

**AUTOMATED SIMULTANEOUS ANALYSIS OF  
ANIONS, MONOVALENT AND DIVALENT CATIONS**

by

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## EXECUTIVE SUMMARY

Since its inception in 1975, ion chromatography has quickly become a powerful tool in many areas of analytical chemistry. Of particular interest to an analytical service laboratory is the automated simultaneous analysis of the three groups of major ions, namely anions (such as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ), monovalent cations ( $\text{Na}^+$  and  $\text{K}^+$ ), and divalent cations ( $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ). For the first time, such an analysis is described in this paper. It has been shown that this approach is suitable for routine use and is more cost effective than the conventional methods, in which each of the ions has to be analysed separately using atomic absorption spectrometry, flame photometry and colorimetry.

## ABSTRACT

This paper describes for the first time an automated simultaneous analysis of the three groups of major ions, namely anions (such as  $\text{SO}_4^{=}$ ,  $\text{Cl}^{-}$ ), monovalent cations ( $\text{Na}^{+}$ ,  $\text{K}^{+}$ ) and divalent cations ( $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ). It was shown that this approach is suitable for routine use and is more cost effective than the conventional methods, in which each of these ions has to be analysed separately, using atomic absorption, flame photometry and colorimetry.

## SOMMAIRE ADMINISTRATIF

Depuis qu'on a commencé à l'utiliser en 1975, la chromatographie ionique a fait ses preuves dans de nombreux domaines de la chimie analytique. Ainsi, les laboratoires analytiques peuvent être particulièrement intéressés par la technique d'analyse simultanée automatisée des trois principaux groupes d'ions, soit les anions ( $\text{SO}_4^{=}$ ,  $\text{Cl}^-$ ), les cations monovalents ( $\text{Na}^+$  et  $\text{K}^+$ ) et les cations bivalents ( $\text{Mg}^{++}$  et  $\text{Ca}^{++}$ ). Dans cette communication, on décrit pour la première fois cette nouvelle technique d'analyse. On a démontré qu'elle peut être employée de façon régulière et à coût moindre que les techniques classiques nécessitant l'analyse individuelle de chaque ion au moyen de la spectrométrie d'absorption atomique, de la photométrie de flamme et de la colorimétrie.

## SOMMAIRE

Dans cette communication, on décrit pour la première fois une technique d'analyse simultanée automatisée de trois principaux groupes d'ions notamment les anions ( $\text{SO}_4^{=}$ ,  $\text{Cl}^-$ ), les cations monovalents ( $\text{Na}^+$ ,  $\text{K}^+$ ) et les cations bivalents ( $\text{Mg}^{++}$  et  $\text{Ca}^{++}$ ). On a pu démontrer que cette technique peut être employée régulièrement et qu'elle est plus économique que les méthodes classiques s'appuyant sur l'analyse individuelle de chaque ion au moyen de la spectrométrie d'absorption atomique, de la photométrie de flamme et de la colorimétrie.

Analyse simultanée automatisée d'anions et de cations monovalents et bivalents.

## INTRODUCTION

Since its inception in 1975<sup>1</sup>, ion chromatography (IC) has quickly become a powerful tool for the analyses of many different chemical parameters such as anions, cations, amino acids, organic acids, alcohols, speciation of metals and inorganic acids, and trace metals<sup>2-6</sup>. Of particular interest to an environmental analytical service laboratory is the simultaneous analysis of the three groups of major ions (anions, monovalent cations and divalent cations) because this approach is potentially more cost effective than the existing methods, where the ions have to be analysed separately and with different methods.

