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Spectrophotometric flow-injection determination of sulphate in soil solutions

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Abstract

A flow-injection procedure for spectrophotometric determination of sulphate in soil solutions is proposed. Samples are directly soaked from the soils under field conditions, in-line filtered through ceramic plates, and preserved with thymol. The method involves reaction with barium dimethylsulphonazo(III) (DMSA) in the presence of dimethylsulphoxide (DMSO) with further measuring the decrease in absorbance at 668 nm. A linear response is observed up to about 5 mg l^{-1} SO_4, and detection limit (3σ criterion) is 0.1 mg l^{-1} SO_4. Only 4.5 μg DMSA is consumed per determination. The system is rugged and baseline drift is not observed during extended operation periods. About 60 samples are injected per hour, and the results are precise (r.s.d. <2%) and in agreement with ion chromatography.

Keywords: Sulphate; Flow analysis; Soil solution; Spectrophotometry

1. Introduction

Sulphate is the predominant sulphur species available to the plants [1], therefore its determination in soil solution is of relevance. A literature survey reveals, however, that methods for this determination are relatively scarce especially in relation to concentrations lower than 0.5 mg l^{-1}.

The turbidimetric determination of sulphate in different matrices has been often reported [2], and presents favourable characteristics of simplicity, low requirements for instrumentation, ruggedness and speediness. The method involves barium (or lead) addition in order to form a reproducible and stable suspension to be quantified. Uniform conditions should then be established, and this is achieved by improving the sample/reagent mixing conditions and timing, as well as the rate of turbidity formation. In this context, addition of colloid protectors is beneficial [2]. The procedure is recommended by the Environment Protection Agency [3] but cannot be directly applied to samples with sulphate contents lower then 2 mg l^{-1}.

Regarding soil analysis, large deviations in results are generally noted, due to the lack of analytical procedures for low-level determination of sulphate, the difficulties inherent to the turbidimetric procedures, and the intrinsic soil heterogeneity.

Reliable results can be obtained by taking advantage of flow-injection analysis [4], as the analyser is an excellent system for solution management [5], providing also a precise timing control. In view of its simplicity, easy of automation and amenability to miniaturization, the flow-injection analyser is rugged and versatile. The sample is reproducibly handled and the involved equilibria are not necessarily reached. This opens the feasibility of establishing the favourable conditions required for the turbidimetric determination of sulphate [6–9].

With regard to low concentration levels, spectrophotometry should be highlighted, as sensitivity tends to be better in relation to turbidimetry. Moreover, suspended matter sometimes found in the samples generally less affects results. In general, BaL-type reagents are used, and variation in ab-

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sorbance is quantified after formation of the slightly soluble barium sulphate and liberation of the L^{2-} ligant. Different ligands such as chloranilate [10], chromate [11], methylthymol blue [12], dimethylsulphonazo(III) [13], etc. have been used.

The main purpose of this work was then to develop a highly sensitive spectrophotometric procedure for sulphate determination in soil solutions. Dimethylsulphonazo(III), herein referred to as DMSA, was selected by considering that it proved to be suitable in relation to large-scale water analysis [13]. The procedure might be implemented in a flow-injection analyser, which is able to provide conditions for avoiding turbidity formation [7,14]. In spite of the relevance of the sulphate determination in soil solutions, exploitation of this method in the context of soil analysis seems to be novel.

2. Experimental

2.1. Reagents, standards, samples

All solutions were prepared with deionised water and analytical-reagent quality chemicals.

The 1000 mg l^{-1} SO_4 stock standard solution was prepared by dissolving 1.376 g $(NH_4)_2SO_4$ in 1000 ml of water. Working standard solutions within the 0.00–5.00 mg l^{-1} SO_4 range were daily prepared by water dilutions of the above stock.

The R reagent (Fig. 1) was daily prepared by adding 8.0 ml of 0.01 mol l^{-1} DMSA solution, 7.0 ml of 0.01 mol l^{-1} Ba (as barium chloride dihydrate) solution, 5.0 ml of 1.0 mol l^{-1} LiCl solution, 20 ml of a buffer (0.05 mol l^{-1} acetic acid/0.05 mol l^{-1} sodium acetate, pH 4.7) solution, 4.0 ml of a 0.1 mol l^{-1} sodium dodecylsulphate (SDS) solution and 800 ml of dimethylsulphoxide (DMSO) to 1000 ml volumetric flask, and filling the volume with water. A 0.1 mol l^{-1} HNO_3 solution was used as the E eluent, and water as the C sample carrier stream.

