

# Application Bulletin



Of interest for:  
General

No. 211/1 e

## Sample preparation for ion chromatography

### Summary

The sample preparation for ion chromatography is divided into steps which should generally be implemented to preserve the column and into steps which should be performed to obtain an improved chromatogram. The goal is to have the test substance in **ionic form in solution** without the presence of interfering substances.

### Contents

1. Dilution of the sample	1
2. Filtration	2
3. Solid phase extraction	2
3.1. Cation exchangers (IC-H)	2
3.2. Anion exchangers (IC-OH)	3
3.3. Cation exchangers $\text{Ag}^+$ (IC-Ag) or $\text{Ba}^{2+}$ form	3
3.4. Non-polar solid phase extraction (IC-RP)	3
3.5. Polar solid phase extraction	3
3.6. Adsorption	3
4. Digestions	4
5. Combustion	4
6. Extraction	4
7. Literature	4
8. Ordering designations	4
9. Treatment of ion exchangers	5
9.1. Regeneration of 6.1012.010 IC-H cation exchanger cartridges	5
9.2. Conditioning and regeneration of the cation exchanger (batch process)	5
9.3. Regeneration of 6.1012.030 anion exchanger cartridges	5
9.4. Activation and regeneration of 6.1012.000 IC-RP cartridges	5
10. Application examples	6
10.1. Fluoride, chloride, nitrate and sulphate in a water sample	6
10.2. Cation determination in acid	7
10.3. Sulphate determination in sodium chloride	8
10.4. Fluorine, chlorine and sulphur determination in organic material	9

## 1. Dilution of the sample

For **anion analysis** dilution is performed with water or eluent, with the eluent dilution producing a somewhat smaller front and system peak. It is appropriate to dilute with eluent when low concentrations ( $< 0.5$  mg/L) have to be analysed. In general, dist. water with addition of eluent concentrate can also be used for dilution.

For **cation analysis**, dilution is effected with  $c(\text{HNO}_3) = 1$  mmol/L. The pH should be set to 3 (check). The entire sample preparation is performed in plastic vessels (e.g. PP) as particularly Na would be leached out of glass by the nitric acid.

### When should dilution be performed?

- When the concentration of an analyte ion is greater than 100 mg/L. In the ideal case, the concentrations lie in the range 0.5 to 50 mg/L. In cation analysis, it must be ensured that work is performed with the 10  $\mu\text{L}$  loop.
- When the total concentration of the anions or cations is greater than 1000 ppm.
- When the content is unknown, work is first performed with highly dilute samples.

## Sample preparation for ion chromatography

### 2. Filtration

For the filtration, 0.45  $\mu\text{m}$  (possibly 0.2  $\mu\text{m}$ ) microfilters, which can be obtained from various manufacturers, are used.

To preserve the column, it is advisable to filter all samples.

With a high solid content, coarse filtration or centrifuging can be used to remove the major part. However, it must always be borne in mind that this fraction and any ions adsorbed on it will not be detected.

### 3. Solid phase extraction

The solid phase extraction or **SPE** employs the same principles for a selective retention as liquid chromatography. The extraction columns (cartridges) are filled with various packing materials (sorbents).

The sequence of such an extraction can be divided into different steps:

- Conditioning
- Retention
- Wash step
- Elution
- Regeneration

All steps are not needed in every case. Often, interfering substances are retained on the cartridge and the analyte ions are present in the eluate. Washing and elution are thus not necessary.

The matrix from which impurity substances should be removed frequently dictates the type of extraction to be used. With an aqueous matrix, substances with non-polar or ionic functional groups can generally be extracted with non-polar or ion exchanger sorbents. Polar sorbents are suitable for the extraction of polar substances from a non-polar medium.

#### 3.1. Cation exchangers (IC-H)

For anion analysis, the sample can be treated with a cation exchanger in the  $\text{H}^+$  form.

##### When is this step necessary ?

- When the front peak is too broad owing to cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and hence anions which are eluted early are masked (see Fig. 1.b)
- For the removal of carbonate/bicarbonate (possibly also treated briefly in an ultrasonic bath or with nitrogen) (see Fig. 1.c)
- With alkaline samples ( $\text{NaOH} + \text{R-SO}_3^- \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{R-SO}_3^- \text{Na}^+$ )
- For the removal of cations from samples for ion exclusion chromatography.

Metrohm offers the **6.1012.010 IC-H** cation exchanger cartridge.

