

## Chapter (non-refereed)

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# Non-suppressed ion chromatography in 'acid rain' analysis

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## 1 Introduction

The ITE Edinburgh and Banchory Research Stations have been collecting and analysing rain samples since late 1977. Recently, interest has turned to more intensive sampling of rainfall events in addition to bulk monthly samples, and to the study of cloudwater chemistry. Until 1984, chemical analyses were performed at ITE Edinburgh using a variety of methods, including continuous flow colorimetry, ion-selective electrodes and atomic absorption/emission. A non-suppressed ion chromatograph was commissioned during 1984 and has been performing all the chemical analyses, with the exception of pH, for about a year. It has allowed a greater number of samples to be analysed within the constraints of staff time.

## 2 Theory

The use of a single chromatographic column to separate anions and their subsequent direct detection by conductivity were described by Gjerde *et al.* (1979) and developed by the same group to include cation analysis (Gjerde *et al.* 1980; Fritz *et al.* 1980). Their approach differed from the earlier ion chromatographic techniques of Small *et al.* (1975), developed commercially by Dionex, in that the background conductivity of the eluant was subtracted electronically, rather than chemically, thereby eliminating the need for a chemical 'suppressor' column to reduce eluant conductivity after the chromatographic column. However, the separation method is similar, using a low-capacity ion exchange column with an aqueous eluant at a controlled pH. Initially, anion separations were performed using phthalic acid (normally *ortho*-, but the 2 other isomers have been used (Glatz & Girard 1982)) at a pH less than 6.0, the highest pH which may be used with a silica-based column. More recent column technology using resin-based columns has allowed the use of pH range 1–12, and a wider range of buffer eluants such as p-hydroxy benzoic acid at pH 8.5. Monovalent cations are generally separated using dilute nitric acid ( $2 \times 10^{-3}$  M), and separation of divalent cations is achieved by using a complexing agent such as ethylenediamine. Detection of the ions after separation can be achieved by measuring conductivity changes. For an eluant such as phthalic acid with low background conductivity, the presence of an inorganic anion, eg chloride, in the detector cell increases the conductivity, and a positive peak is produced. In cation analysis, where the nitric acid

eluant has a larger conductivity, the presence of an ion such as sodium produces a decrease in the conductivity and a negative peak. In either case, both peak heights and areas are linearly related to the amount of each ion injected on to the column. Alternative detection methods have been employed, and for anions these may be significantly more sensitive than straightforward conductivity detection. Small and Miller (1982) in the USA, and Cochrane and Hillman (1982) in the UK reported the use of indirect ultra-violet detection with phthalate as eluant. The UV absorption of the phthalate eluant is decreased as non-absorbing anions pass through the detector. This method has the added advantage of allowing the estimation of an unknown ion's valency from the variation of retention time with eluant concentration. The response (expressed as the area of the negative peak) also depends only on the concentration of the ion present in a sample, when measured in equivalents per litre, so that the response is independent of the ion and allows quantitative estimation of an unknown (Small & Miller 1982).

A similar technique, but using changes in refractive index, has been applied by Haddad and Heckenberg (1982) to the analysis of both anions and cations.

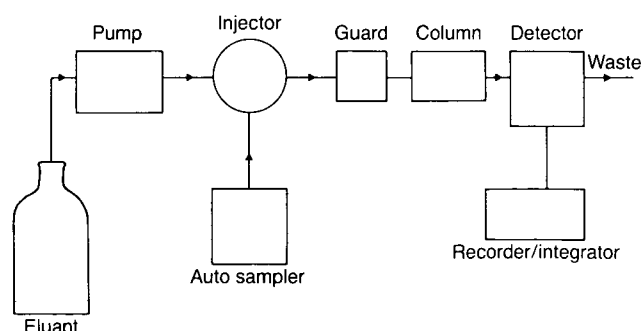


Figure 1. Schematic ion chromatography system based on standard HPLC equipment

## 3 Practice

The great practical advantage of non-suppressed ion chromatography over suppressed (ie using a chemical suppressor column) is that a system can be built from readily available standard components for high-performance liquid chromatography (HPLC). A schematic diagram of such a system is shown in Figure 1, and the equipment used at ITE Edinburgh is listed in Table 1. Other detectors (eg UV detector) could be used

in place of the conductivity detector. For a laboratory with existing HPLC equipment, only a suitable column needs to be purchased to achieve a capability for ion chromatography.