The Dowex 50W-X8 cation exchange resin (100–200 mesh, H^+ form) was used to fill a cylindric (i.d. = 1.0 mm, h = 3.0 cm) mini-column that was made from Tygon tubing. Glass wool plugs (ca 1 cm) were placed at mini-column ends

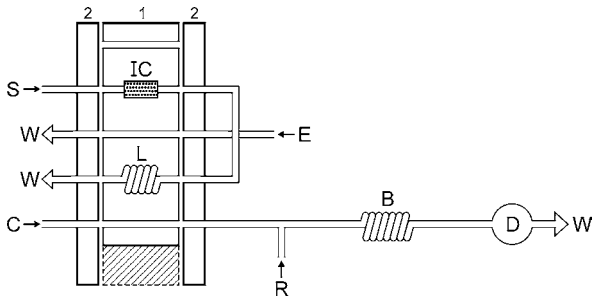

Fig. 1. Flow diagram. S: sample; C: sample carrier stream; R: reagent; E: eluent; 1: central sliding portion of the injector-commutator; 2: external fixed portions of the injector-commutator; IC: ion-exchange mini-column; L: external sampling loop; B: reaction coil; D: detector; W: waste.

in order to avoid resin losses during system operation. Filling of resin was accomplished by aspirating a stirred water resin suspension with the peristaltic pump. In this way, resin packing was attained without an excessive hydrodynamic pressure.

Soil solutions were collected at different depths (10–150 cm) by a set of Plexiglas extractor devices provided with ceramic capsules [15]. The collected material underwent filtrations, first through a Whatman #1 paper filter and then through a 0.45 μm cellulose acetate membrane filter [16].

2.2. The flow-injection system

The flow set up comprised a model IPC-8R Ismatec peristaltic pump equipped with Tygon pumping tubes, a manually operated injector-commutator [5], a model USB 2000-UV-vis Ocean Optics spectrophotometer furnished with a acrylic Z-shaped flow cell (optical path = 10 mm; inner volume = 18 μl), and accessories. The manifold was build-up with 0.5 mm i.d. Teflon tubing, and accessories.

The flow system operates as follows. When the injector-commutator rests in the sampling position specified in Fig. 1, the sample is pumped through the resin mini-column filling the external sampling loop that precisely selects the sampled volume. Switching the injector-commutator to the alternative position inserts the selected sample volume (200 μl) into its carrier stream (0.6 ml min^{-1}) and places the mini-column into the eluent stream allowing the sorbed ions to be discarded towards waste. A sample zone is established and pushed forwards by the carrier stream. The R reagent (0.75 ml min^{-1}) merges with the sample zone at the confluence point, and the chemical reactions take place inside the following reaction coil (250 cm). Details of the involved chemistry are given elsewhere [13]. When the sample passes through the flow cell, the absorbance monitored at 668 nm undergoes a transient lessening, which is recorded as an inverted peak with height proportional to the sulphate content in the sample.

2.3. Procedure

The proposed method involves formation of the slight soluble barium sulphate; therefore crystal growth might result in turbidity formation. As a vector sum of the analytical signal (absorbance lessening) plus that related to turbidity (absorbance[1] increase) was involved, this might lead to a sensitivity drop. In this way, experiments were done in order to verify if turbidity was formed. To this end, the blank and the 3.00 mg l^{-1} SO_4 standard solutions were placed instead of the sample carrier stream, establishing an steady situation (sample "infinite volume" [17]) and the measurements were done at either 580 nm (isosbestic point) or 700 nm (negligible absorption by the Ba-DMSA complex).

Influence of acidity of the reaction medium was investigated by adding different acetic/acetate solutions

[1] This term is used here instead of turbidance.

($3.0 < pH < 5.5$) to the R reagent. DMSA concentration in this reagent was investigated within 5.0×10^{-4} and 10.0×10^{-4} mol l^{-1} DMSA. Regarding the DMSO solvent, its concentration inside the main reactor was varied within the 40–65% (v/v) range; for >40% (v/v) concentrations, the R reagent was prepared with 80% (v/v) DMSO and the C/R flow rate ratio and concentrations of the other chemical species were varied accordingly. Establishment of a micellar medium to improve system performance was investigated by adding different surfactants (0.01–0.1% (m/v) gelatine, Tween-80, glycerol; 1.0×10^{-3}–10×10^{-3} mol l^{-1} sodium dodecylsulphate) to the R reagent.