Several authors have attempted the simultaneous analysis of the major ions. Tejada et al.<sup>7</sup> in 1978 devised an ion chromatographic system, which allowed them to analyze for either  $\text{SO}_4^{=}$  or  $\text{NH}_4^+$  by simply flipping a switch. Barkley et al.<sup>8</sup> in 1979 used a dual channel system with one detector to analyse some monovalent cations and anions; however, they had to switch the detector, within the same run, from cationic analysis to anionic analysis, and in the process lessened the ability to analyse for  $\text{Cl}^-$  ion. Using ethylenediaminetetraacetic acid as eluent, Yamamoto et al.<sup>9</sup> were able to analyse simultaneously the anions and divalent cations (as anionic complexes). Jones et al.<sup>10,11</sup> successfully determined anions and monovalent cations using two possible eluents, as well as anions and

divalent cations using a more acidic eluent; however, possible problems of  $\text{Cl}^-$  peak broadening and precipitation of  $\text{Li}_3\text{PO}_4$  and  $\text{PbSO}_4$  could occur. This would be undesirable in routine use. Iskandarani and Miller<sup>12</sup>, using an indirect photometric chromatography (IPC) and a dual wavelength UV detector, was able to analyse both anions and monovalent cations simultaneously. (IPC uses a light-absorbing eluent and a photometer to detect "transparent" ionic species<sup>13</sup>). However, none of the above approaches can analyse simultaneously all three groups of ions.

This paper describes the simultaneous analysis of the three groups of ions and the automation of the analysis via a single sample loading system. The method is simple to operate, cost effective, and is suitable for routine use in an established or newly formed service laboratory.

## EXPERIMENTAL

Milli-Q water (18 megohm) was used. All chemicals used were of reagent grade:  $\text{NaNO}_2$ ,  $\text{NaNO}_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{KBr}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaF}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{LiCl}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{HCl}$ ,  $\text{CuCl}_2$ , diaminopropionic acid.HCl(DAP), L-histidine.HCl.H<sub>2</sub>O,  $\text{Na}_2\text{EDTA}$ , LiHphthalate, Li acetate, m-phenylenediamine.2HCl,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{NaCO}_3$  and  $\text{NaHCO}_3$ .

For each salt, a stock of 1000 ppm anion (or cation) was prepared. Several standards were then made containing the analytes of interest ranging from very low to high levels, which were readily available for analysing a wide range of samples. Calibration curves were not necessary as one-point calibrations by peak height were found to be adequate for most analyses in each class of waters (soft waters, hard waters, ...).

A dual channel ion chromatograph, Dionex 2020, was replumbed so that it could be used as a single sample loading system. The waste line of the first loading valve (channel 1) was connected to the second loading valve (channel 2) with the smallest possible dead volume between the two valves. The first loading valve was then connected to a Milton Roy loading pump (NSI-33R) and a Technicon autosampler IV (Fig. 1). With this configuration the dual channel system could be simultaneously loaded and manually injected. With a programmable controller (Auto ion 100, Dionex Corporation), the complete system was automated to operate unattended for a day or longer. The anions were detected by a conductivity detector and recorded by a recorder/integrator (HP3390). The cations were likewise detected and recorded. The operating conditions are presented in Table 1 and Figure 1. The instructions on using Dionex instruments and columns were followed.

Barium hydroxide had to be very carefully prepared and kept under  $N_2$  atmosphere at all times to avoid precipitation of  $BaCO_3$  and subsequent malfunction of the suppressor. The 18 megohm water



(usually 8 litres) was first purged for one hour with high purity  $N_2$  gas introduced from the container spigot. Then the hydroxide (usually 152 g) was added, and the container shaken under  $N_2$  atmosphere until complete dissolution.

## RESULTS AND DISCUSSION

### a. Choice of eluents

Several potential known eluents were tested on HPIC-AS4 and HPIC-CS3 analytical columns. First, the columns were placed in series (single channel) as done by Jones et al.<sup>10,11</sup> using each of the following eluents -- lithium carbonate/lithium acetate, lithium hydrogen phthalate, and sodium ethylenediaminetetraacetic acid<sup>9</sup>. Under each of these conditions, there were fewer peaks than expected, some peaks were ill-defined, and the background conductivity was quite high, which is undesirable for low level works.