**Table 1.** Ion chromatography equipment used at ITE Edinburgh

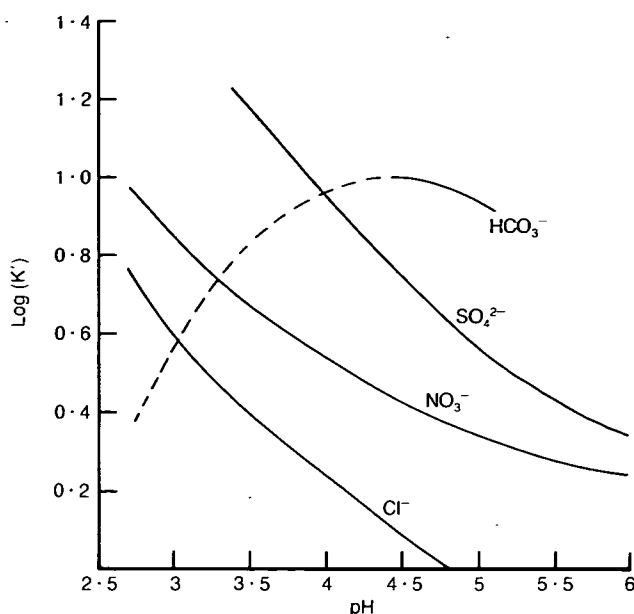
Pump: Kontron 414 single-piston pump with pulse dampener
Autosampler: Kontron MSI660 with pneumatic injector (Rheodyne) capacity 60 × 2 ml vials
Column holder and detector: Wescan ion chromatography module (conductivity)
Recorder/integrator: Shimadzu C-R1A single channel printer/plotter

The operation of the system requires the same care as any HPLC equipment. All samples are filtered through a disposable 0.2 µm filter, and eluants are also filtered through an 0.2 µm 'candle' filter before use. Initially, problems were found with the quality of the laboratory supply of deionized water which, although 'pure' in that its conductivity was around 0.1 µS, had sufficient colloidal material present to accumulate on the guard column and create a high back-pressure. Analytical columns are not cheap (£200–£600), but the use of a guard column and care in sample preparation permits several thousand injections without serious loss of column efficiency. The size of the injection loop can be varied to suit the samples: for normal rain samples, we use a 200 µl loop, but for cloudwater samples, which generally have much larger concentrations, a 20 µl loop has been used successfully.

The limits of detection are around  $2 \times 10^{-6}$  M for direct injection. Other workers (eg Roberts *et al.* 1981) have pre-concentrated samples on a short column in place of the sample loop. Up to 10 ml of sample may be passed through the concentrating column; the ions are retained at the head of the concentrating column and are then flushed on to the analytical column by pumping eluant backwards through the concentrating column. In this way, concentrations down to  $10^{-8}$  M may be detected, but at these levels the likelihood of contamination is very great, and precautions such as using pre-soaked polycarbonate labware and a dust-free environment must be observed to obtain reproducible results.

