

Automation of sample dilution and injection for the determination of anions by ion chromatography

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Abstract

An automated system is described for sample dilution and subsequent injection into an ion chromatograph for the determination of anions in process solution. The system is controlled by FlowTEK, a program developed at Mintek. Anions such as chloride, nitrate, and sulphate have been successfully diluted with a dialysis unit and determined by ion chromatography using this program. The concentration ranges of anions that can be diluted and determined are 10 to 2 000 mg/l for chloride, and 40 to 10 000 mg/l for both nitrate and sulphate.

Introduction

Automation, as defined by the International Union for Pure and Applied Chemistry (IUPAC), refers to "the use of combinations of mechanical and instrumental devices to replace, refine, extend or supplement human effort and facilities in the performance of a given process, in which at least one major operation is controlled without human intervention, by a feedback mechanism" (Stockwell, 1990). Although there are a number of factors that stimulate the need for automation in a chemical laboratory, a major motivation is one of cost-effectiveness. In clinical laboratories, automated analysers have been used with considerable success. Industrial laboratories are devoting much attention to automation at present. Automated methods of analysis, using flow-injection analysis (FIA) techniques for the determination of ions, have become established, and automated analysers, either commercial or constructed in-house, have become features in many analytical laboratories. However, generally only individual ions can be determined at one time.

Since its inception in 1975, ion chromatography (IC) (Small et al., 1975) has become a powerful tool for the simultaneous analysis of many different ions in one chromatographic run. Although the dilution of sample solutions containing macroamounts of anions such as chloride, nitrate, and sulphate is a time-consuming task, automatic dilution in IC has received little attention. The problem associated with this type of analysis is the need to automatically dilute macroamounts of anions to within the range required for the IC determination. Dialysis (Barnes, 1994; Hansen and Ruzicka, 1976; Martins et al., 1985; and Van Staden, 1986) has been used for the removal of interferents based on the selective permeation of solutes through a membrane i.e. as a separation method. The technique is also ideally suited to the dilution of either anions or cations (Hansen and Ruzicka, 1976; Martins et al., 1985; Van Staden, 1986). In principle, dialysis is a process that separates different solutes by means of their unequal transport rates through membranes. The driving force for dialysis is the concentration

gradient across the membrane. The use of suitable membranes in continuous flow systems has made it possible to selectively and reproducibly transfer the analyte from a relatively unknown sample stream into a carrier or collector stream of known composition. The reproducibility of sample transfer, provided all other parameters remain constant, can be utilised for the dilution of the samples (Martins et al., 1985; Van Staden, 1986).

FlowTEK (Marshall and Van Staden, 1992) software for analyser control developed at Mintek, is a program that is able to provide a flow-based analyser with microprocessor control and data acquisition capabilities. The program has numerous user-defined set-up options, and is relatively easy to use to improve data quality in automated systems.

In this investigation, a method for the automatic IC determination of chloride, nitrate, and sulphate, using the FlowTEK program, was developed. When dilution of macroamounts of anions was required, the use of a dialysis unit for sample dilution was investigated because of the ease of use, and the reproducibility and speed of solute transport. In addition, the feasibility of placing the dialysis unit ahead of the IC system was assessed in an attempt to avoid peak-broadening and consequently longer elution times. The removal of interferents prior to automatic injection was also considered.

Experimental

Apparatus

A schematic of the automated system is shown in Fig. 1. A Dionex Model 2000i ion chromatograph equipped with an air-actuated 8-port injection valve with 2 sample loops (7 and 50 μ l), a low-capacity ion exchanger (AS4 separator column), and a Dionex micromembrane suppressor was used for the chromatographic determinations of the anions. A sample changer, equipped with 50 sample containers of 5 ml capacity, was connected to a Gilson Minipuls 2HP8 pump with Teflon tubing of 0.5 mm inner dia. When dilution was required, a dialysis unit containing a Technikon Autoanalyser Type C membrane was placed between the sample changer and the injection port of the IC system. The unit was constructed from 2 perspex blocks as described elsewhere (Barnes and Jones, 1989). An Epson PC, with the FlowTEK program installed and a colour monitor, was used to monitor the sequence of events.