The above eluents and others (including sodium carbonate/sodium bicarbonate, HCl, phenylenediamine/HCl, HCl/DAP/histidine, and  $CuCl_2$ /HCl/DAP/histidine) were then tested on each column separately. It was found that the carbonate/bicarbonate eluent was most compatible with AS4 column for anions, and the HCl/DAP/histidine eluent most compatible with CS3 column for mono- and divalent cations.

b. Control of Regenerant Flow Rates

The gravity feed or pressure feed of regenerants recommended by the manufacturer was not rugged enough to provide a steady and reliable flow rate for each regenerant. This sometimes resulted in baseline shifts. The problem was remedied by connecting each of the two regenerant waste lines to a Technicon proportioning pump. By using Technicon tubing of required volumes, not only were we able to keep the flow steady but were also able to make simple and reliable flow rate changes.

c. Eluent flow rate and guard columns for anions

With repeated analysis of organic-contaminated colored waters<sup>14</sup>, the separator column rapidly became poisoned and the retention times became progressively shorter with use. To circumvent this problem, an extra guard column, MPIC-NGI (used in mobile phase chromatography) was placed before the HPIC-AG4 (guard column) and HPIC-AS4 (separator column) as shown in Table 1 and Figure 1.

The use of an eluent flow rate of 1.0 ml/minute, instead of the usually recommended 2.0 ml/minute, was found to be advantageous. It gave better resolution to the anionic analytes with close retention times but with markedly different concentrations, and it provided an optimum working pressure range of 700-800 PSI. Furthermore, the analysis time of 13 minutes for anions (Table 1) was well within the 20 minutes required by an EPA ion chromatographic method<sup>15</sup> for the analysis of the same six anions listed in Table 1.

d. Mono- and divalent cations analysis

The cation system uses two gradient eluents -- a weak one for monovalent cations and a strong one for divalent cations (Table 1). The optimum flow rate was 1.1 mL/minute. A run consists of a weak eluent phase, a strong eluent phase, and a weak eluent phase. It begins with the weak eluent at time 0.0 minute (injection) to 3.2 minute, changes to the strong eluent from 3.2 to 11.0 minute, and returns to weak eluent from 11.0 to 14.0 minute, when an analysis ends (Fig. 2); the run continues with weak eluent from 14.0 to 18.4 minute to reestablish the baseline for a new run. The bottom part of Fig. 2 depicts a chromatogram of such an analysis of a standard. The top part is the anion chromatogram simultaneously obtained from the same standard.

For low level divalents, an analysis is hindered by two problems -- significant baseline shift during the transition from weak to strong eluent; and background divalents being retained (during the two weak eluent phases) and later eluted with the analyte divalents by the strong eluent. To help smooth out the baseline, it was necessary to change the flow rate from 1.1 to 1.2 mL/min at time interval 7.6-10.5 minute. (This flow rate change also works well at higher level divalents). To eliminate the background divalents from the weak eluent, only the strong eluent should be used. This way, the cation system operates as a "divalent system" for divalents only.

If only monovalents are desired, the cation system can also operate as a "monovalent system", using the weak eluent only.

However, some care should be exercised. The strong eluent should be used occasionally to flush out the retained divalents, thus avoiding column overload and subsequent interference.

e. Recovery data and detection limit

The waters we studied covered a hardness range of 0.3-200 ppm  $\text{CaCO}_3$  and, according to Thomas<sup>16</sup>, ranged from very soft to very hard waters. Thomas classified waters as follows:

<u>Hardness</u> <u>ppm <math>\text{CaCO}_3</math></u>	<u>Water Type</u>
1 - 60	soft
61 - 120	medium hard
121 - 180	hard
>180	very hard

The recovery data agree with the certified values and interlaboratory medians, and range from 98 to 102% for all the water types studied: a very soft water Standard Reference Material<sup>17</sup> (Table 2), a very soft quality control sample<sup>18</sup> and a soft water (Table 3), a soft and a medium hard water (Table 4), and a medium hard and a very hard water (Table 5). The analytical results were also precise as evidenced by the small standard deviations, s.d., of three replicate analyses. Much harder waters or salt waters were not

studied, but with proper dilution are likely analyzable without overloading the analytical columns.

