

The application of single-column ion chromatography for the determination of sulphate in rain-water samples

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Abstract

Single-column ion chromatography using potassium hydrogen phthalate at pH 5,0 or sodium benzoate at pH 6,8 as mobile phase, was compared to a methylthymol blue continuous flow method for the analysis of sulphate in rain-water samples. Statistical evaluation indicated comparable results between the ion chromatographic and continuous flow methods. Sulphate recovery using the ion chromatographic method was 96 to 100% and the continuous flow method 100 to 108%.

Introduction

The separation of several common anions chromatographically in only a few minutes was described for the first time by Small et al. (1975). Their technique commonly known as suppressed ion chromatography used basic eluents to separate sample anions on a low capacity anion-exchange column. The eluent then flowed through a second suppressor column, which was a high capacity cation-exchange column in the hydrogen form. This converted the eluent into a low-conducting weak acid and the sample anions into highly conducting acids.

Gjerde et al. (1979; 1980) introduced a new system for anion chromatography, which allows for the elimination of the suppressor column, made possible by the use of a special anion-exchange resin of very low capacity and the adoption of an eluent having a very low conductivity.

Single-column chromatography has been used for water/environmental samples and accurate results have been obtained (Hern et al., 1983). An effective analytical method for determining parts per billion concentrations of chloride and sulphate in very pure water such as steam condensates using single-column ion chromatography was demonstrated by Roberts et al. (1981).

It is still widely believed that suppressed ion chromatography is the preferred method to single-column ion chromatography. This paper aims to illustrate that accurate analyses can be done without the need for a suppressor column, and compares 2 different methods for determining sulphate in rain-water samples, namely single-column ion chromatography and a continuous flow system method.

In addition to illustrating the effectiveness of single-column ion chromatography, it was decided to develop a method for the determination of sulphate in rain-water samples using ion chromatography. Although sulphate analysis can be done on the Auto Analyser at a higher rate with less cost per analysis, the ion chromatography technique exhibits a wider dynamic range (0,1 mg/l to 40 mg/l) as well as being the more sensitive method and it is for this reason that ion chromatography is considered the conventional method for determining sulphate in rain-water samples. An added advantage of using ion chromatography is that a number of anions can be determined simultaneously, whereas with an Auto Analyser, a number of Auto Analysers with various methods are needed.

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Experimental

Apparatus

Ion chromatograph

A Shimadzu HIC-6A ion chromatograph with the following components was used for the evaluation of sulphate in rain-water samples:

- LC-6A liquid pump
- CTO-6A column oven
- COD-6A conductivity detector
- SCL-6B system controller
- SIL-6B auto injector

Parameter settings were as follows:

Flow rate : (i) sodium benzoate: 1,5 ml/min
(ii) potassium hydrogen phthalate: 1,2 ml/min
Oven temp.: 30°C
Polarity : positive
Gain : 0,1 μ S/cm
Range : 64
Response : standard

A Hamilton PRP-X100 column consisting of a trimethylammonium strong base ion exchanger was used.

The number of theoretical plates for the sulphate peak using a 2 mM solution of potassium hydrogen phthalate, at a flow rate of 1,2 ml/min and a pH of 5,0, was calculated to be 4399.

The areas of the chromatograph were calculated using a Hewlett Packard 3359A chromatographic work system.

Auto analyser

The determination of sulphate is based on the reaction, at an acidic pH, of sulphate ions with barium ions to form barium sulphate (Badenhorst et al., 1992). This is followed by measurement, at high pH, of the increase in absorbance at 480 nm, due to the removal of the barium methylthymol blue complex. The sample is first passed through a sodium-type cation-exchange column to remove multivalent metal ions. Since the chemistry is non-linear, a solution containing 5 mg/l sulphate is added to improve the linearity. The sample containing sulphate is then reacted with an alcohol