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OPTIMIZATION OF ION CHROMATOGRAPHY USING COMMERCIALLY AVAILABLE DETECTION SYSTEMS AND SOFTWARE

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SUMMARY

An ion chromatographic system is described which is composed of a high-performance separator column, a micro-membrane suppressor system, dedicated software and various detection systems. The system is built for the analysis of fluoride, chloride, nitrate and sulphate in precipitation samples. In this system conductivity detection is used in series with UV detection (for nitrate) and an ion-selective electrode (for fluoride).

A linearizing software programme for suppressed conductivity, UV and ion-selective electrode detection was developed in our laboratory and added to the commercial software together with modules for calibration, quality control and automatic recalibration. The total system allows more than 100 samples a day to be analyzed automatically. The calibration procedure involves the analysis of only two standards for a linear range of 0.2–80 mg/l for chloride, nitrate and sulphate, 0.2–40 mg/l for nitrate and 10–1000 μg/l for fluoride with conductivity, UV and ion-selective electrode detection, respectively.

Using a 130-μl injection loop detection limits are obtained of 10, 20, 40 and 60 μg/l for fluoride, chloride, nitrate and sulphate, respectively. The repeatability within a analyzing cycle of ten samples is of the order of 1–3%. The reproducibility is better than 5% as automatic recalibration is performed at this level.

INTRODUCTION

The determination of inorganic anions by ion chromatography, introduced by Small *et al.* in 1975[1], has widely replaced classical wet chemical techniques, especially in the field of environmental research. Favourable features, such as the simplicity, the sensitivity and the multi-component character, have made ion chromatography very popular.

To achieve sufficiently low detection limits, good selectivity, high speed and linear calibration curves over a large concentration range, our laboratory has generally applied detectors, analytical columns, suppressor column systems and linearizing programmes and other software of our own design[2–4]. However, high-performance separator columns, a sophisticated membrane suppressor system, multi-detector systems and dedicated software have recently become commercially available[5]. A

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modular ion chromatograph based on these recent developments with multi-detectors for the analysis fluoride, chloride, nitrate and sulphate ions in rain, mist and dew samples is the main subject of this paper.

The application of a low-pulsation pump and a thermostatted conductivity detector, based on a four-electrode system, results in improved detection limits. So the 1600-μl sample loop combined with a concentrator column, as applied in a previous configuration, has been replaced by a 130-μl sample loop. The resulting low sample loadings favour the use of high-speed columns, which are otherwise easily overloaded, which results in a loss of selectivity.

The sensitivity of ion chromatography with conductivity detection is enhanced by the use of a suppressor system. In the case of determination of anions a cation-exchange column in the H^+ form was originally used, which minimized the conductivity of the eluent and increased the conductivity of the eluting solutes. A recent development is the introduction of a micro-membrane suppressor system, which eliminates the regeneration of a two-columns-in-tandem system[2]. The dead volume of the membrane-based hollow-fibre suppressor used to be a problem, but the introduction of the micro-membrane suppressor has reduced the void volume considerably so it is now comparable with that of a small suppressor column.

The selectivity of ion chromatography, which by "classical" definition is based on conductivity detection, can be improved by combining different detectors in series[2]. This approach has two advantages: (1) in the case of very weak acids, *e.g.* sulphide and cyanide electrochemical detection offers an excellent alternative for conductivity detection in combination with a suppressor system[6]; (2) selective detectors can solve the analytical problems in cases of poor separation, *e.g.* fluoride, which elutes partly in the "waterdip", or bromide in the presence of a high concentration of nitrate. In our laboratory, conductivity detection is used in series with UV detection (for nitrate) and an ion-selective electrode (for fluoride or chloride).

Since 1975 there has been an expanding commercial market in ion chromatography. After Dionex, other manufacturers of ion chromatographic equipment arrived on the scene. One consequence is the possibility of buying an ion chromatography system built from various modules instead of a system from just one supplies. In our laboratory an ion chromatograph is built from a Sycam pump, a Dionex injection valve, a Dionex column, a Dionex micro-membrane suppressor, a Waters conductivity detector, a Shimadzu UV detector and a Metrohm ion selective electrode in a holder of our own design.

As the price of microcomputers has fallen over the past five years, dedicated bench microcomputers have entered the laboratory. So on-line control of analytical parameters, such as peak search, background correction, automatic calibration and re-analysis of samples, have become common practice. However, until recently, users had either to develop their own software or to accept a "black box", which offered few possibilities for specific adaptations. Recently, commercial software has become available in the form of modules, which offer the opportunity to develop specific applications. A linearizing submodule developed at our laboratory was added to the commercial software, together with modules for calibration, quality control and automatic recalibration.