Table 6 compares the detection limits of the eleven ions studied. The results indicate that the present method using a direct injection of just 50  $\mu\text{L}$  has better detection limits than many of those by the conventional methods<sup>19</sup>. With a larger sample loop and/or a concentrator column used in conjunction with each of the analytical columns, further improvement of the detection limits can be achieved.

f. Interference

It is a known fact that organic ions such as acetate, formate, and maleate interfere with  $\text{F}^-$  and  $\text{SO}_4^{=}$  determinations due to their similar elution time. Fortunately, in the rain or other samples we normally analyse, these organics are not present in significant quantity. However, it's been recently reported that in stemflow and throughfall waters, these and other organic ions can be present in sufficient quantity so as to interfere with  $\text{F}^-$  and  $\text{SO}_4^{=}$  determinations, thus producing poor ionic balances<sup>20</sup>. If confronted with such problems, we would use sodium borate and/or sodium carbonate plus sodium hydroxide as eluent to separate and quantitate these ions<sup>21</sup>.

For analysis of low level  $\text{F}^-$ , a known amount of eluent concentrate must be added to the sample, specifically 100  $\mu\text{L}$  to 10 mL of sample, in order to eliminate the "water dip interference". But this addition of concentrate of  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  alters the original  $\text{Na}^+$

concentration. Fortunately,  $\text{Na}^+$  can be determined relatively fast by using the monovalent system (weak eluent only).

The concentration interference occurs when two analytes of close retention time have markedly different concentration levels. Sodium and ammonium are a good example as  $\text{Na}^+$  in water samples is often much more concentrated than  $\text{NH}_4^+$ . Thus, the  $\text{NH}_4^+$  peak becomes a  $\text{Na}^+$  peak shoulder, which is difficult to quantitate. This type of interference, however, is often solved by diluting the eluent and/or decreasing the eluent flow rate coupled with diluting the sample itself.

Strontium could interfere with the determination of monovalents if a new injection is made too soon after the  $\text{Ca}^{++}$  peak. However, in routine analysis a new injection is made only after 18.4 minute time when  $\text{Sr}^{++}$  has already eluted and the monovalents' baseline has reestablished itself. Furthermore,  $\text{Sr}^{++}$  is not very sensitive and its concentration in natural waters is usually very small compared to those of the common major cations.

g. Advantages and disadvantages

The primary advantage of the proposed method is the simultaneous analysis of the three groups of major ions. The method is also versatile in that it can operate as an independent anion system, cation system, monovalent system using the weak eluent only, divalent system using the strong eluent only, or a joint system with any combination the analyst desires.

The major disadvantage is the relatively long time taken for routine determinations of cations, which lengthens the whole analysis time. If one is interested in only one ion or two similar ions (such as  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ), it would be faster to use the relevant conventional method.

### **COST EFFECTIVENESS**

#### **a. Initial capital expenses**

To analyse routinely the 12 ions (Table 1), using conventional methodologies, an established analytical service laboratory usually requires a total capital expenditure of around \$108,000 to acquire an automated flame photometry for  $\text{Na}^+$  and  $\text{K}^+$  analysis; an atomic absorption spectrophotometer for  $\text{Li}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ; an automated colorimetry system for  $\text{F}^-$ ,  $\text{SO}_4^{=}$  and  $\text{Cl}^-$ ; and an additional automated colorimetry system for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{HPO}_4^{=}$ . On the other hand, the system we are using costs only about 57% of the cost of the conventional systems.

#### **b. Analysis time**

According to the Directory of Services<sup>22</sup>, the time required for a test for each of the cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ) is 0.03

hour/test. (A test is defined as an analysis of a constituent in a standard, a quality control sample or an actual sample). The other times/test are 0.04 hr for  $\text{SO}_4=$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ; 0.05 hr for  $\text{F}^-$ ; 0.02 hr for  $\text{Li}^+$ ; and 0.06 hr for  $\text{HPO}_4=$ . Thus the total time required for 1000 tests of the 12 ions (i.e. 100 tests/ion) will be 45 hours by the conventional methods. Using the proposed method, even if we give 25 minutes/run of twelve tests to cover instrument warm up and data handling, it will take 41 hours to finish the equivalent 1000 tests. Thus the analysis time is about the same for both the IC and the conventional methods. However, the IC method requires one analyst only to do the above tests, whereas the conventional methods in an operational service laboratory utilize three analysts -- one for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ; one for  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4=$ ; and one for the nutrients  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and  $\text{HPO}_4=$ .