Instead of the exchanger cartridges, work can also be carried out with ion exchanger material (batch process). Note here that the exchanger must be conditioned (see Chap. 9).

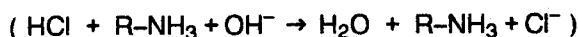
## Sample preparation for ion chromatography

### 3.2. Anion exchangers (IC-OH)

For **cation analysis**, the sample can be prepared using an anion exchanger in the OH<sup>-</sup> form.

#### When is this step necessary ?

- With highly acidic samples (pH < 2), the pH value can be raised and then set to pH = 3 with HNO<sub>3</sub> (see Fig. 2.b).



Metrohm offers the **6.1012.030 IC-OH** anion exchanger cartridge.

Instead of the exchanger cartridges, work can also be carried out with ion exchanger material (batch process). Note here that the exchanger must be conditioned (see Chap. 9).

### 3.3. Cation exchangers in the Ag<sup>+</sup> (IC-Ag) or Ba<sup>2+</sup> form

Cation exchangers are also available with Ag<sup>+</sup> or Ba<sup>2+</sup> ions in place of H<sup>+</sup> counter ions. With these cartridges, certain anions that are in excess and which would hence interfere with the chromatogram can be removed (e.g. determination of ca. 10 ppm sulphate in salt).

**Ag<sup>+</sup> form:** Removal of the halides (chloride, bromide, iodide)  
(The content of fluoride, nitrite, nitrate and sulphate is influenced only to a minor extent or not at all.) (see Fig. 3.b)

Metrohm offers the **6.1012.020 IC-Ag** cation exchanger cartridge.

To retain excess silver, the sample must be injected via a cation exchanger cartridge (e.g. 6.1012.010 IC-H).

**Ba<sup>2+</sup> form:** Removal of sulphate  
(This type of removal of sulphate has not proved successful in our experiments as large losses due to adsorption were found.)

### 3.4. Non-polar solid phase extraction (IC-RP)

The following non-polar sorbents are available in cartridge form: C18 (octadecyl), C8 (octyl), C2 (ethyl), PH (phenyl), CH (cyclohexyl), etc. The one most frequently used is probably the C18 (or RP-18), which is available by Metrohm as **6.1012.000 IC-RP** sample preparation cartridge.

#### When is this type of solid phase extraction necessary ?

- When organic substances which could interfere with the chromatogram or harm the column have to be removed.
- For the enrichment of heavy metals as a complex and subsequent determination (also extraction from an interfering matrix, e.g. heavy metals in brine).

### 3.5. Polar solid phase extraction

The following polar sorbents are available in cartridge form: CN (cyanopropyl), 2OH (diol), SI (silica), AL (aluminium oxide), etc.

#### What are these cartridges used for ?

- For the extraction of sulphate when this is in excess (aluminium oxide).  
(Fluoride is also removed, use only when necessary.)
- Enrichment of sulphate. Subsequently elute with ammonia (aluminium oxide).
- Enrichment of polar substances from a non-polar matrix.

### 3.6. Adsorption

A further possibility to remove interfering organic materials (e.g. colloids, dyestuffs) is by adsorption on activated carbon and subsequent filtration. The spectroscopic grade activated carbon used must be as pure as possible (AOX quality).

## Sample preparation for ion chromatography

### 4. Digestions

For cation analysis, various mineralisation processes can be employed. Dry digestion, dry digestion after addition of acid and also wet digestions are used.

In all methods, ensure that

- the content is changed as little as possible (blank value)
- the organic matrix is completely destroyed
- the digestion reagents are removed as completely as possible

Dry ashing in a platinum crucible has been used for different samples. The residue was taken up in a small amount of nitric acid, diluted and used for the analysis. In some cases, e.g. in the determination of iron, warming the sample with hydrochloric acid (possibly nitric acid) before and after ashing resulted in an improvement.

Wet ashing results in a higher blank value, but can also produce residues with better solubility in some cases.

For anion analysis, these "open" procedures can not be used. Instead, digestions in closed vessels with subsequent absorption in an alkaline medium must be employed (see *Metrohm AB 171*).

Fusion with  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  has been used for the determination of divalent cations and silicate in silicate samples.

### 5. Combustion

Combustions following Schöniger or similar methods can be used for the determination of halogens and sulphur in organic substances. The method is not suitable for trace analysis. The content in the sample should be in the percent range, but at least 0.01 ... 0.1% (e.g. investigation of solvent wastes) (see *Fig. 4a*).