The ion chromatograph is automated as we are engaged in large-scale environmental programmes, which necessitates the analysis of 100 samples of rain, mist and

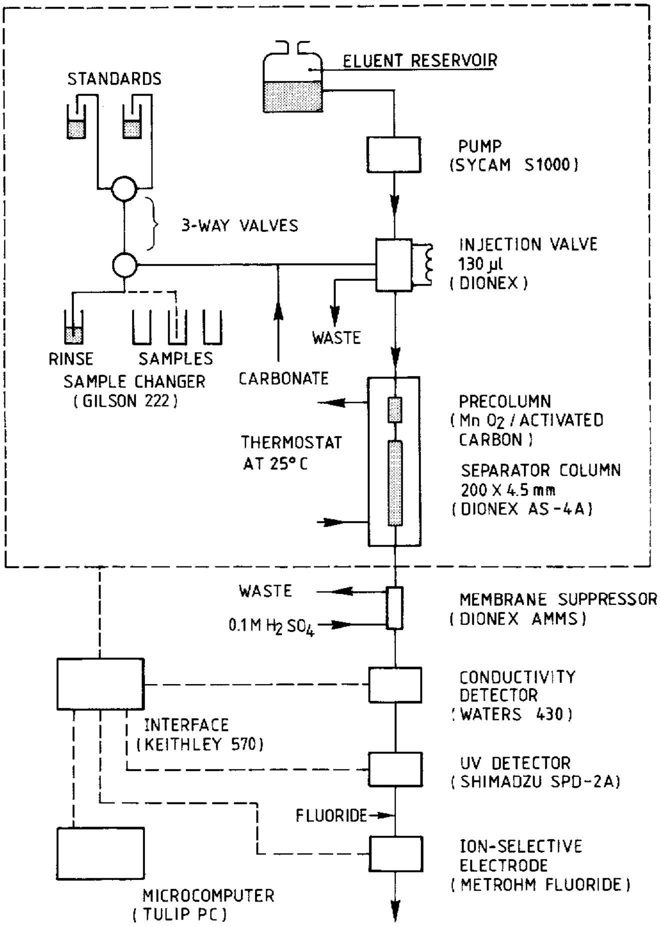

Fig. 1. General set-up of the ion chromatograph.

dew per day. In this paper a modular ion chromatograph, built at a cost of *ca.* Dfl. 80 000 is described, with the emphasis on multi-detection, automation and linearization of calibration graphs.

EXPERIMENTAL

Apparatus

The ion chromatograph is shown diagrammatically in Fig. 1. Samples are injected from a Gilson 222 sample changer, which is controlled by the microcomputer and offers arbitrary re-analysis of a sample. The samples are mixed on-line with 0.1 *M* sodium carbonate in a ratio of 1:20 before the injection loop. The injection volume is 130 μl. The 200 × 4.5 mm I.D. Dionex AS-4A column is thermostatted at 25°C. The eluent is a standard Dionex mixture of $1.8 \cdot 10^{-3}$ *M* sodium carbonate and $1.7 \cdot 10^{-3}$ *M* sodium bicarbonate. The eluent is pumped by a Sycam pump S1000 at a flow-rate of 1.2 ml/min.

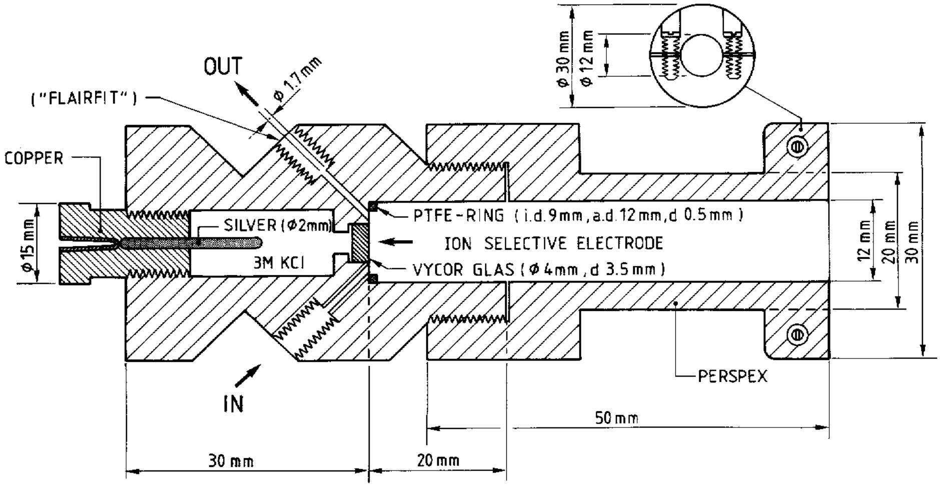

Fig. 2. Holder for ion-selective electrodes. i.d. = Internal diameter; a.d. = outer diameter; d = thickness; ∅ = outer diameter.