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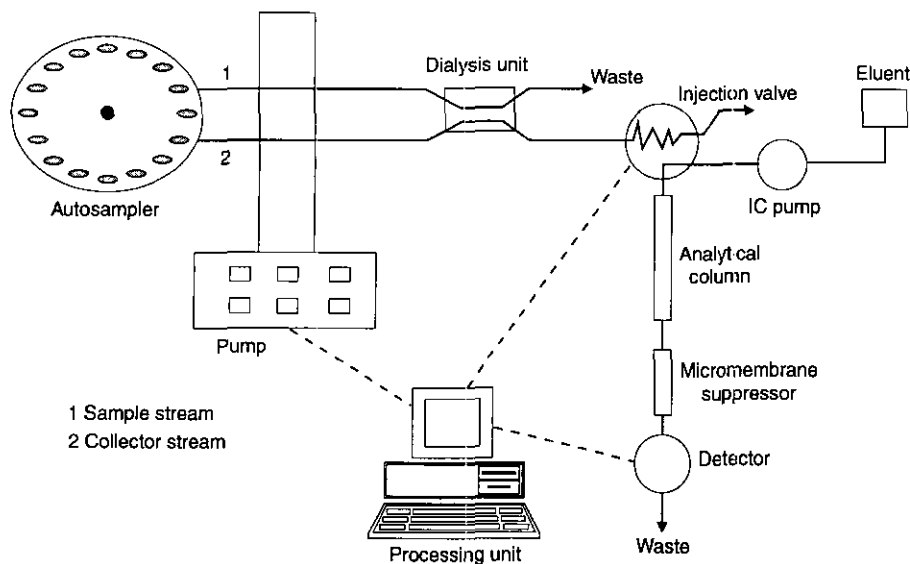


Figure 1
Schematic of an
automated IC system

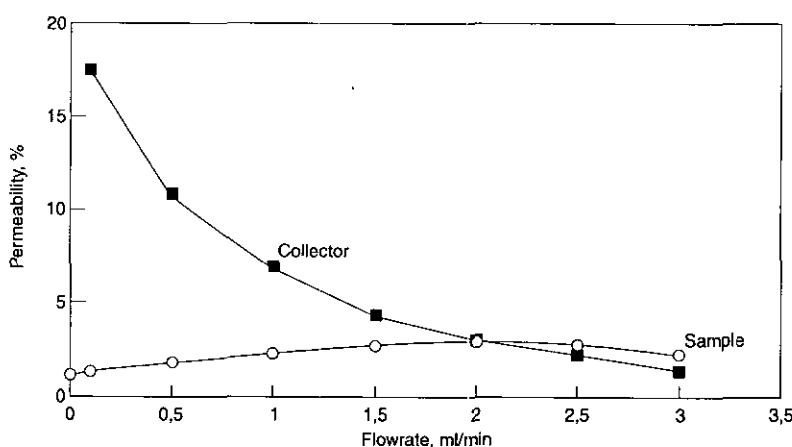


Figure 2
The effect of flow rate on permeation

Reagents

Individual stock solutions containing 10 g/l of chloride, nitrate, and sulphate were prepared by dissolution of their respective sodium salts (Merck AR) in water. Calibration solutions of the anions in the range 2 to 10 mg/l for chloride and 10 to 40 mg/l for nitrate and sulphate were prepared by suitable dilution of the stock solutions. For calibration curves for concentrated anion solutions that would require dilution by dialysis prior to IC measurement, working standard solutions were prepared in the ranges 10 to 2 000 mg/l for chloride and 50 to 10 000 mg/l for nitrate and sulphate. The eluent was a carbonate-bicarbonate solution (244 mg/l and 235.2 mg/l respectively), and 1.226 g/l sulphuric acid was used as the regenerant solution. Distilled water was used as the collector stream in the dialysis unit throughout the investigation.