### 6. Extraction

For the analysis of ions in oil or solvent samples, extraction with water or eluent is advisable. The solvent fraction which passes into the aqueous phase in such an extraction can be removed by means of solid phase extraction.

Should, however, the entire element content need to be determined, combustion is required.

### 7. Literature

- Feige, M. / Schäfer, J. / Frahne, D.  
*Halogen- und Schwefel-Bestimmung mit IC nach Verbrennung der Probe*  
GIT Fachz. Lab. 35 (1991) 443-447
- Saari-Nordhaus, R. / Anderson, J.M. / Henderson, I.K.  
*Sample preparation for ion chromatography using solid phase extraction*  
Int. Lab. 25 (1990) 36-42
- Haddad, P.R.  
*Sample cleanup methods for ion chromatography*  
J. Chrom. 482 (1989) 267-278
- METROHM Application Bulletins

### 8. Ordering designations

- |                                      |            |
|--------------------------------------|------------|
| • IC-RP sample preparation cartridge | 6.1012.000 |
| • IC-H sample preparation cartridge  | 6.1012.010 |
| • IC-Ag sample preparation cartridge | 6.1012.020 |
| • IC-OH sample preparation cartridge | 6.1012.030 |

## Sample preparation for ion chromatography

### 9. Treatment of ion exchangers

#### 9.1. Regeneration of 6.1012.010 IC-H cation exchanger cartridges

\*HCl p.a. 10% (10 mL) is forced slowly through the cartridge using a syringe or sucked through by vacuum. The filter is then flushed free from chloride with ultrapure water (control injection).

If the regenerated exchanger cartridge is not used for quite some time (2 days), it should be flushed again with 5 mL ultrapure water before use.

\* Another acid (e.g. HNO<sub>3</sub> p.a. 15%) can be used instead of HCl p.a. 10%, depending on the ions which have to be determined.

#### 9.2. Conditioning and regeneration of the cation exchanger (batch process)

To ca. 60 g ion exchanger are added 150 mL \*HCl p.a. 10% and the mixture stirred for 15 min. The solution is decanted off, ultrapure water added and decanting again performed. This procedure is repeated until the decanted solution is free from chloride (control injection).

The exchanger is now stored under ultrapure water. After relatively long standing (2 days), the solution should be decanted off and renewed before the exchanger is used.

\* Another acid (e.g. HNO<sub>3</sub> p.a. 15%) can be used instead of HCl p.a. 10%, depending on the ions which have to be determined.

#### 9.3. Regeneration of 6.1012.030 IC-OH anion exchanger cartridges

Anion exchangers are regenerated in the same way as cation exchangers. A base, chiefly NaOH p.a. or KOH p.a., is used in place of acid.