#### 4 Analysis of anions

The 3 major anions in rainwater (chloride, nitrate and sulphate) are readily separated and detected, and, by choice of a suitable eluant, other inorganic ions such as fluoride and phosphate may be separated and measured. The order of elution is



**Figure 2.** Retention of major inorganic ions in rainwater as a function of pH, using  $4 \times 10^{-3}$  M phthalate eluant (after The Wescan Ion Analyser, 4, 3 (1982), Wescan Inc., Santa Clara, California)

determined by the concentration of the eluant and its pH. For a phthalate eluant, the optimum pH is between 4 and 5 to achieve elution of the sulphate ion in reasonable time. The sensitivity of the method increases as eluant concentration is decreased, but a compromise must be sought between elution time (which increases with decreasing concentrations) and sensitivity. For a  $4 \times 10^{-3}$  M solution of potassium hydrogen phthalate, Figure 2 shows the effect of changing pH on retention of the common anions. For rainwater analysis, a pH must be chosen sufficiently high to elute sulphate quickly without 'losing' the chloride peak in the initial 'solvent' peak. After some trial and error, we have adopted as standard an eluant for anion analysis of 0.332 g o-phthalic acid, 24.0 ml 0.1 M NaOH and 10 ml methanol per litre of deionized water. This is equivalent to a phthalate concentration of  $2 \times 10^{-3}$  M at pH 4.74. Addition of a small quantity (1%) of methanol alters the retention characteristics to some extent, but has been found useful for avoiding bubble formation in the detector, which can occur even with vacuum-degassed eluant. Methanol (5%) is also added to the wash-water of the autosampler to prevent droplet formation in the PTFE (polytetrafluoroethylene) sample tubing. This eluant allows the separation of the 3 major ions in less than 15 minutes at a flow rate of 3 ml min<sup>-1</sup> using a 25 cm × 4 mm column. A typical analysis is shown in Figure 3 for a rainwater sample. Calibration is achieved by inserting a single standard solution (usually  $200 \times 10^{-6}$  M Cl<sup>-</sup>,  $50 \times 10^{-6}$  M, NO<sub>3</sub><sup>-</sup>,  $50 \times 10^{-6}$  M SO<sub>4</sub><sup>2-</sup>) after every 5 samples. Response factors are calculated automatically by the integrator and used for

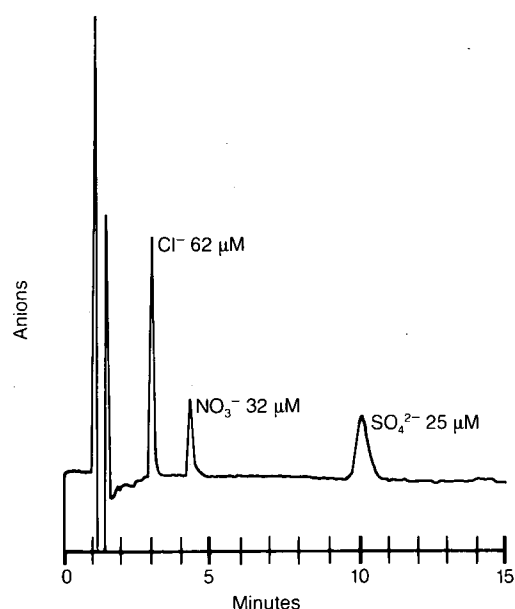


Figure 3. Anion analyser of rainwater sample from Great Dun Fell, Cumbria (17 April 1985). Flow rate:  $3 \text{ ml min}^{-1}$ ,  $100 \mu\text{l}$  injection; eluant:  $2 \times 10^{-3} \text{ M}$  phthalate at pH 4.74 in 1% methanol; column: Vydac 302IC  $25 \text{ cm} \times 4 \text{ mm}$

subsequent samples. Analysis of a range of standard solutions has demonstrated a rectilinear response through the origin (Figure 4), which

