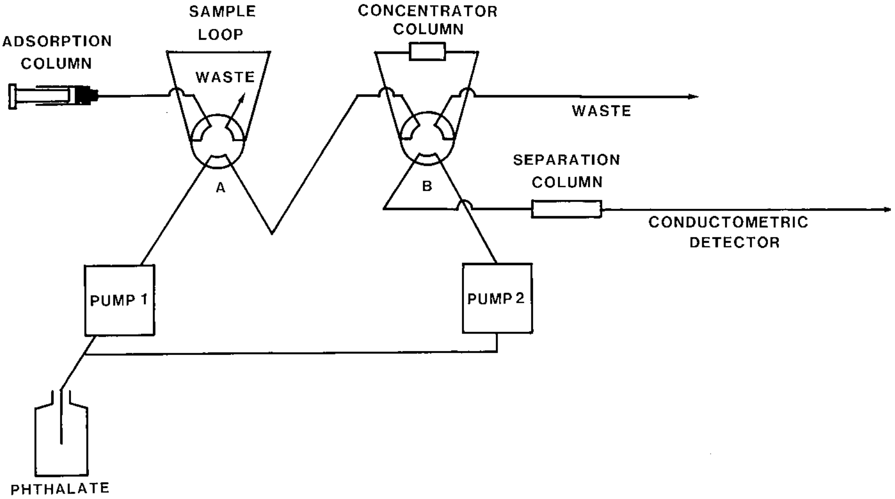

FIGURE 1 Chromatographic set-up.

Columns

For the specific adsorption of humic substances Bond-Elut-NH_2 disposable extraction cartridges (Analytichem, Harbor City, CA, USA) were used. These devices consist of a syringe barrel packed with 40 μm chemically bonded amino silica particles. Using a suitable plunger, samples can easily be pressed through the packing. Before use, the columns were rinsed and conditioned by sequentially pumping through them 5 mL aliquots of hexane, ethanol, water, 1,000 ppm K_2SO_4 and finally 14 mL of water. During the conditioning and the determinations of breakthrough capacity, a plastic adapter with low dead volume permitted the adsorption columns to be connected to a flow system.

For the concentration a high capacity Mono Q anion exchange resin (Pharmacia, Uppsala, Sweden) was used. It was packed into a specially made column (id 2 mm, bed length 5 mm) which permitted the length of the resin bed easily to be adjusted and optimized.

The separation column consisted of an anion exchange resin (Dionex, Sunnyvale, CA) packed into a glass column (5 mm id, bed length 50 mm, Pharmacia).

Procedure

Removal of humics:
2.0 mL of sample was pressed through the clean-up column (see Figure 1) into the 1,000 uL loop connected to valve A. The volume was large enough to give a steady state concentration of ions in the loop.

Concentration of anions:
After switching injector A, the sample was concentrated on top of the concentrator column during 3.0 minutes. The mobile phase was phthalate (3.5×10^{-4} M, pH 4.8) and the flow rate was 0.45 mL min^{-1}.

Separation of anions:
By switching injector B, the concentrator and separation columns were connected, and the mobile phase from pump 2 backflushed the concentrator. The anions were desorbed and separated in the separation column at a flow rate of 2.0 mL min^{-1}.

RESULTS AND DISCUSSION

Characteristics of the clean-up cartridges

An important parameter of the material used is the adsorption capacity for humic substances. Two different lots of cartridges were recently examined[15] and the adsorption capacities found were 68 and 170 μg of humic acid per cartridge, respectively. The RSD within each lot was 10–15%. The large difference between lots is probably due to different yields in the synthesis of the chemically bonded material. The capacity of each cartridge is sufficient to remove humics from a limited amount of water only and it is strongly advisable to test each lot of cartridge with representative samples for sufficient removal of humics. This can be checked by UV spectrophotometry. Figure 2 shows UV-spectra of a water sample before and after the clean-up procedure.