Automated sample introduction

Each of the sample containers was filled with about 5 ml of the sample and placed in the sample changer. The IC system was set to the parameters given in Table 1 and allowed to run until a stable baseline was obtained. The sample and collector flow rates were maintained at 1.5 ml/min. Samples and standards should be of the same concentration range and were treated in the same way. The FlowTEK program was started to control the following events. The

sample arm of the sample changer placed the sampling tube into a sample cup, where it remained for 1 min to load the sample via the dialysis unit into the injection valve of the IC system. This time was shown to be sufficient for washing the sample line and the sample loop to remove any contamination from the previous sample, and filling the sample loop with another sample. After loading of the injection loop, the sample was injected, and the sample arm remained at the bottom of the sample cup for a set period of time, which was determined by the retention time of the last component to be eluted. The sampling tube was then transferred to the next sample cup, a process that was completed in 6 s, and the sequence of events repeated for the following sample solution.

Results and discussion

In order to achieve dilution using FIA systems, earlier investigators (Martins et al., 1985, Van Staden, 1986) placed the dialysis unit after the point of introduction of the sample plug. In FIA, this type of sample dilution resulted in a large dispersion of the sample plug in the collector stream, and broad peaks with low sensitivity were recorded. Similar disadvantages were expected in an IC system. This could result in band-broadening, and therefore in a loss of resolution and an increase in the time of the analysis. It was therefore decided to place the dialysis unit ahead of the IC injection point, and to use it to dilute macroamounts of the anions prior to IC analysis. As the membrane is capable of withstanding the often difficult conditions expected when dealing with real samples i.e. very acid or alkaline solutions, placing it directly into the sample stream did not pose a problem. It has been shown previously that the parallel channels in the dialysis unit allowed different configurations of the flow paths of both the sample and the collector streams to obtain the dilution required for a particular analysis (Barnes and Jones, 1989).

To determine the effect of flow rate, the flow rate of a sulphate sample was varied from 1 to 3 ml/min, while the flow rate of the collector stream was kept constant (1 ml/min). Next, the collector stream flow rate was varied between 0.5 and 3 ml/min while the flow rate of the sample stream was kept constant (1 ml/min). In each case, the permeation of the sulphate anion was measured. The results are shown in Fig. 2. Variation of the flow rates of the sample and collector streams had a marked but opposing effect on