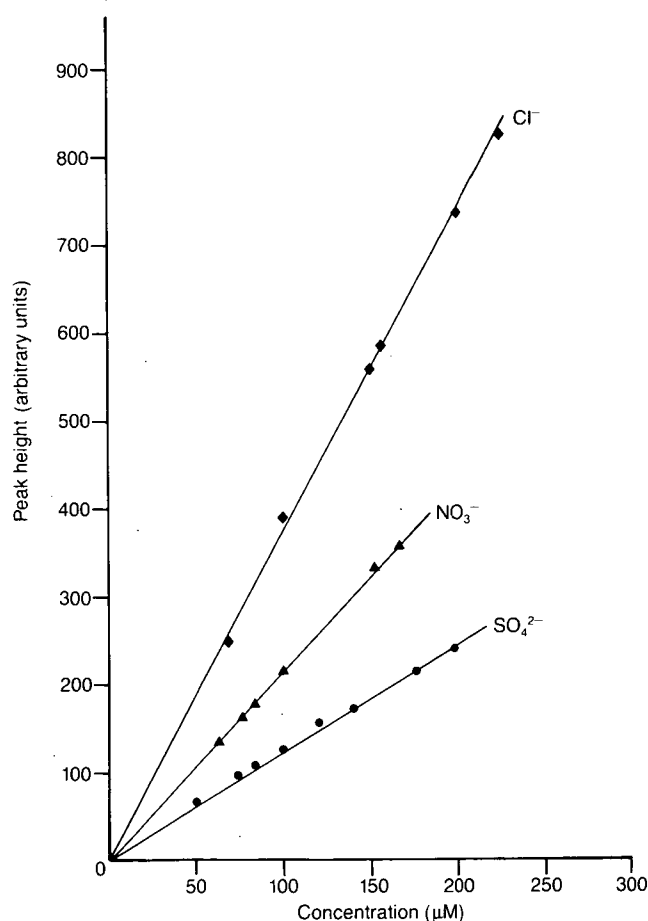


Figure 4. Calibration of anion analyser using a range of standard solutions. Conditions as for Figure 3

permits the routine use of a single-point standard. Most samples are analysed in duplicate, with agreement usually to within 2%. The limits of detection vary, and are best for chloride ( $<1 \times 10^{-6} \text{ M}$ ) and worst for sulphate ( $1-2 \times 10^{-6} \text{ M}$ ), but are adequate for rainwater samples, where systematic errors introduced in the process of sampling may be up to 30% (Fowler & Cape 1984).

### 5 Analysis of cations

With the exception of hydrogen ions, the most important cations in rainwater analysis are sodium, potassium, ammonium, calcium and magnesium. Although potassium concentrations are usually rather small, they are a good indicator of contamination of a sample from bird droppings, etc. Large concentrations of ammonium and high pH are not sufficient in themselves to designate a sample as 'contaminated', as they could arise from dissolution of atmospheric ammonia (Cape *et al.* 1984). As yet, no simple and reliable method is available for simultaneous analysis of monovalent and divalent cations by non-suppressed ion chromatography, so samples must be analysed using 2 different eluants.

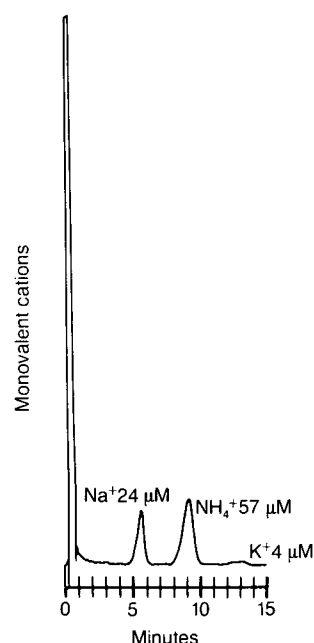


Figure 5. Monovalent cation analysis of rainwater sample from Castlelaw, Midlothian (24–27 March 1985). Flow rate:  $1.7 \text{ ml min}^{-1}$ ,  $200 \mu\text{l}$  injection; eluant: nitric acid at pH 2.50 in 1% methanol; column: Wescan cation  $25 \text{ cm} \times 4 \text{ mm}$