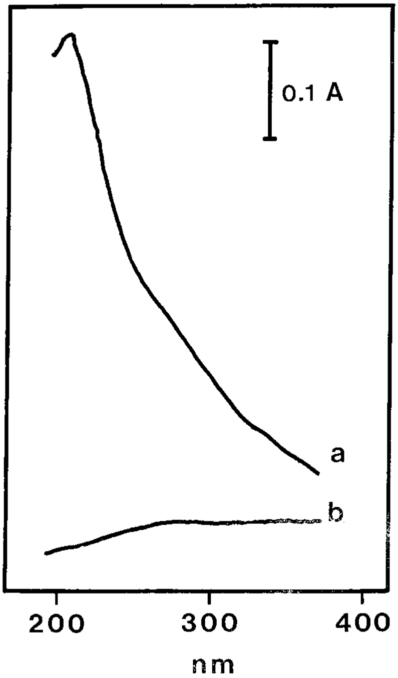

FIGURE 2 UV-spectra of a natural water sample before (a) and after (b) the clean-up procedure.

To obtain a higher degree of automation than is possible with the set-up described, some experiments were performed in which the adsorption cartridge was connected between the injection valves A and B in Figure 1. Thus, water was continuously pumped through the cartridge and samples were injected by valve A in the usual way. Unfortunately, this approach failed due to hydrolysis of the silica material. Silicate ions formed were concentrated on the concentrator column, creating severe interferences in the separation step. Also, the adsorption capacity gradually decreased. The use of a bonded phase material of higher quality would probably reduce these disadvantages. Problems of this kind were not experienced with a Nucleosil-NH_2 material in a similar set-up.[12]

Some adsorption losses of nitrate and sulfate were noted when the clean-up cartridges were used directly, without deactivation. This is probably due to permanent anion exchange sites. Deactivation of these sites can be made with sulfate ions, which are more strongly adsorbed than the individual charged groups of the humic acid. Hence, the humic acid will not appreciably displace the deactivating sulfate ions and determination of sulfate in water containing humic acid can still be made. The deactivation with sulfate decreases the adsorption capacity for humics with about 30%.[15]

Sample concentration and separation

To investigate the capacity of the enrichment column, the breakthrough volume of nitrate and sulfate was determined in the following way: The column was equilibrated with 3.5 mM phthalate solution (pH 4.8). A solution of nitrate and sulfate (50 mg L^{-1} each) in water was pumped through the column and the effluent was monitored by the conductometric detector. As is seen in Figure 3, the breakthrough volume for nitrate is ca 2 ml and for sulfate ca 4 ml. The 1 ml loop which was chosen should thus be adequate.

After desorption by phthalate eluent which is performed by reversing the flow of eluent through the concentrator column, the ions are eluted in a small volume of eluent (ca 100 uL). Thus, the concentration is raised ca ten times, permitting an easy quantification and separation of small amounts of anions. The detection limit was below 1 mg L^{-1} for both nitrate and sulfate. By an increase of the capacities of the concentrator and the clean-up columns, larger sample volumes can be used which permits lower detection limits of anions. This would make the investigation of the anion exchange capacity for different humic substances in various natural waters

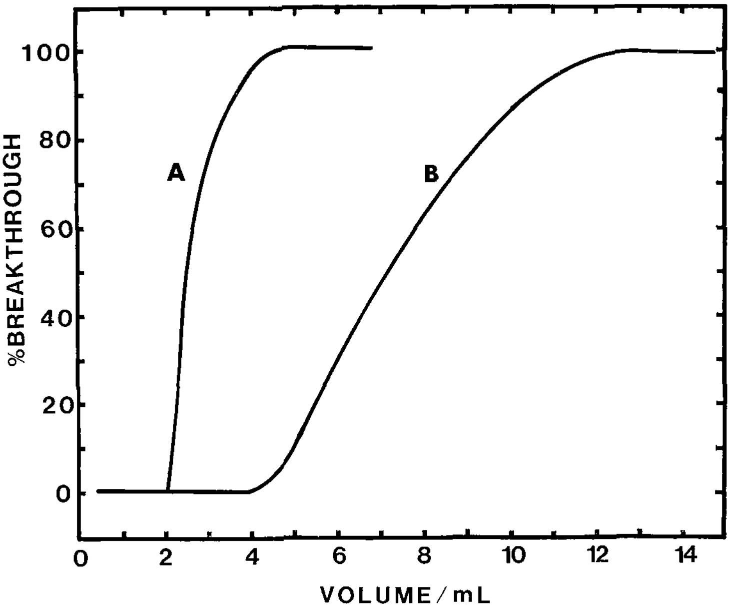

FIGURE 3 Breakthrough curves of nitrate (A) and sulfate (B) on the concentrator column, determined as described in the text.

possible. The amount of water that is injected into the separation column is greatly reduced, which minimizes the problems with the so-called pseudo water peak (see below). These advantages are gained at the expense of a somewhat decreased resolution, which can be compensated for by careful optimization of the separation conditions.