### CONCLUSION

In conclusion, the proposed IC method is cost effective and is suitable for routine use. Furthermore, due to the great versatility of IC, as indicated in the introduction, its excellent sensitivity and its ease of operation, the system should be a definite asset for any operational service laboratory.



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**TABLE 1 Operating conditions**

Loading System	Eluent	Flow Rate ml/min	Guard Columns	Separator Columns	Suppressor	Regenerant	Analytes	Analysis Time minutes
Single Sample	1.8 mM Na <sub>2</sub> CO <sub>3</sub>	1.0	MPIC-NG1 (4x50 mm)	HPIC-AS4 (4x250 mm)	Anion Fibre Suppressor	0.025 N H <sub>2</sub> SO <sub>4</sub> 2 mL/min	F <sup>-</sup> , Cl <sup>-</sup> , HPO <sub>4</sub> <sup>=</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>=</sup>	13
	2.2 mM NaHCO <sub>3</sub>		HPIC-AG4 (4x50 mm)					
Single Sample	weak and strong eluents*	1.1 and 1.2**	HPIC-CG3 (4x50 mm)	HPIC-CS3 (4x250 mm)	Cation Micromembrane Suppressor	60 mM Ba(OH) <sub>2</sub> 7 mL/min	Li <sup>+</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , K <sup>+</sup> , Mg <sup>++</sup> , Ca <sup>++</sup>	14

\* Weak eluent = 12 mM HCl + 0.25 mM DAP.HCl+0.25 mM histidine.HCl

(a) For analysis of monovalents = from injection to 3.2 minute time

(b) For reestablishing baseline = from 11.0 minute to 18.4 minute time.

Strong eluent = 48 mM HCl + 4 mM DAP.HCl + 4 mM Histidine.HCl.

For analysis of divalents = from 3.2 minute to 11.0 minute time.

\*\* The change in flow rates helped smooth out the baseline for low level divalents = 1.1 mL/minute throughout a run, except for the time interval 7.6-10.5 minute where 1.2 mL/minute was used.

Note: The exact operating times may slightly vary from one set-up to another.

**TABLE 2. Recovery data for a very soft simulated rainwater = NBS  
Standard Reference Material 2694-II (0.3 ppm hardness)**

Ions	Certified* ppm	Found± S.D. ppm
Na <sup>+</sup>	0.419±.015	0.418±.003
NH <sub>4</sub> <sup>+</sup>	(1.0)	1.025±.006
K <sup>+</sup>	0.106±.008	0.108±.002
Mg <sup>++</sup>	0.051±.003	0.047±.001
Ca <sup>++</sup>	0.049±.011	0.047±.002
F <sup>-</sup>	0.098±.007	0.103±.010
Cl <sup>-</sup>	(1.0)	1.098±.004
NO <sub>3</sub> <sup>-</sup>	7.06±.15	7.11±.14
SO <sub>4</sub> <sup>=</sup>	10.9±.2	10.75±.05

\* Value in ( ) is uncertified.

**TABLE 3. Recovery data for very soft and soft waters: snow melt (0.9 ppm hardness) and spiked snow melt (9 ppm hardness)**

Snowmelt		Ions	Spiked Snowmelt	
Interlaboratory median <sup>18</sup> , ppm	Found $\pm$ S.D. ppm		Total Recovery $\pm$ S.D., ppm	% Recovery
-	-	Li <sup>+</sup>	0.503 $\pm$ .003	101
0.320	0.324 $\pm$ .003	Na <sup>+</sup>	3.729 $\pm$ .018	99
0.100	0.106 $\pm$ .002	NH <sub>4</sub> <sup>+</sup>	1.317 $\pm$ .011	98
0.150	0.156 $\pm$ .003	K <sup>+</sup>	2.074 $\pm$ .009	102
0.050	0.049 $\pm$ .002	Mg <sup>++</sup>	0.558 $\pm$ .005	100
0.280	0.283 $\pm$ .001	Ca <sup>++</sup>	2.774 $\pm$ .038	100
-	-	F <sup>-</sup>	2.257 $\pm$ .009	100
0.472	0.474 $\pm$ .003	Cl <sup>-</sup>	4.880 $\pm$ .032	100
-	-	HPO <sub>4</sub> <sup>=</sup>	1.495 $\pm$ .007	99
0.138	0.138 $\pm$ .005	NO <sub>3</sub> <sup>-</sup>	1.363 $\pm$ .005	99
0.360	0.351 $\pm$ .008	SO <sub>4</sub> <sup>=</sup>	3.801 $\pm$ .011	99