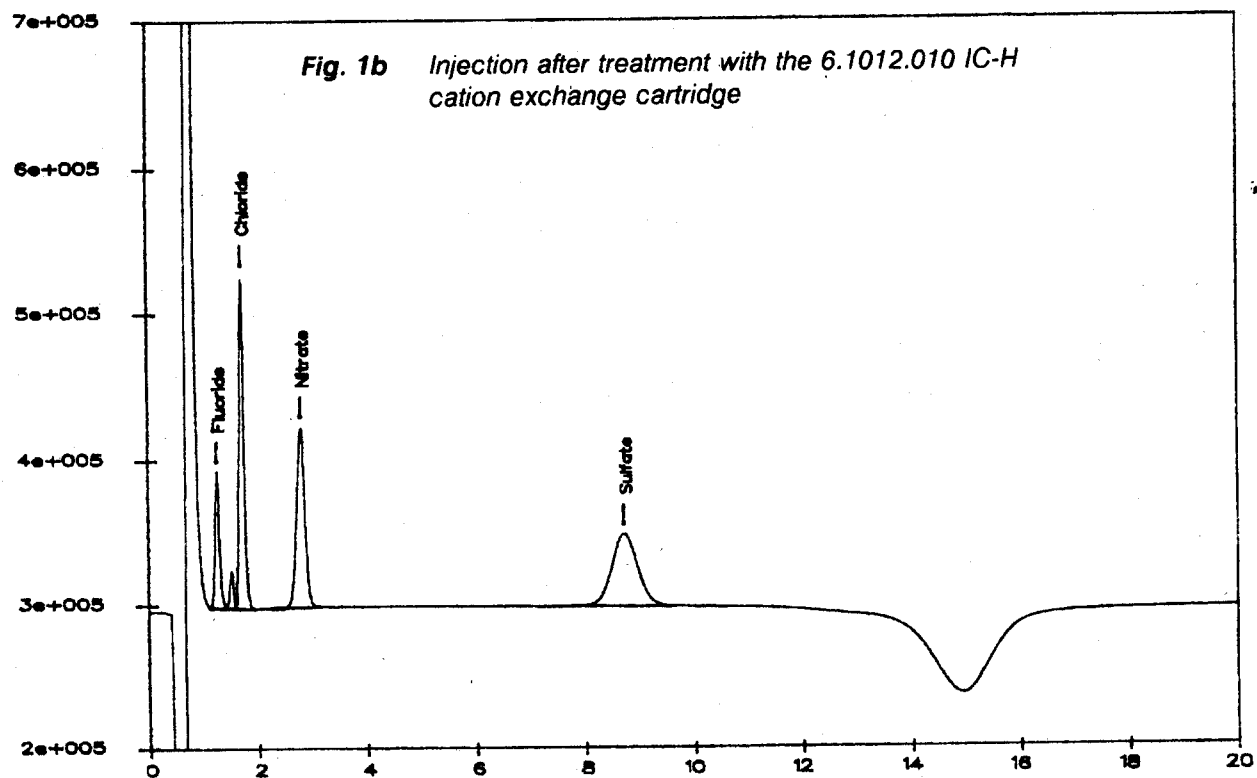
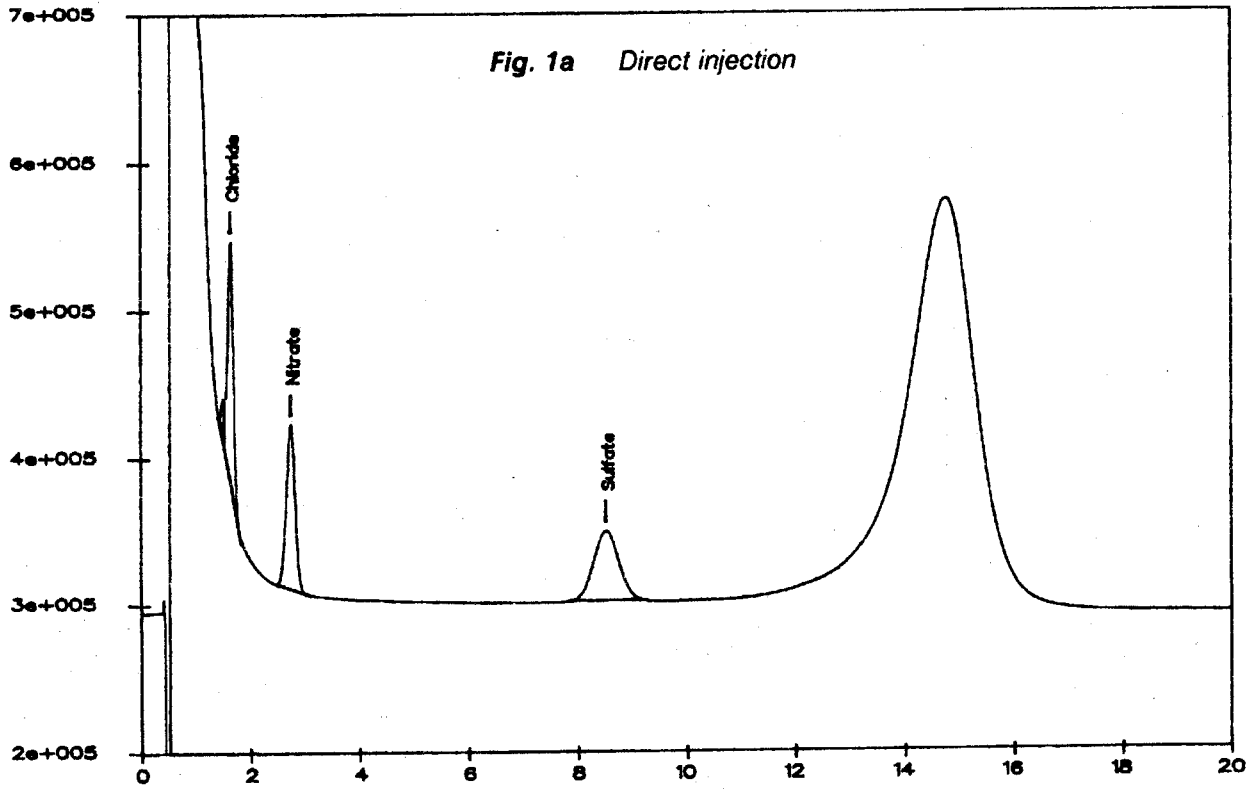
#### 9.4. Activation and regeneration of 6.1012.000 IC-RP cartridges

Before IC-RP cartridges are used, they must be activated with 10 mL methanol p.a. and flushed with 10 mL deionised water.

