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Comparison of the determination of anions in dissolved organic carbon-loaded water samples by ion chromatography and photometric methods

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ABSTRACT

Dissolved organic carbon (DOC) in water samples can cause strong interferences in photometric detection methods using complexing reactions. Ion chromatography was demonstrated to minimize DOC effects on the determination of anions. Further, it can be used to examine the accuracy of photometric methods by calculating the difference in the ion balance using ion chromatographic values.

INTRODUCTION

Ion chromatographic and photometric methods are often used for the routine laboratory determination of anions in water samples [1,2]. Therefore, the question arises of which method is applicable to reduce matrix effects, especially those caused by dissolved organic carbon (DOC).

EXPERIMENTAL

To answer the above question, 160 samples of seepage water prepared from lysimeters underneath the humus layer and cup lysimeters (ceramic material; installation depth 40 cm) were analysed for sulphate, chloride and nitrate by both methods. Because of the installation depth of the lysimeters, these water samples contain high concentrations of DOC ranging up to 50 ppm whereas samples prepared from cup lysimeters in the mineral soil horizon are nearly free from DOC, generally lower than 0.8 ppm [2].

Ion chromatographic detection was carried out with a Dionex 4010i instrument using micromembrane suppression (AMMS-1) and an HPIC-AS3 analytical column under standard conditions [1].

The following methods for photometric analysis

with an automated wet chemistry (AWC) system were used: nitrate at 520 nm after reduction to nitrite as an azo dye [3]; sulphate at 490 nm indirectly by releasing an azo dye [1,8-dihydroxy-2-(4-sulphobenzeneazo)-naphthalene-3,6-disulphonic acid] from the corresponding thorium(IV) complex [4]; and chloride at 480 nm indirectly as iron(III) thiocyanate equivalent after reaction with mercury(II) thiocyanate [5].

RESULTS

Both the ion chromatographic and photometric methods gave accurate results for the determination of sulphate, nitrate and chloride of DOC-free cup lysimeter samples (Fig. 1). On the other hand, DOC had a strong influence on the photometric determination of sulphate and chloride. Both methods are based on complexing reactions with metal cations. As a consequence of the complexing character of DOC, high results for the determination of sulphate and chloride in samples from lysimeters containing high concentrations of DOC were found (Fig. 1).

On account of the detection wavelength (>440 nm), self-absorption of the DOC can be excluded as a reason for these high results. Because a total organic carbon analyser was not available, the DOC

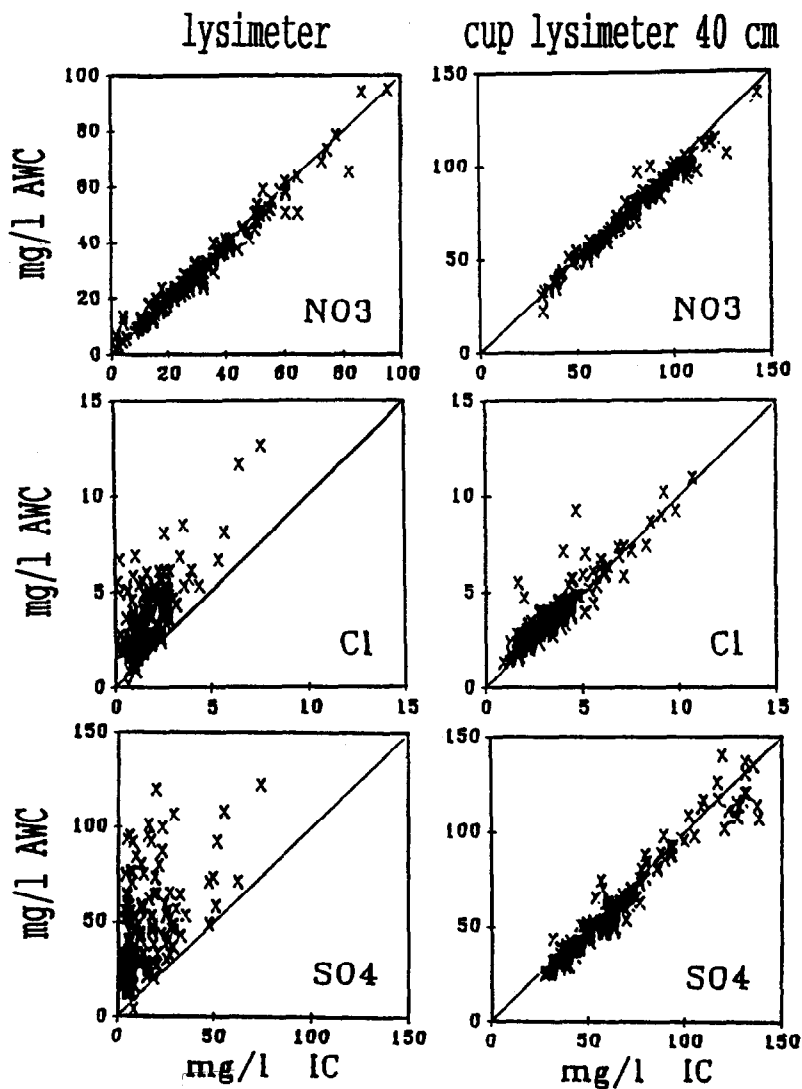


Fig. 1. Comparison of the values obtained using AWC photometric methods (AWC) and ion chromatography (IC).

content of the water samples had to be calculated indirectly as the difference in the ion balance (cations minus anions) using ion chromatographic (IC) values for the anions, inductively coupled plasma values for the cations and the pH (values not given here). The relationship between the DOC content and the overestimation of sulphate and chloride can be seen in Fig. 2.

The effect of DOC on the photometric methods can be reduced but not completely removed by sol-

id-phase extraction with reversed-phase material because polar carbon compounds will not be adsorbed on this material.

DISCUSSION

Ion chromatography is applicable for the specific determination of anions in DOC-loaded water samples using a reversed-phase material for protection of the analytical column. The advantage of ion

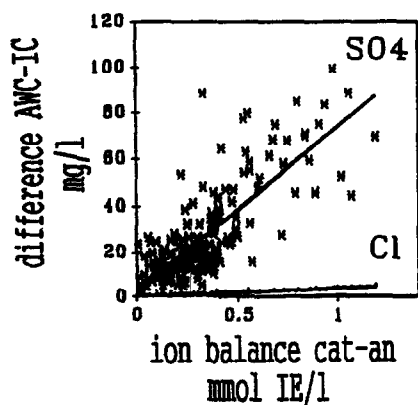


Fig. 2. Influence of DOC on the values obtained by photometric (AWC) methods (DOC calculated as the difference in the ion balance, based on IC values). cat = Cations; an = anions. IE = ion equivalent.

chromatography over photometric methods lies in its insensitivity to DOC interferences. Therefore, it is possible to calculate the relative influence of DOC on photometric methods using IC values. Finally, ion chromatography of anions produces less toxic waste than most photometric methods and is much easier to handle.

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