**TABLE 4. Recovery data for soft and medium hard waters: Lake Superior water (44 ppm hardness) and spiked Lake Superior water (84 ppm hardness).**

L.S. Water Found±S.D. ppm	Ions	Spiked L.S. water	
		Total Recovery ±S.D., ppm	% Recovery
-	Li <sup>+</sup>	0.197±.001	100
1.246±.005	Na <sup>+</sup>	3.369±.006	102
-	NH <sub>4</sub> <sup>+</sup>	0.392±.007	98
0.492±.003	K <sup>+</sup>	1.277±.002	99
2.693±.016	Mg <sup>++</sup>	5.225±.077	101
13.067±.076	Ca <sup>++</sup>	25.171±.270	98
0.087±.004	F <sup>-</sup>	0.587±.005	100
1.222±.005	Cl <sup>-</sup>	2.277±.010	101
-	HPO <sub>4</sub> <sup>=</sup>	0.666±.005	98
0.306±.002	NO <sub>3</sub> <sup>-</sup>	0.585±.005	99
3.104±.013	SO <sub>4</sub> <sup>=</sup>	6.209±.096	102

**TABLE 5. Recovery data for medium hard and very hard waters: Fraser River water (111 ppm hardness) and spiked Fraser River water (200 ppm hardness).**

F.R. Water Found±S.D. ppm	Ions	Spiked F.R. water	
		Total Recovery ±S.D., ppm	% Recovery
-	Li <sup>+</sup>	3.040±.020	101
6.823±.142	Na <sup>+</sup>	11.920±.043	99
-	NH <sub>4</sub> <sup>+</sup>	7.543±.022	101
8.371±.175	K <sup>+</sup>	13.922±.028	98
16.921±.282	Mg <sup>++</sup>	30.720±.045	99
16.407±.268	Ca <sup>++</sup>	28.381±.064	99
0.143±.008	F <sup>-</sup>	0.631±.008	99
11.858±.249	Cl <sup>-</sup>	25.494±.049	100
0.192±.002	HPO <sub>4</sub> <sup>=</sup>	6.830±.024	99
2.953±.008	NO <sub>3</sub> <sup>-</sup>	5.411±.005	102
12.014±.246	SO <sub>4</sub> <sup>=</sup>	23.637±.090	101

TABLE 6. Comparison of detection limits, ppm.

Constituents	Conventional Methods <sup>16</sup>	This Work (IC)* better than
F <sup>-</sup>	0.05	0.005**
Cl <sup>-</sup>	0.1	0.005
HPO <sub>4</sub> <sup>=</sup> (P)	0.001	0.05
NO <sub>3</sub> <sup>-</sup> (N)	0.005	0.004
SO <sub>4</sub> <sup>=</sup>	1.0	0.01
Li <sup>+</sup>	0.005	0.005
Na <sup>+</sup>	0.1	0.02
NH <sub>4</sub> <sup>+</sup>	0.001	0.02
K <sup>+</sup>	0.1	0.05
Mg <sup>++</sup>	0.005	0.05
Ca <sup>++</sup>	0.04	0.05

\* Direct injection of 50 µL sample (without concentrator).

\*\* Concentrate eluent is used in sample to eliminate the water dip.



