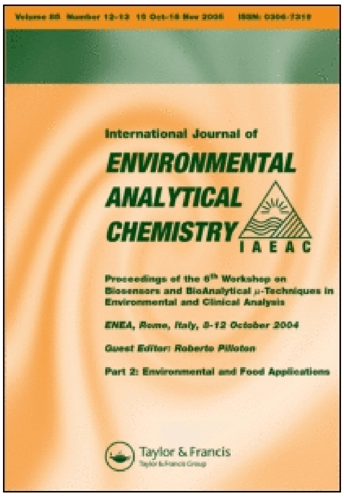

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A Simple Reverse Phase Column Clean Up for the Determination of Sulfate in Aqueous Leachates Containing Organic Compounds

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An analytical method has been developed for the determination of sulfate in leachates of soils and leaves laden with colored organic compounds. Reserve-phase chromatography proved to be an effective means for removing organic compounds from aqueous leachates without loss of sulfate. This simplistic pretreatment, employing Sep-Pak C_{18} cartridges, is rapid, cost effective, and extends the utility of the conventional methylthymol blue colorimetric method for sulfate.

KEY WORDS: Sulfate, colorimetric, organic, leachates, soil, leaf, chromatography.

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INTRODUCTION

An increased environmental awareness has led to widespread monitoring for the presence of specific chemicals in selected environmental samples. These samples often contain substances, other than those of interest, that may limit the applicability of conventional analytical methods. For example, the presence of colored organic compounds in aqueous leachates of soils and leaves can introduce serious errors in the colorimetric determination of sulfate.[1,2]

Methods have been reported that suggest means to destroy organic interferences or ways to circumvent their effects. One method involves oxidizing the organic compounds with hydrogen peroxide in conjunction with ultraviolet irradiation to decolorize the solution.[1] Without prior knowledge of the organic compounds in the sample, this time-consuming decolorizing technique may convert some or all sulfur species present to sulfate.

Indirect methods for sulfate have been devloped to circumvent the interference of organic compounds. One method removes sulfate as insoluble barium sulfate followed by a determination of the unreacted barium by atomic absorption spectrophotometry,[3] while another converts sulfate to sulfide and measures the sulfide level with a silver/silver sulfide ion-selective electrode.[4]

A rather simple pretreatment procedure has been developed that negates the need for both time-consuming decolorization and indirect methods. The procedure makes use of reverse-phase chromatography to remove organic compounds from aqueous solutions. This pretreatment procedure extends the utility of the methylthymol blue colorimetric method for sulfate to opaque leachates that could not be analyzed colorimetrically and to the analysis of certain transparent leachates that could be analyzed but with sulfate recoveries as low as 30%. Other techniques[1] for the removal of organic compounds were investigated, but poor sulfate recoveries were observed.

PROCEDURE

Ionized acidic organic compounds are converted to nonpolar forms at a pH of less than 2. (Addition of 15 μl of concentrated Ultrex HCl to 10 ml of aqueous sample is usually adequate.) The C_{18} column (Sep-Pak, Waters Associates, Inc.) rejects sulfate but retains nonpolar compounds on beads, which are coated with octyl-decyl alkyl chains.

After the pH of a sample is adjusted to below pH 2, sufficient solution is withdrawn into a volumetric pipet. On end of a short length of Tygon tubing is attached to the pipet tip and the other end to a C_{18} cartridge. The flow of sample solution through the cartridge is initiated with a rubber bulb placed atop the pipet. After flow has started, only gravity flow is recommended. Faster flow rates do not provide adequate time for complete interaction of the sample with the column matrix. The first liquid passed through the column ($\sim\frac{1}{2}$ml) is discarded. The remaining solution is collected in a clean vial.

Since the barium-methylthymol blue reaction must take place at pH 12.5–13.0,[5] a measured portion of the treated sample is evaporated to dryness on a hot plate to drive off excess hydrogen ions. The residue is dissolved with warm deionized water and diluted to a desired volume. A portion of the solution is taken for automatic analysis by the methylthymol blue colorimetric method. For comparison with a noncolorimetric method, selected samples were split and analyzed by both colorimetry and ion chromatography.[6]

The columns are cleaned after use by back-flushing with 10 ml of reagent-grade methanol followed with deionized water rinse. Longevity of Sep-Pak C_{18} columns is dependent on color intensity of the sample. The columns may be re-used as many as 10 times with slightly colored solutions, but only 2 or 3 times with highly colored solutions.