The micro-membrane suppressor system (Dionex AMMS) is continuously regenerated by 0.1 *M* sulphuric acid at a flow-rate of 0.7 ml/min by a Watson-Marlow pump.

The Shimadzu SPD-2A UV detector, with a cell volume of 8 μl, is set at 220 nm to detect nitrate. The Waters 430 conductivity detector, internally thermostatted at 35°C and equipped with a unique four-electrode design, offers a very stable baseline. The fluoride ion-selective electrode (Metrohm) is mounted in our laboratory-made holder with a void volume of 25 μl shown in Fig. 2. For fluoride measurements the eluent is mixed 1:10 with a 1 *M* acetic acid–acetate buffer at pH 4.7 and 1000 μg/l fluoride.

Automation

For automation purposes the ion chromatograph is equipped with a Tulip PC microcomputer (512 Kbyte, 20 Mbyte hard disk) interfaced with a Keithley 570 data acquisition system. The software performs calibration, sample injection, data acquisition and calculation of concentrations.

For years we have been working with laboratory-designed software but recently we have bought commercial computer programmes. The idea of a modular approach is also used in the software set-up. The main programme is written in GW BASIC (MS-DOS V3.0). User interface, graphic presentation of results and quality control are part of the main programme. Modules such as data acquisition, chromatography software, statistic operations are activated from the main programme using the GW BASIC "SHELL" function. Data transfer between the modules is realized using standard Input/Output on hard and RAM disk (see Table I).

For data acquisition from the detectors and calculation of concentrations by the software the following tasks are performed: (i) the detector response is measured each second; (ii) a peak-search routine indicates the start, maximum and the end of each peak in preset time windows for chloride (50–90 s), nitrate (120–140 s) and

TABLE I

DESCRIPTION AND FUNCTIONS OF THE SOFTWARE

Module (supplies)	*Functions*
Data acquisition module	
Labtech Notebook (Lab Technologies)	Data collection of detector signals Control of valves Real-time graphic presentation of raw data
Interpretation modules	
Labtech Chrom (Lab Technologies)	Peaksearch and integration
Corval (Fortran 77) (our laboratory)	Linearization of conductivity signal by eqn. 1 Linearization of UV signal Linearization of ion-selective electrode by eqn. 2
Non Linear Least Squares (IMSL Fortran Library)	Estimation of response factors in eqn. 2

sulphate (270–310 s); (iii) the baseline is determined before and after the peak and the mean value of the baseline is subtracted from each point of the chromatogram; (iv) depending on the type of detector, the non-linear response is corrected for by means of mathematically derived equations. The non-linear responses of the conductivity detector, the UV detector and the ion-selective electrode have different origins.

The non-linear behaviour of the suppressed conductivity detection is a result of the changes in the background conductivity of the eluent in presence of the eluting solutes after the suppressor system. In this eluate the eluent is a weak acid and the solutes are strong acids, the H^+ ions of which suppress the ionization of the weak acid. Consequently, the contribution of the eluent to the conductivity is not constant, but decreases as the solute concentration increases. So the reduction of the background conductivity and the enhancement of the conductivity of the solutes result in non-linear calibration graphs.

The calibration graphs can be linearized by a correction of the measured conductivity based on the acid–base equilibrium of the eluent after suppression and the displacement of eluent ions from the separator column by solute ions.

In earlier work a quadratic equation in the unknown concentration c_x of the eluting solute was derived[4]. By means of the square-root formula (eqn. 1), the sample concentration at each point of a conductivity chromatogram is calculated:

$$c_x = [-B + (B^2 - 4AC)^{1/2}]/2A \qquad (1)$$

where A, B and C are functions of the measured conductivity of the solute, the cell constant of the conductivity cell, the capacity factor of the solute, the pK_1 of HCO_3^-/H_2CO_3, the eluent concentration and the specific conductivity of H^+, bicarbonate and the solute. The capacity factor is calculated from chromatographic retention data of the solutes, and the cell constant is determined by calibrating the conductivity cell with potassium chloride solutions of known concentrations.The non-linear calibration graphs for the conductivity detection can be linearized by integration of c_x for chloride, nitrate and sulphate.