Effect of temperature was studied within 20 and 50 °C by immersing the main reaction coil and the C and R solution bottles inside a controlled-temperature water bath. After each temperature adjustment, a 5-min delay was needed for attainment of thermal equilibrium.

In order to investigate the progress of the involved reactions, the sample carrier stream was replaced by a 3.00 mg l^{-1} standard solution, and the peristaltic pump was stopped for 0–10 min after achievement of the steady situation.

After system design, the cation-exchange mini-column was placed and the eluting conditions were investigated by using different eluent solutions (0.1–1.0 mol l^{-1}, HCl or HNO_3) at different flow rates. Thereafter, the main figures of merit of the proposed procedure were evaluated and the system was applied to large-scale analyses.

3. Results and discussion

Turbidity formation was not observed under all the investigated situations as confirmed by the measurements performed at the isosbestic point or at 700 nm. This is a very positive aspect, as the soil solutions present colloid particles that could act as primary nuclei. $BaSO_4$ crystal growth was relatively slow and did not affect sensitivity or repeatability. It should be emphasised that rate of turbidity formation was lower than that already reported [14], as lower concentrations of sulphate and barium ions were involved.

3.1. System dimensioning

Regarding acidity of reaction medium, a sensitivity drop was observed under too acidic conditions (Fig. 2) due to combined effects of DMSA protonation and increasing the rate of crystal growth. On the other hand, alkaline conditions are not recommended in view of the possibility of occurrence of side reactions, e.g. formation of slightly soluble carbonate and/or hydroxides involving Ba^{2+}. In order to avoid the interference of carbonate and taking into account the higher analytical signals at $4.0 < pH < 5.0$, the pH value of the buffer solution added to R reagent was selected as 4.5. This is a favourable aspect, as this pH value matches the pK_a of the acetic/acetate buffer system inside the DMSO solvent [18], thus guaranteeing a suitable buffer capacity.

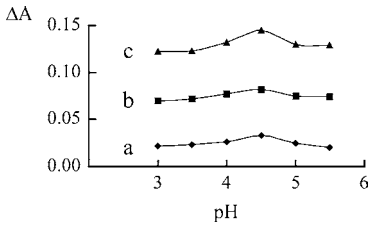

Fig. 2. Influence of acidity. Δ*A*: peak height, in absorbance; pH refers to the buffer solution added to reagent R; curves a, b and c refer to 0.50, 1.00 and 1.50 mg l^{-1} SO_4.

The DMSA concentration was selected as 8.0×10^{-4} mol l^{-1}, corresponding to a baseline of about 0.9 absorbance. For lower concentrations, sensitivity underwent a proportional lessening. Higher concentrations are not recommended in view of the baseline instability observed under conditions of very low transmitted radiation. The Ba^{2+} concentration was selected as 7.0×10^{-4} mol l^{-1} as a guarantee that this cation is quantitatively linked with DMSA. With equimolar concentrations, the detection limit was sometimes affected, probably because other chemical species might be linked to DMSA.

DMSO proved to be a relevant parameter in system design too, as increasing its concentration in the reaction medium increased sensitivity. However DMSO concentration could not be increased at will in order to avoid an excessive analyte dilution at the confluence point. Best sensitivity was noted for the DMSO concentration of 57% (v/v).

Among the investigated surfactants, SDS proved to be the most efficient, and better sensitivity was observed when its concentration was 3.0×10^{-3} mol l^{-1} SDS (Fig. 3). Moreover, the establishment of an organized medium through the addition of this surfactant led to a pronounced enhancement in the signal-to-noise ratio. This favourable aspect is due to the improved mixing conditions, the ability of the surfactant as a colloid protector and the increased punctual analyte concentration [19]. Moreover, crystal deposition on the inner walls of the tubing and flow-cell was not noted, leading to improved system washing and baseline stability.

Temperature was not a relevant parameter in the system design, as only slight variations (<10%) in the slope of the analytical curve were observed by varying the water bath temperature within 25 and 60 °C. Regardless of the pre-set temperature, the system was always stable, and baseline drift was

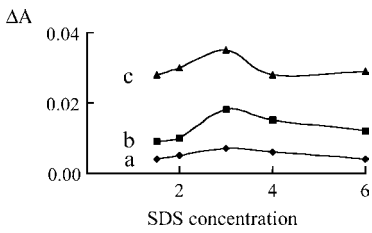

Fig. 3. Influence of surfactant concentration. Δ*A*: peak height, in absorbance; SDS concentration expressed in mmol l^{-1}; curves a, b and c refer to 0.50, 1.00 and 1.50 mg l^{-1} SO_4.

not observed even for lower temperatures. In order to reduce the possibility of air-bubbles liberation under higher temperatures, it was decided to operate the system under laboratory conditions (25 °C). In this way, the controlled-temperature water bath is not necessary.