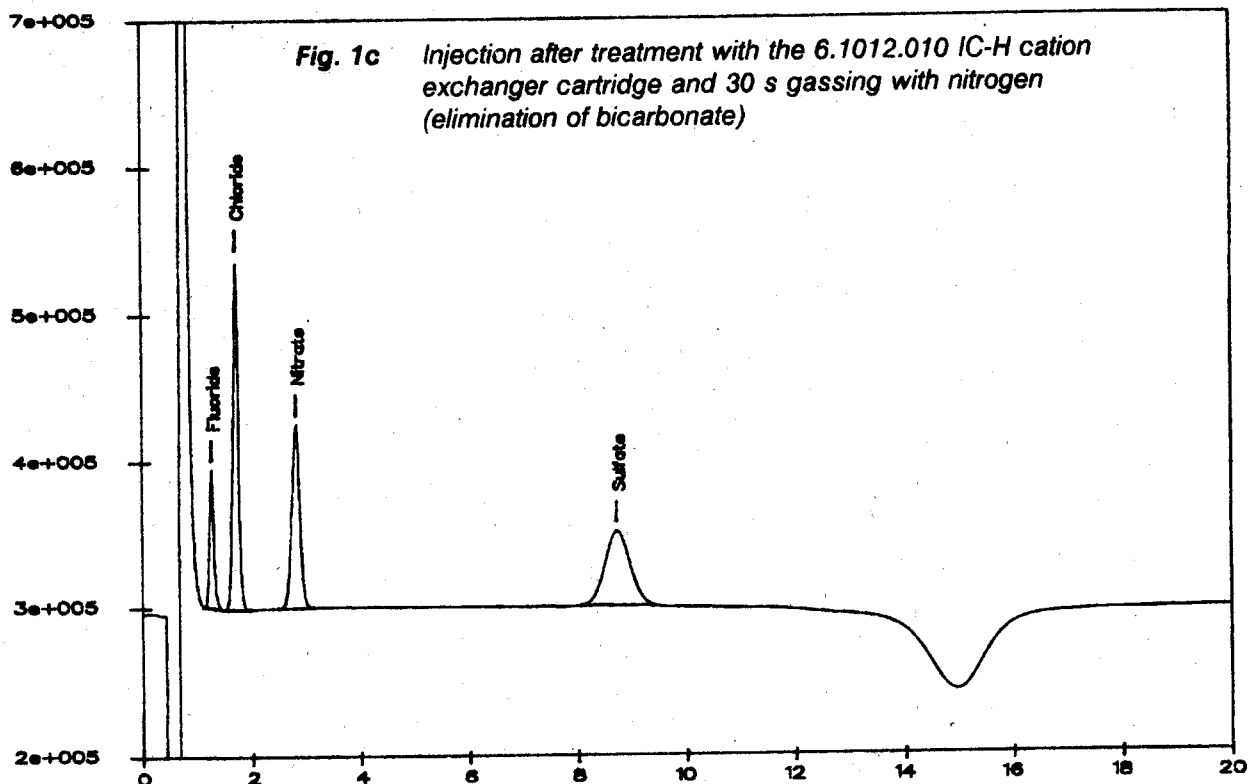
Regeneration is performed in the same manner, except that the amount of methanol is increased to ca. 20 ... 50 mL.

**Sample preparation for ion chromatography****10. Application examples****10.1. Fluoride, chloride, nitrate and sulphate in a water sample**

IC anion column: PRP X-100 (Metrohm 6.1005.000)  
Eluent: 2 mmol/L phthalic acid in 10% acetone, pH = 5.0  
Flow: 2 mL/min  
Inj. Vol.: 100  $\mu$ L  
Full Scale: 4  $\mu$ S/cm  
Polarity: +