RESULTS AND DISCUSSIONS

The procedure was first tested to determine if either the column or sample treatment changed the detectable sulfate concentration of standard sulfate solutions. Standards were subjected to the same treatment discussed in the previous section. Table I shows that this procedure did not significantly alter sulfate concentration of the standards.

Water blanks were also subjected to the same treatment that samples would undergo in order to determine if any sulfate initially present in the column could contaminate the sample. The tests also determined if any acids or glassware used affected the sample sulfate concentration. Results indicated that water blanks acidified with concentrated Ultrex HCl did not exhibit any sulfate peaks but that water blanks acidified with concentrated Ultrex HNO_3 exhibited signals as high as 1.2 ppm sulfate. The same results occurred when acidified water blanks were evaporated without being passed through the column.

Natural soil and leaf leachate samples were treated as described. The samples were then analyzed by ion chromatography and the methylthymol blue procedure. Results are given in Table II. All values agree within 10%.

Table III shows that excellent sulfate recovery is obtained by our

TABLE I
Analysis of sulfate standards undergoing treatment

Sulfate present (μg/ml)	Sulfate found (μg/ml)	Percent recovery
1.0	1.1	110
3.0	3.0	100
4.0	4.2	105
20.0	21.0	105

TABLE II
Analyses for SO_4^{2-} in treated natural samples by colorimetric method and ion chromatography (IC)

	Sulfate, μg/ml		
Sample number	IC	Colorimetry	Percent deviation
1[a]	60.8	66.0	8.6
2[a]	60.0	60.0	0
3	16.2	17.6	8.6
4	7.8	8.5	9.0
5[a]	50.4	50.2	0.4

[a] Denotes coloured sample.

TABLE III
Recovery of sulfate added to natural samples (samples 6–10 were soil leachates while sample 11 was a leaf leachate)

Sample number	Percent recovery
6[a] (+3 ppp)[b]	99
7[a] (+3 ppm)[b]	95
8 (+2 ppm)[c]	100
9[a] (+2 ppm)[c]	92
10 (+2 ppm)[c]	95
11 (+2 ppm)[c]	95

[a] Denotes colored sample.
[b] SO_4^{2-} added before column treatment.
[c] SO_4^{2-} added after column treatment.

method. Sample color and sulfate levels had no effect on the efficiency of Sep-Pak C_{18} cartridges for the removal of interfering organic compounds. A sample containing approximately 150 ppm cystine, was analyzed without pretreatment by the methylthymol blue procedure to determine if sulfate was present. No sulfate was found. Cystine was studied because it was found to be a typical type of organic sulfur compound present in the leachates. The sample was then analyzed after column pretreatment to determine if any of the organic sulfur was converted to sulfate. If Ultrex HCl was used to adjust the pH prior to column treatment, no sulfate was found. When Ultrex HNO_3 was used to adjust the pH, the sample contained approximately 7 μg/ml. This procedure is acceptable as long as Ultrex HCl is used.

While our initial organic sulfur experiments utilized cystine, other types of organic compounds will be studied in the future. In particular, ester sulfates may comprise significant portions of the total dissolved sulfur in soil and vegetation leachates and are known to decompose under heat and acid conditions to yield inorganic sulfate resulting in possible overestimates of total sulfate concentrations. Existing methods[1] for dealing with highly colored samples use u.v. and H_2O_2 oxidation to reduce organic content prior to analysis by colorimetry. While the effects of this method on ester sulfates are not known, we have determined that the H_2O_2-u.v. method does oxidize the sulfur in cystine to sulfate to some extent.

This method for sulfate determination allows use of the conventional methylthymol blue procedure with highly colored organic samples. The procedure is easy to implement and does not require the purchase of additional equipment other than the disposable cartridges. Several hundred samples using this procedure have been analyzed without encountering any difficulties.

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