Regarding influence of sample residence time inside the analytical path, proportional to the available time interval for sample/reagent interaction, it was observed that chemical equilibrium was not reached. The experiments involving sample "infinite volume" and peristaltic pump stopping revealed that absorbance related to the steady situation decreased in about 30% after 2–3 min of resting time. This aspect is not a drawback, as attainment of chemical equilibrium is not always necessary in flow-injection analysis [4]. In this way, a reaction time of ca. 10 s (1.35 ml min^{-1} total flow rate) was selected by taking into account that the increase in sensitivity was too low, that possibility of turbidity formation would increase, and that loss in sampling rate would be pronounced for a 3-min sample residence time. It should be stressed that an additional time interval of ca. 30 s was provided for proper resin mini-column re-conditioning.

The mini-column was very efficient to circumvent effects of the presence of potential interfering chemical species such as Ca^{2+}, Al^{3+}, K^+ and Mg^{2+}. With this artefact, concentrations as high as 5, 5, 40 and 20 mg l^{-1}, respectively, could be tolerated as deviations <2% were noted in relation to the determination of 0.25–1.50 mg l^{-1} SO_4. These concentrations (added to typical samples) are not likely to occur in soil solutions. A noteworthy feature of this ion-exchange architecture is that the analyte does not participate in the separating step, which is an additional guarantee for the measurement repeatability; moreover, the hydrodynamic pressure can be maintained low. With this strategy, resin deterioration due to soil organic matter was not observed. The elution step towards waste is not critical and 0.1 mol l^{-1} HNO_3 (1.0 ml min^{-1}) was selected as eluent.

3.2. Figures of merit

Beer–Lambert law is followed within 0.00 and 5.00 mg l^{-1} SO_4 and a typical equation describing the analytical curve is

$$\Delta A = 0.0947C + 0.0175, \quad r > 0.9977, n = 6$$

where ΔA is the lessening in absorbance; C the analyte concentration in mg l^{-1} SO_4.

The system handles about 60 samples per hour, meaning 4.5 μg DMSA per determination. Measurement precision is fair, relative standard deviation of results being estimated as <2% after 10 repetitive runs of typical soil solution samples. Detection limit was estimated [20] as 0.1 mg l^{-1} SO_4 (3σ criterion). Accuracy was confirmed by running some samples already analysed by ion chromatography [21], and results are presented in Table 1. No statistical differences between methods were found at the 95% confidence level (estimated and limit t-values: 0.397 and 2.262).

Table 1
Sulphate concentrations in soil solutions as determined by the proposed method and by ion chromatography [21] (data (mg l^{-1}) based on five replications; deviations specified by 0.00 refer to <0.005)

Sample[a]	Flow-injection system	Ion chromatography
1	0.60 ± 0.02	0.58 ± 0.01
2	0.22 ± 0.01	0.24 ± 0.01
3	0.53 ± 0.02	0.51 ± 0.00
4	0.22 ± 0.01	0.19 ± 0.01
5	0.15 ± 0.00	0.15 ± 0.01
6	0.26 ± 0.01	0.29 ± 0.00
7	0.22 ± 0.00	0.26 ± 0.00
8	0.49 ± 0.02	0.46 ± 0.01
9	0.94 ± 0.02	0.91 ± 0.00
10	1.55 ± 0.03	1.64 ± 0.01

[a] Collected at the Amazon region (Presidente Figueiredo AM, Brazil).

4. Conclusions

The proposed system exploits spectrophotometry is simple and rugged. As a consequence, precise results are obtained and baseline drift is not observed during extended working periods. In view of its favourable characteristics of sample/reagent consumptions, sampling rate, sensitivity, selectivity and easy of implementation, it can be recommended for large-scale analysis of soil solutions. The flow-injection system can be regarded as a "closed laboratory" where the involved reactions take place without contact with the ambient. Alternatively, sample losses and/or contamination are avoided. Waste generation is minimal, only 450 μl DMSO and 45 μg DMSA per sample, which meets the requirement of the modern tendency towards Clean Chemistry.

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