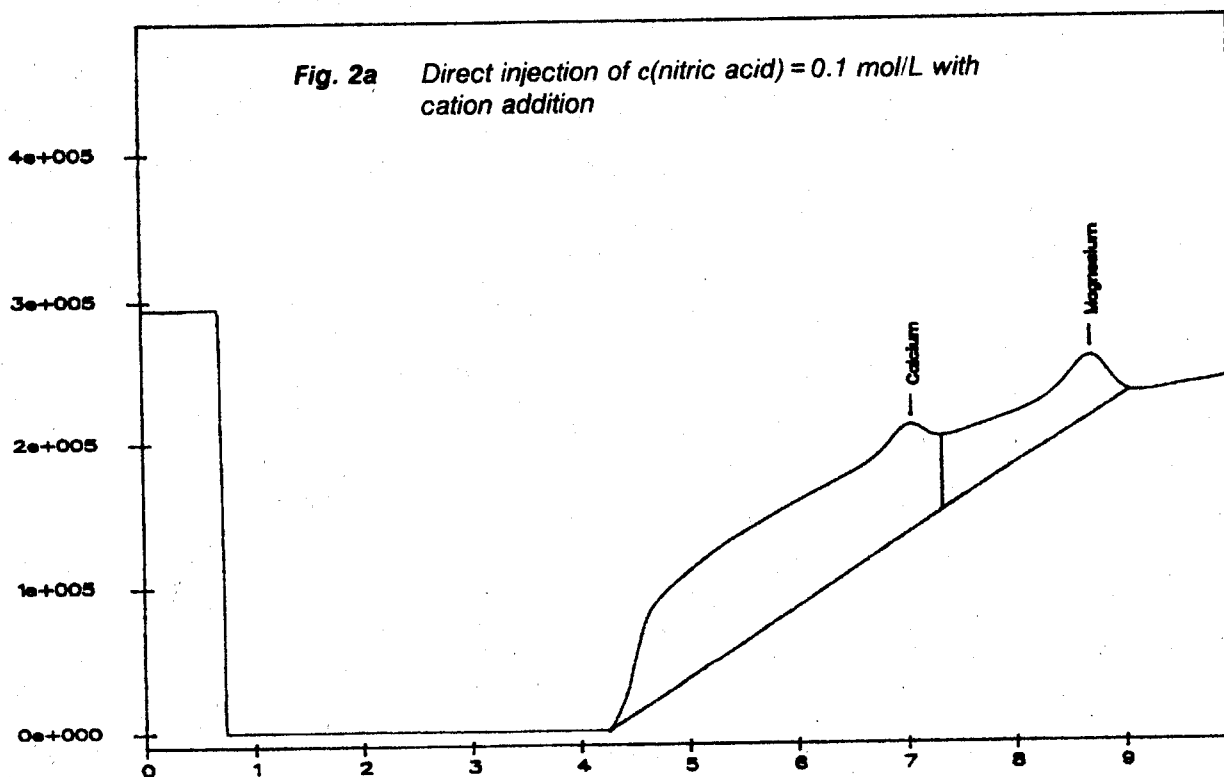


## Sample preparation for ion chromatography

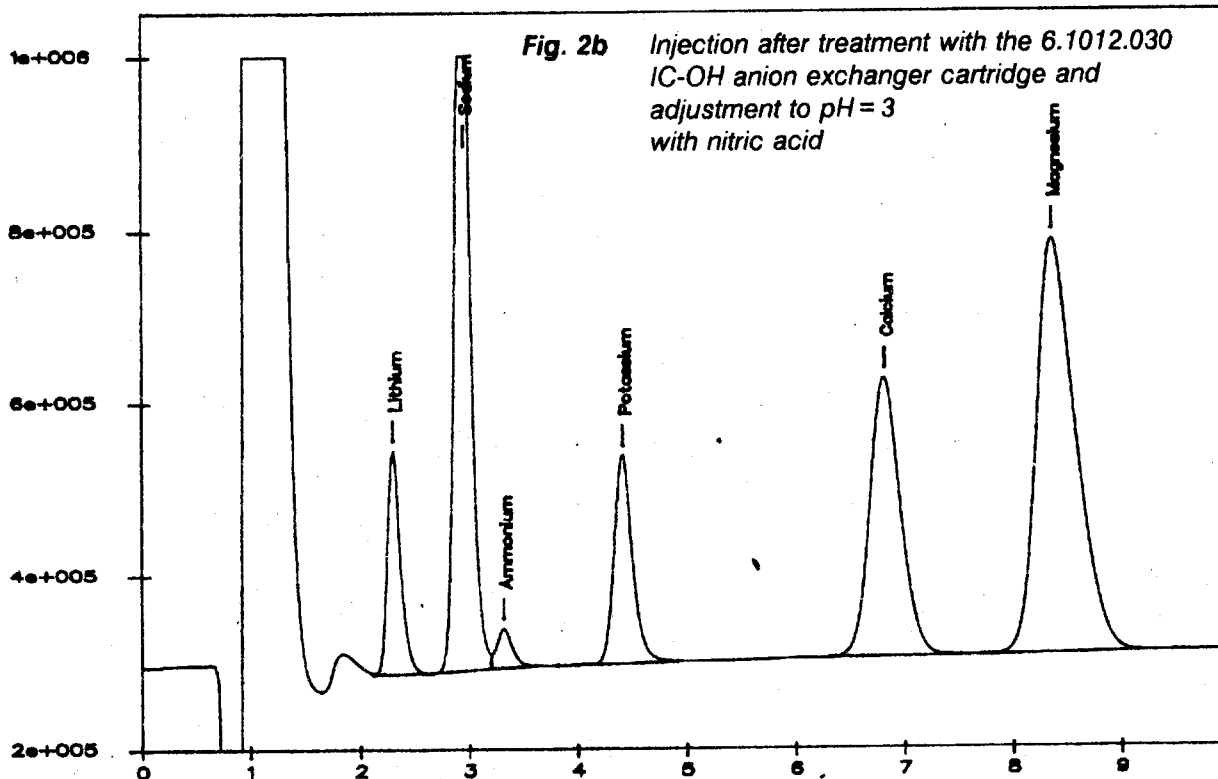


## 10.2. Cation determination in acid

IC cation column: SUPER-SEP (Metrohm 6.1009.020)  
Eluent: 5 mmol/L tartaric acid, 0.75 mmol/L dipicolinic acid in water  
Flow: 1 mL/min  
Inj. Vol.: 10  $\mu$ L  
Full Scale: 5  $\mu$ S/cm  
Polarity: -