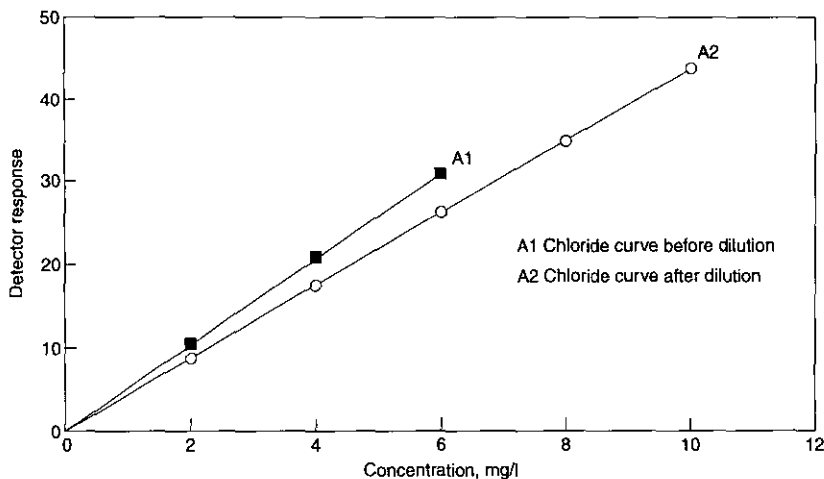


Figure 3
The effect of dilution on chloride curves

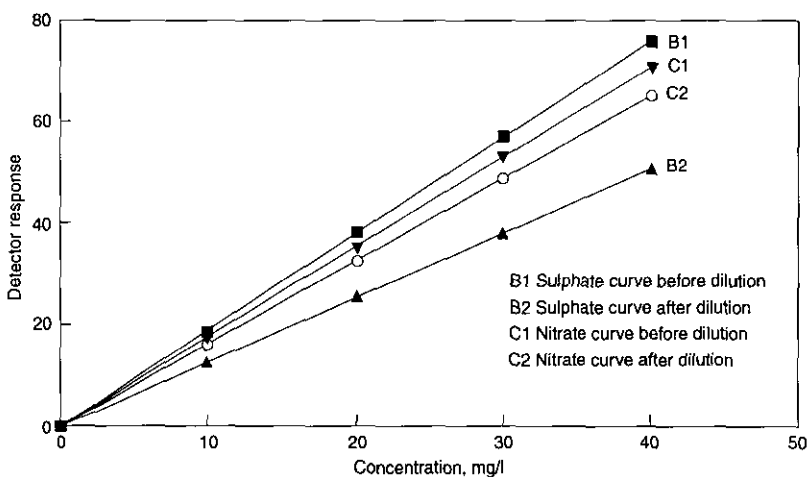


Figure 4
The effect of dilution on nitrate and sulphate

TABLE 1 INSTRUMENTAL SETTINGS	
Parameter	Value
Sample flow rate	1.5 ml/min
Collector flow rate	1.5 ml/min
Eluant flow rate	1.0 ml/min
Detector output range	100 μ S
Recorder range	1 V
Sample volume	50 μ l

permeation. Increasing the sample flow rate gradually increased the permeation of the sulphate through the membrane, resulting in a decrease in dilution. The flow rate of the collector stream had a strong influence on the amount of solute that diffused through the membrane, and an increase in the flow rate of the collector stream

was accompanied by an increase in dilution (Fig. 2). The rate of permeation remained the same. However, the fast collector stream flow rate means that an increased volume collects the solute, and therefore the achievable dilution is increased. Percentage permeation is defined as the concentration of the collector stream divided by the concentration of the donor stream times one hundred. When the logarithm of the percentage permeation vs. the flow rate of the collector was plotted, a near straight-line graph was obtained. From the results it is apparent that, depending on the dilution required for a particular sample, the flow rates of the 2 streams can be adjusted to obtain either a larger or a smaller dilution. In the present investigation it was decided that, for the sake of system simplicity, a compromise flow rate of 1.5 ml/min for both the sample and the collector streams would be used.

The automated system, with and without dilution by dialysis and with the instrumental settings given in Table 1, was used to obtain calibration curves for chloride, nitrate, and sulphate in the ranges 2 to 10 mg/l and 50 to 300 mg/l for chloride, and 10 to 40 mg/l and 500 to 2000 mg/l for nitrate and sulphate using a 50 μ l sample loop. As expected, straight-line calibration curves were obtained. The calibration curves for chloride, nitrate, and sulphate are compared to those obtained for concentrated solutions after dilution as shown in Figs. 3 and 4. In all 3 cases, the slopes of calibration curves obtained from standards that were not diluted with the dialysis unit were higher than calibration curves obtained from standards that were diluted using the dialysis unit. However, good calibration curves were obtained after dilution and these curves could be used for the determination of anions after automated sample dilution.

Another means of desensitising IC is to adjust the injected sample volume. This approach can be coupled with dialysis to achieve a larger working range. The results in Table 2 show the working range that can be obtained when different injection volumes are used. When dialysis is coupled with the practice of varying the injection volume, a wide range of samples can be determined. For example, sulphate can be determined up to 40 mg/l in the absence of the dilution apparatus, whereas with dilution, using an appropriate flow rate for both the sample and the collector streams and a sample volume of 7 μ l, the range of determination is extended to 10 000 mg/l.

To bridge the range of dilution between that obtained using the instrumental settings given in Table 1 and the undiluted standard range, the conductivity detector output was lowered from 100 μ S to 30 μ S and 10 μ S (Table 3). From the precision and accuracy comparisons at these different settings, dilution by dialysis can be carried out with a reasonable degree of confidence.