Monovalent cations are separated (with a suitable low-capacity cation exchange column) using an eluant containing high-purity nitric acid at pH 2.50 in 1% methanol at a flow rate of  $1.7 \text{ ml min}^{-1}$ . An analysis takes less than 15 minutes, but the length of the column (25 cm) and consequent pressure drop precludes larger flow rates. Again, a balance must be found between speed of analysis (larger

eluant concentrations) and sensitivity (smaller eluant concentrations). A typical analysis is shown in Figure 5 for a rain sample. The calibrations are again linear, permitting the routine use of a single standard (usually  $200 \times 10^{-6}$  M  $\text{Na}^+$ ,  $100 \times 10^{-6}$  M  $\text{NH}_4^+$ ,  $50 \times 10^{-6}$  M  $\text{K}^+$ ). However, peak areas must be used, as divalent cations accumulate on the column and retention times decrease systematically as ion exchange sites are filled, giving rise to higher peaks and shorter retention times. The original column performance can be restored using a 'sample' of 1% nitric acid injected routinely every 6 samples prior to the calibration standard. Sensitivity is better than  $1 \times 10^{-6}$  M for sodium and  $1-2 \times 10^{-6}$  M for potassium, with reproducibility similar to the anion analysis.

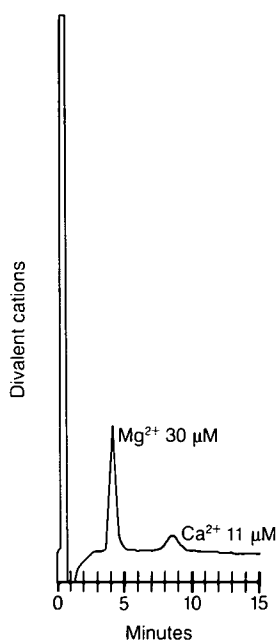


Figure 6. Divalent cation analysis of rainwater sample from Achnagoichan, Speyside (January 1983). Flow rate:  $1.5 \text{ ml min}^{-1}$ ,  $200 \mu\text{l}$  injection; eluant:  $0.84 \times 10^{-3}$  M ethylenediamine at pH 6.0 adjusted with conc. nitric acid in 1% methanol; column: Wescan cation  $25 \text{ cm} \times 4 \text{ mm}$

Divalent cations are separated on the same column but using an eluant comprising  $56 \mu\text{l}$  ethylenediamine per litre of 1% methanol, adjusted to pH 6.0 with concentrated nitric acid ( $0.84 \times 10^{-3}$  M in ethylenediamine). A typical analysis (Figure 6) takes 10 minutes at a flow rate of  $1.5 \text{ ml min}^{-1}$ . Calibrations using peak heights or areas are linear, and standard solutions (usually  $50 \times 10^{-6}$  M  $\text{Ca}^{2+}$ ,  $50 \times 10^{-6}$  M  $\text{Mg}^{2+}$ ) are used to recalibrate automatically every 6 samples. Detection limits are not quite as good as for the other analyses, being around  $2 \times 10^{-6}$  M under optimum conditions.

## 6 Discussion

The main advantage of any form of ion

chromatography over other methods (eg colorimetry, ion-selective electrodes) is that all anions or cations present in a sample are analysed simultaneously. This means that interferences from components which are not expected can be identified, where separate analysis for individual ions would perhaps not show the presence of a 'contaminating' ion. This advantage is best illustrated by means of an example: a monthly bulk rainwater sample (from Waterhead, SW Scotland, July 1984) had been contaminated by (presumably) bird droppings, given the large  $\text{NH}_4^+$  and  $\text{K}^+$  concentrations and high pH. Re-analysis of this sample for anions after one year gave the trace shown in Figure 7, in which the additional peak (cf Figure 3) was identified as nitrite ion. In the previous