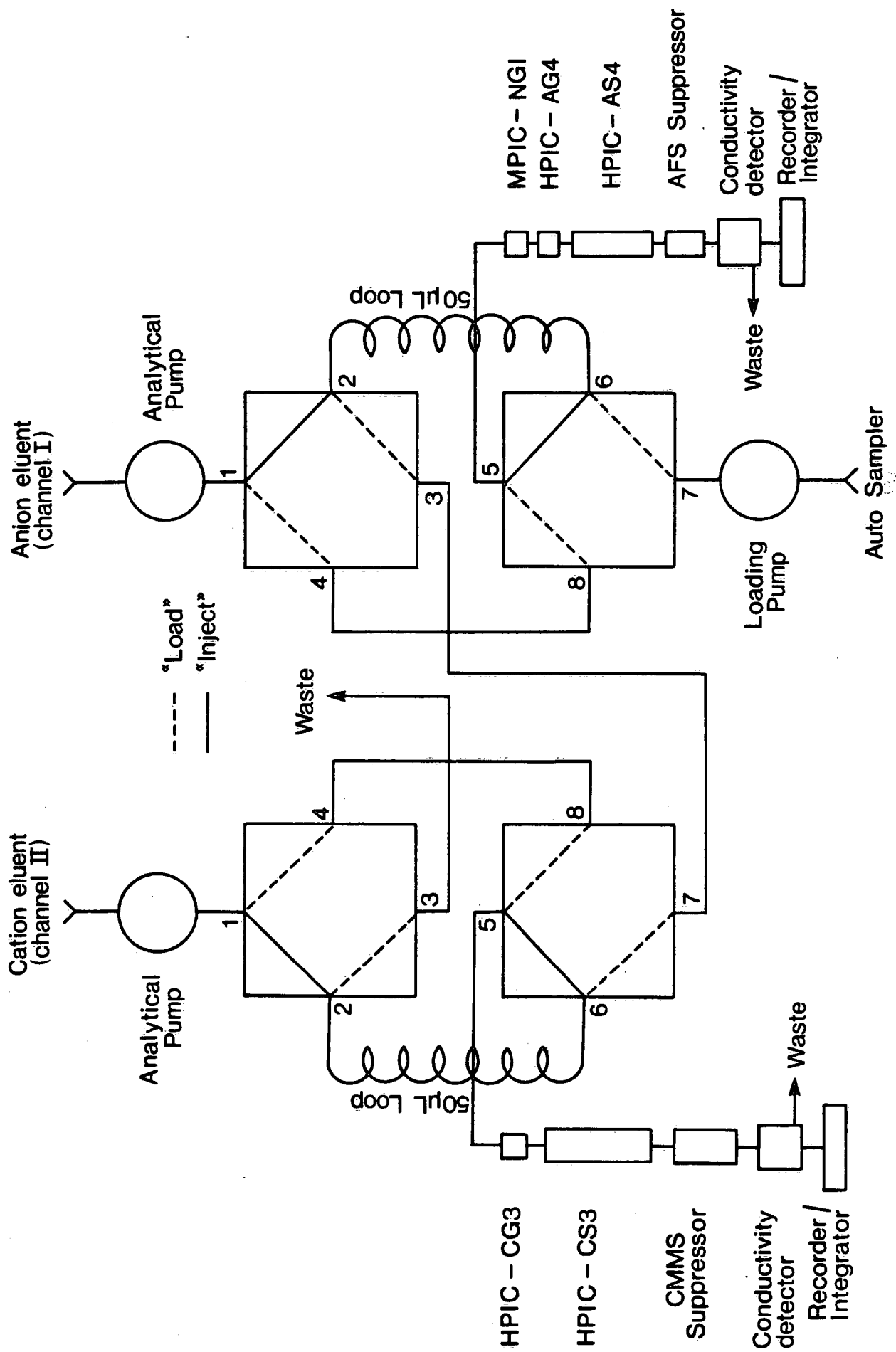


Fig.1 SINGLE SAMPLE LOADING AND INJECTION CONFIGURATION FOR ANALYSIS OF ANIONS AND CATIONS.