In the case of UV detection the response is also non-linear, as the background UV absorption depends on the concentration of the solute. The variation of the background UV absorption results from variation in the eluent displacement and shifting of the HCO_3^-/H_2CO_3 equilibrium as function of the solute concentration. Like the linearization of the conductivity detection, this is corrected for by a BASIC routine in the main programme.

In the case of ion-selective electrodes, which have a logarithmic response, the non-linearity is corrected for by using eqn. 2:

$$c_x = c_B(10^{(\mathrm{d}E/S)} - 1) \qquad (2)$$

where c_B is the added background concentration of the solute; S is the slope of the electrode response; and dE is the peak height of the detector signal. Eqn. 2 is derived from the difference in the electrode response for the solute: $E_{c_x} + E^0 + S\log(c_x + c_B)$ and the background: $E_{c_B} = E_0 + S\log(c_B)$.

After analysis of two standards, the values of c_B and S are calculated by means of a commercial programme, "Non Linear Least Squares".

The advantage of the linearization procedure is a detection range of 0.2–80 mg/l for chloride, nitrate and sulphate, 0.2–40 mg/l for nitrate and 10–1000 μg/l for fluoride by calibration with two standards and conductivity, UV and ion-selective electrode detection, respectively.

Theoretically no calibration is necessary as soon as the parameters in eqns. 1 and 2 are determined. However, for quality control reasons, a standard is measured every cycle of ten sample analysis. The system is automatically stopped if the measured data exceeds a $\pm 5\%$ variation with the absolute data.

RESULTS AND DISCUSSION

The separator column is guarded by means of a pre-column filled with a 1:1 mixture of manganese dioxide (100–200 mesh) and active carbon. Any hydrogen peroxide present in precipitation samples, which reduces the lifetime of the separator column, is eliminated by manganese dioxide[7], and organic components are adsorbed on the active carbon.

The use of fast separation conditions cause the complete disappearance of the fluoride peak and the partial disappearance of the chloride peak in the "water dip" of the sample injection. This results in unidentified fluoride and chloride peaks by the commercial software peak-search routine. By means of the addition of carbonate the negative injection peak is eliminated, which offers conductivity detection of chloride. In Fig. 3 an ion chromatogram is shown of a standard containing 1 mg/l chloride, nitrate and sulphate.

In the case of fluoride the sensitivity and selectivity of conductivity detection is not sufficient when precipitation samples are analysed. As the fluoride concentration in these samples generally does not exceed 0.5 mg/l, components such as formic acid and acetic acid present in atmospheric samples will interfere. By means of an ion-selective electrode these analytical problems can be overcome. Fluoride is mixed with the eluate just before the ion-selective electrode in order to increase the response time and the linear range of the electrode. As metal fluoride complexes are decom-

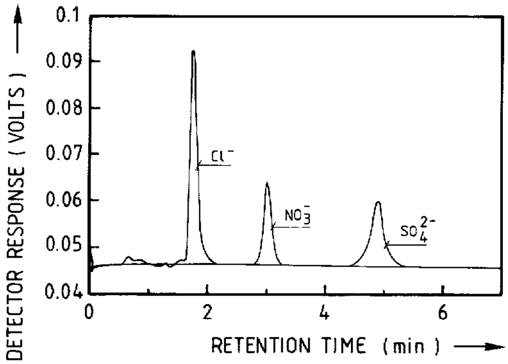

Fig. 3. Ion chromatogram of a standard containing 1 mg/l chloride, nitrate and sulphate.

TABLE II

PEAK AREAS OBTAINED FOR CHLORIDE BY CONDUCTIVITY DETECTION WITH AND WITHOUT LINEARIZATION CORRECTION

Injection volume 130 μl; $n = 5$.

Standard injected (mg/l)	*Corrected peak area*		*Non-corrected peak area*	
	Direct	*Normalized**	*Direct*	*Normalized**
0.2	0.73	0.99	0.44	0.59
1.0	3.65	0.99	2.33	0.65
4.0	15.1	1.03	10.3	0.70
8.0	29.8	1.02	22.4	0.76
16.0	59.0	1.01	49.8	0.85
40.0	146.0	1.00	117.0	0.80
80.0	295.0	1.01	245.0	0.84

* Calculated with eqn. 3.

TABLE III

PEAK AREAS OBTAINED FOR NITRATE BY CONDUCTIVITY DETECTION WITH AND WITHOUT LINEARIZATION CORRECTION

Injection volume, 130 μl; $n = 5$.