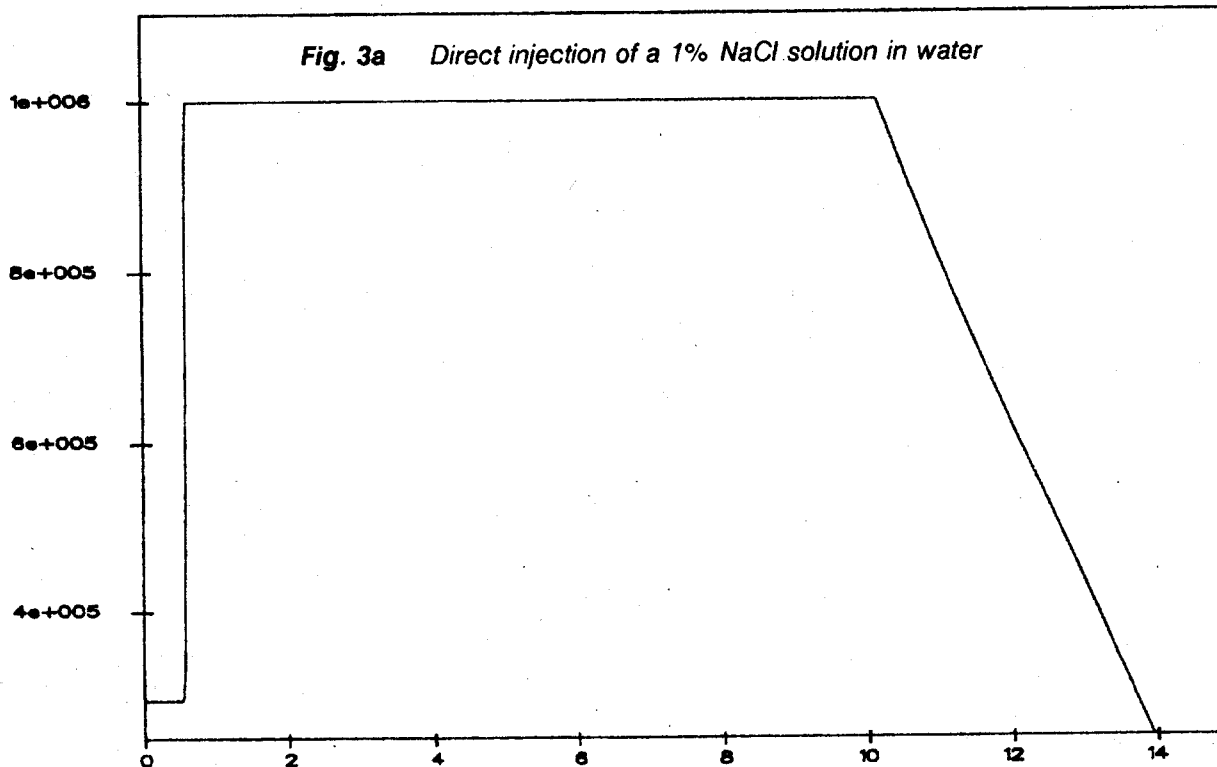


Sample preparation for ion chromatography



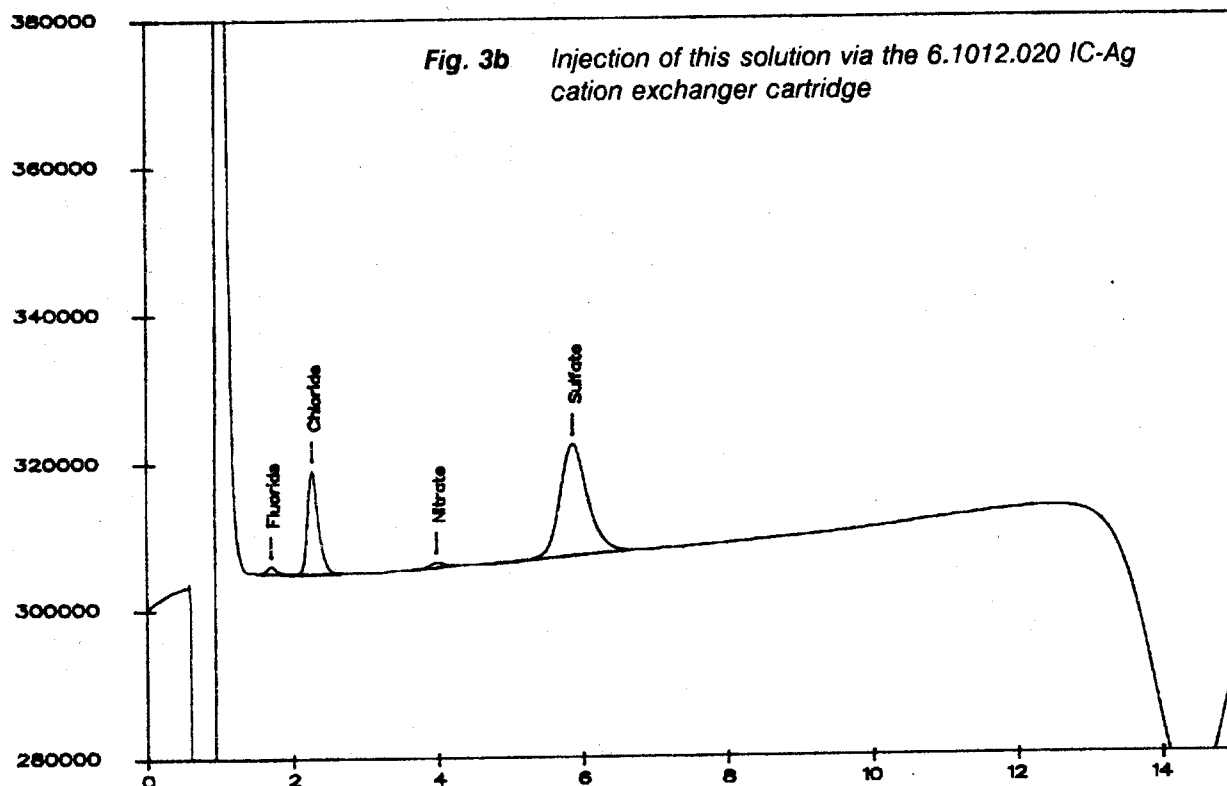
10.3. Sulphate determination in sodium chloride

IC anion column: SUPER-SEP (Metrohm 6.1009.000)  
 Eluent: 2.5 mmol/L phthalic acid in 5% acetonitrile, pH = 4.2  
 Flow: 1.5 mL/min  
 Inj. Vol.: 100 µL  
 Full Scale: 4 µS/cm  
 Polarity: +





## Sample preparation for ion chromatography



## 10.4. Fluorine, chlorine and sulphur determination in organic material

IC anion column: SUPER-SEP (Metrohm 6.1009.000)  
Eluent: 2.5 mmol/L phthalic acid in 5% acetonitrile, pH = 4.2  
Flow: 1.5 mL/min  
Inj. Vol.: 100  $\mu$ L  
Full Scale: 4  $\mu$ S/cm  
Polarity: +