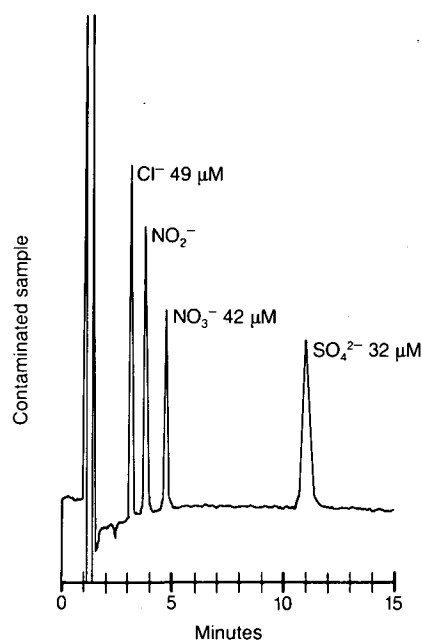


Figure 7. Anion analysis of contaminated rainwater sample after one year's storage, showing the presence of nitrite in solution. Conditions as for Figure 3

colorimetric technique, it would have appeared as nitrate, as the method did not distinguish between nitrite and nitrate. In practice, this is not usually a problem in rainwater analysis as nitrite ions are rarely, if ever, present. It appears, in this case, that the nitrite ions were produced by oxidation of ammonium ions in the sample over the year, even though the sample was kept at  $4^\circ\text{C}$  in an unlit coldroom. However, the sample was grossly contaminated, and there has been no evidence of similar oxidation in uncontaminated samples with a lower pH.

A secondary, but very important, advantage of ion chromatography is its ease of automation, and non-suppressed ion chromatography has the added advantage that there is no need to regenerate a suppressor column (although in

practice this problem is not insuperable). The system used at ITE Edinburgh routinely runs 24 hours per day for 5 days a week. Samples are analysed in batches for anions, monovalent cations and divalent cations over a period of about one month using a single analyser. In this way, about 100 samples per month can be analysed in duplicate for 9 ions (including  $H^+$  from pH) by one technician. This figure allows for re-analysis using appropriate standards and/or sample injection loops where one ion (eg  $Cl^-$ ) may be present in very large concentrations.

Planned improvements to the present system include active control of the column and detector temperatures, which is expected to reduce baseline noise and drift and to improve sensitivity and reproducibility. There has been an occasional problem when the system has been left running unattended overnight in an unheated laboratory.

### 7 Summary

The technique of ion chromatography may be employed using conventional HPLC hardware and low-capacity ion exchange columns. For conductivity detection, eluants must have conductivities very different (greater or smaller) than the ions to be measured. Modern detectors have the capacity to suppress the background conductivity electronically, in a manner similar to the chemical background suppression used in 'suppressed' ion chromatography (eg Dionex).

The routine use of non-suppressed ion chromatography for the analysis of rainwater and cloudwater, both for anions and cations, is described. Care must be taken in sample preparation to remove particles in order to prolong column life, but this is not usually a problem for this type of sample. The major anions of interest ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) are separated using a  $2 \times 10^{-3}$  M solution of phthalic acid in 1% methanol, adjusted to pH 4.74 with NaOH. The monovalent cations ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ) are separated using pH 2.5 nitric acid, while divalent cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ) are separated using  $0.84 \times 10^{-3}$  M ethylenediamine solution adjusted to pH 6.0 with  $HNO_3$ . Each analysis takes about 15 minutes.

Peak heights (recorded on a dedicated integrator) are linearly related to concentration over at least 3 orders of magnitude. Using a 200  $\mu$ l injection loop, sensitivity is better than  $2 \times 10^{-6}$  M and reproducibility is usually within 1% for multiple analyses.

An autosampler, autoinjector and integrator allow for continuous operation, with up to 40 duplicate analyses per day. There is no suppressor column to be regenerated, but for rain samples column 'clean-up' is required daily for about 30 minutes.

### 8 References

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