A further benefit from the use of the dialysis unit is that any precipitates, and gases that may be present in a process solution being analysed for anions, do not permeate through the Technicon Autoanalyser Type C membrane, and are therefore prevented from interfering in the chromatographic determination. Only anions that permeate the membrane and which elute at the same time as, or very

TABLE 2 EFFECT OF SAMPLE SIZE ON THE DILUTION RANGE				
Sample size	Range investigated mg/l		Range found mg/l	
	50 μ l	7 μ l	50 μ l	7 μ l
Cl ⁻	0-300	0-2 000	50-300	100-2 000
NO ₃ ⁻	0-2 000	0-15 000	500-2 000	1 000-10 000
SO ₄ ²⁻	0-2 000	0-15 000	500-2 000	1 000-10 000

TABLE 3 PRECISION AS EXPRESSED IN RELATIVE STANDARD DEVIATION (S _r)									
Detector output μ S	Cl ⁻			NO ₃ ⁻			SO ₄ ²⁻		
	Amount mg/l	S _r		Amount mg/l	S _r		Amount mg/l	S _r	
		50 μ l	7 μ l		50 μ l	7 μ l		50 μ l	7 μ l
100	100	0.018		1 000	0.002		1 000	0.001	
	200		0.011	2 000		0.001	2 000		0.002
30	30	0.019		300	0.002		300	0.070	
	180		0.018	1 800		0.006	1 800		0.011
10	10	0.021		300	0.227		300	0.519	
	60		0.042	1800		0.370	1 800		0.182

TABLE 4 COMPARISON OF DILUTION METHODS FOR ANIONS					
Cl ⁻ mg/l		NO ₃ ⁻ mg/l		SO ₄ ²⁻ mg/l	
Manual	Dialysis	Manual	Dialysis	Manual	Dialysis
70	68	665	700	790	790
106	105	1 600	1 630	1 700	1 690
222.5	220	2 630	2 710	2 650	2 700
480	475	3 520	3 850	3 680	3 725
635	640	4 600	4 500	4 300	4 380
840	830	5 800	5 850	6 000	6 090
1 100	1 130	6 800	6 850	6 925	7 000
1 400	1 450	7 625	8 000	7 840	7 900
1 650	1 630	9 000	9 100	9 500	9 580

close to, chloride, nitrate, and sulphate interfere. The use of more efficient columns for the separation of both the anions of interest and interfering ions can solve this problem.

Samples of process solutions containing low levels of Ca^{2+} , Mg^{2+} , Si^{4+} , As^{3+} , and As^{5+} were analysed for chloride, nitrate, and sulphate. These samples did not require any treatment except dilution where it was necessary, as the cations did not show any kind of interference at the levels present after dilution for the anion analysis. Dilution was carried out both manually and by dialysis. Table 4 shows that there is a good agreement between both methods of dilution, and it can therefore be concluded that dilution by dialysis can be used to obtain accurate and precise results. This method of automatic dilution and sample introduction could be of interest in systems in which the levels of anions require monitoring on a regular basis.

Conclusion

Automated sample introduction of anions such as chloride, nitrate, and sulphate can be achieved using the FlowTEK program, and automatic dilution of macroamounts of the anions can be achieved using a dialysis unit placed before the injection port of the chromatographic system. The amount of dilution can be manipulated by changing the flow rates and flow configurations of the dialysis unit, or by using more than one dialysis unit (Barnes and Jones, 1989). In this investigation 10 to 2 000 mg/l of chloride and 40 to 10 000 mg/l of nitrate and sulphate were diluted so that they fell within the standard calibration curves for chloride (1 to 5 mg/l),

nitrate (10 to 40 mg/l), and sulphate (10 to 40 mg/l). The agreement between dialysis and manual dilution was good. The advantage of this method of dilution is the ease with which it can be incorporated into automated systems. Furthermore it also provides a means of sample clean-up.

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