The concentration process is dynamic and based on the gradual dilution of the phthalate eluent with water from the sample. If the time of concentration is more than 3 minutes, ions are lost to waste.

Pseudo water peak

In non-suppressed ion chromatography, an extra peak is often observed.[12,14,16] related to a disturbance in the protonation equilibrium of phthalic acid, caused by the injection of water (second peak in Figure 4). The retention time of this peak is relatively independent

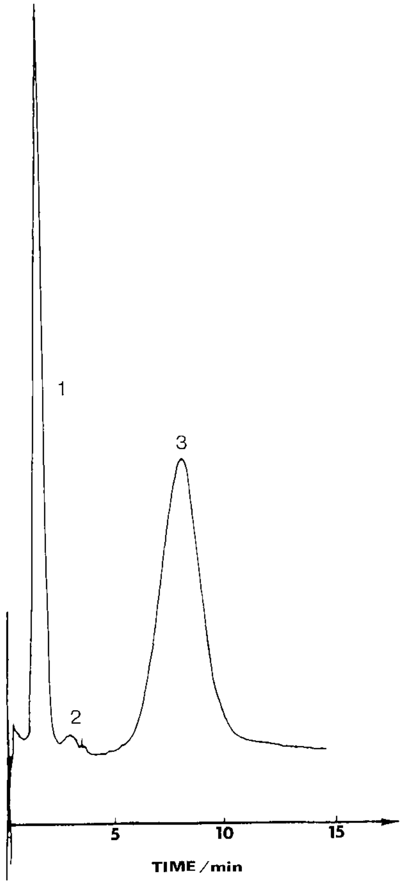

FIGURE 4 Chromatogram of $10\,\mathrm{mg\,L^{-1}}$ nitrate (peak 1) and sulfate (peak 3) after clean-up from a solution also containing $0.9\,\mathrm{mg\,L^{-1}}$ of humic acid. Peak 2 is the pseudo water peak. Eluent: Phthalate $3.5\times10^{-4}\,\mathrm{M}$, pH 4.8. Injected volume: 1 mL, concentrated to 0.1 mL as described in the text.

of pH. The height, however, depends on pH and can be both positive and negative. This unusual phenomenon complicates the choice of optimal pH for the separation. In Figure 5, the height dependence on pH in $3.75\times10^{-4}\,\mathrm{M}$ phthalate is shown. This behaviour is strongly dependent on the phthalate concentration as the buffer capacity of the eluent is very low, which is a necessity in

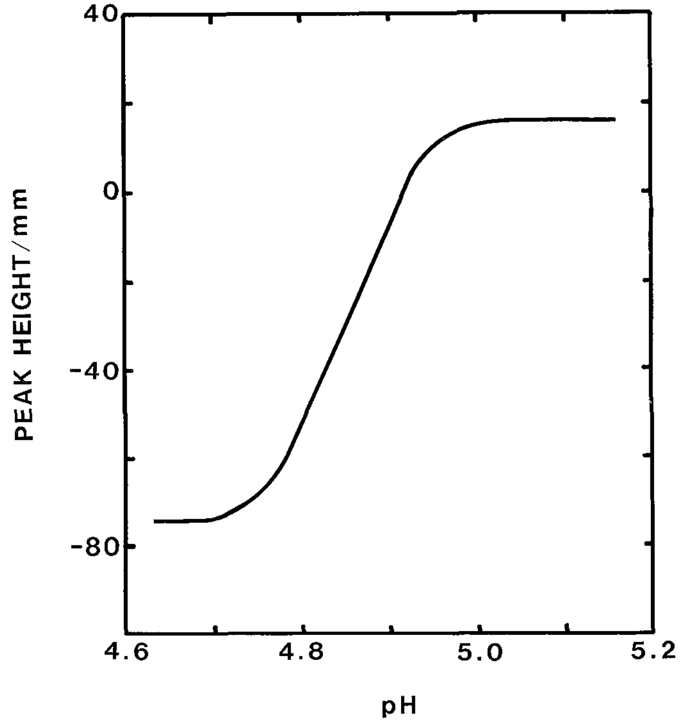

FIGURE 5 The variation of the height of the pseudo water peak with pH. Eluent: Phthalate, 3.75 10^{-4} M.

non-suppressed ion chromatography. To optimize the separation, the best eluent was found to be 3.5 10^{-4} M phthalate, pH 4.8. A typical chromatogram under these conditions is shown in Figure 4.