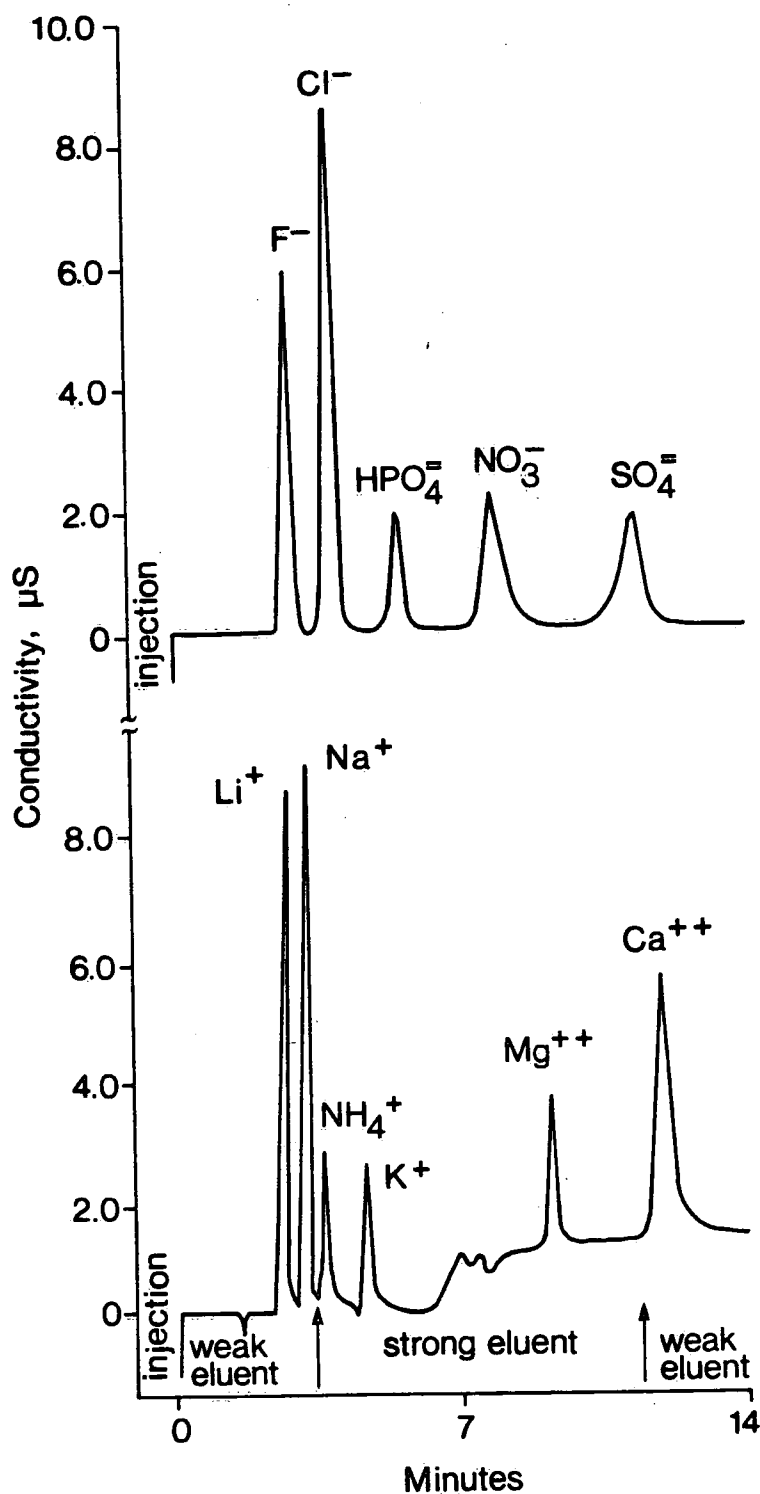


Fig.2 CHROMATOGRAMS FOR SIMULTANEOUS ANALYSIS OF ANIONS AND CATIONS.

In ppm,  $F=2.2$ ,  $Cl=4.9$ ,  $HPO_4-P=1.5$ ,  
 $NO_3-N=1.2$ ,  $SO_4=3.5$ ,  $Li=1.0$ ,  $Na=3.4$ ,  
 $NH_4-N=1.2$ ,  $K=1.9$ ,  $Mg=0.5$ , and  $Ca=2.7$ .