Standard injected (mg/l)	*Corrected peak area*		*Non-corrected peak area*	
	Direct	*Normalized**	*Direct*	*Normalized**
0.2	0.38	0.91	0.17	0.41
1.0	2.03	0.97	0.91	0.43
4.0	8.5	1.02	3.78	0.45
8.0	17.3	1.03	7.58	0.46
16.0	34.5	1.03	15.5	0.46
40.0	81.7	0.98	38.2	0.46
80.0	163.0	0.98	76.4	0.46

* Calculated with eqn. 3.

TABLE IV

PEAK AREAS OBTAINED FOR SULPHATE BY CONDUCTIVITY DETECTION WITH AND WITHOUT LINEARIZATION CORRECTION

Injection volume 130 μl; $n = 5$.

Standard injected (mg/l)	*Corrected peak area*		*Non-corrected peak area*	
	Direct	*Normalized**	*Direct*	*Normalized**
0.2	0.49	0.90	0.28	0.52
1.0	2.64	0.97	1.50	0.55
4.0	10.7	0.99	6.50	0.60
8.0	21.0	1.00	13.6	0.63
16.0	43.2	1.00	29.8	0.69
40.0	103.0	0.95	74.4	0.70
80.0	204.5	0.95	141.2	0.65

* Calculated with eqn. 3.

posed on the analytical column at the pH of the eluent (pH 9), the addition of decomplexing reagents, such as 1,2-cyclohexylene dinitrilotetraacetic acid monohydrate (Merck-Titriplex IV), is not necessary.

Nitrate is detected by the conductivity detector as well as by the UV detector. In this way a quality control is performed as bromide and phosphate possibly present in environmental samples and eluting near nitrate will not be detected by UV at 220 nm. The UV detection is linear over the range 0.2–40 mg/l nitrate. By analysing standards in this range a correlation coefficient of 0.9997 was obtained between conductivity and UV detection.

The efficiency of the linearizing module in the case of conductivity detection was tested by analysing standards in the concentration range 0.2–80 mg/l chloride, nitrate and sulphate. Tables II–IV, present the results for corrected and non-corrected peak areas of the conductivity detection by the linearizing module. The normalized peak areas, calculated from eqn. 3, present the response per μmol of injected solute.

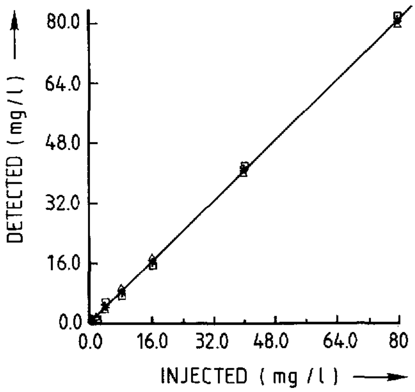

Fig. 4. Linear detection range of chloride (∗), nitrate (△) and sulphate (□).

$$\text{Norm} = (PM)/(Ic_S) \tag{3}$$

where Norm is the normalized peak area, P is the peak area of the detected solute, I is the injection volume (130 μl), c_S is the concentration of the injected sample (mg/l), and M is the equimolecular weight of the detected solute.

The non-corrected peak areas show large variation over the concentration range, indicating non-linear behaviour. For the corrected peak areas, however, the normalized values are constant within a variation of 5% for chloride, nitrate and sulphate, up to a concentration of 80 mg/l.

These results show that linear calibration graphs can be obtained over a large concentration range by taking in account the suppression of the eluent dissociation by the solute ions, the displacement of eluent ions in the separator column by the solute ions, and integration of the total eluted peak area. Linear calibration based on peak heights cannot be obtained as the peak width increases with injected sample concentrations.

The linear range of the system is limited by the capacity of the separator column. At concentrations above 80 mg/l the column becomes overloaded. As shown in Fig. 4, the detection range is linear in the concentration range 0.2–80 mg/l with correlation coefficients of 0.9999 between injected and detected concentrations of chloride, nitrate and sulphate.

As the detection limit is defined as three times the variation of the blank, the detection limits are determined by analysing ten times double demineralized water. The detection limits for fluoride, chloride, nitrate and sulphate are 10, 20, 40 and 60 μg/l, respectively.

The reproducibility is better than 5% as automatic recalibration is performed at this level. The reproducibility is defined as the value below which the absolute difference between two single analyses is obtained after recalibration of the system.

The repeatability is of the order of 1–3%, and is defined as the value below which the absolute difference between two single analyses is obtained within an analysis cycle. An analysis cycle consists of the analysis of ten samples, after which automatic recalibration is performed.

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