Analysis of model solutions

A series of model solutions containing 10 mg L^{-1} each of nitrate and sulfate and 0.00, 0.09, 9.0 and 45 mg L^{-1} of reference humic acid were prepared. Nitrate and sulfate were determined in the solutions using the procedure described in the experimental section.

Reference humic acid with a concentration of 45 mg L^{-1} (without ions added) was separately analyzed for the background level of nitrate and sulfate, giving the following results: 3.7 mg L^{-1} and

$5.2\,\mathrm{mg\,L^{-1}}$, respectively. These background levels were considered in the calculation of the percent recovery of nitrate and sulfate from solutions containing humic acid as compared with pure water solutions (see Table I).

TABLE I
Percent recovery of model solution, nitrate and sulfate containing humic acid.

Ion concn., $\mathrm{mg\,L^{-1}}$%	Recovery for concn. of humic acid added $\mathrm{mg\,L^{-1}}$			
	0.09	0.9	9	45
NO_3^-				
10	97	97	98	104
10	99	89	97	96
10	101	90	90	104
SO_4^{2-}				
10	110	96	99	113
10	111	113	102	125
10	103	110	97	124

Most of the recoveries in Table I are not significantly different from 100%. The general RSD ($n=12$) is 5% for nitrate and 9% for sulfate. The limited precision is partly due to imprecise timing of the valve swichings, which was performed manually.

CONCLUSION

The on-line combination of a clean-up column for the removal of humics and an ion exchange column for separation of anions can not be made by a simple series connection as these processes demand different eluents. A phthalate (or similar) eluent is necessary for the separation step while it would; due to its ion strength, cause unacceptable adsorption of anions if it were used in the clean-up step.[12]

In this work, we show that this problem can be solved using an intermediate column facilitating the necessary solvent exchange. This column also permits a considerable concentration of the sample, resulting in an appreciable lowering of the detection limit.

References

1. K. A. Smith, (Ed.), *Soil Analysis;* (Marcel Dekker: New York, Basel, 1983).
2. R. A. Wetzel, C. L. Anderson, H. Schleicher and G. D. Crook, *Anal. Chem.* **51,** 1532 (1979).
3. R. M. Cassidy and S. Elduck, *J. Chromatogr.* **262,** 311 (1983).
4. T. B. Hoover and G. D. Yager, *Anal. Chem.* **56,** 221 (1984).
5. W. A. Dick and M. A. Tabatabai, *Soil. Sci. Soc. Am. J.* **43,** 889 (1979)
6. M. Ahmed and A. R. Khan, *The Nucleus* **19,** 35 (1982).
7. R. S. Bowman, *J. Chromatogr.* **285,** 467 (1984).
8. T. Darimont, G. Schulze and M. Sonnebom, *Fresenius' Z. Anal. Chemie* **314,** 383 (1983).
9. S. H. Kok, K. A. Buckle and M. Wotton, *J. Chromatogr.* **260,** 189 (1983).
10. S. Rokushika, Z. Y. Qiu and H. Hatano, *J. Chromatogr.* **260,** 81 (1983).
11. M. A. Tabatabai and W. A. Dick, *J. Environ. Qual.* **12,** 209 (1983).
12. G. Marko-Varga, I. Csiky and J. Å. Jönsson, *Anal. Chem.* **56,** 2066 (1984).
13. J. E. Girard and J. A. Glatz, *Int. Lab.* 62 (1981).
14. T. S. Stevens, *Ind. Res. Dev.* **25**(9), 96 (1983)
15. I. Csiky, G. Marko-Varga and J. Å. Jönsson, *Anal. Chim. Acta,* in press.
16. T. Okada and T. Kuwamoto, *Anal. Chem.* **56,** 2073 (1984).