

# Some Modern Approaches to the Chromatographic Determination of Inorganic Anions

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## Introduction

The determination of inorganic anions has traditionally been performed using classical titrimetric, volumetric or spectrophotometric techniques, or with the use of ion selective electrodes. In many cases, these techniques lack selectivity, sensitivity and speed, and are applicable to the determination of only a single species at one time. Conventional ion exchange, with diverse monitoring methods such as conductivity, polarography, spectrophotometry etc. is also inadequate in terms of resolution and sensitivity. These drawbacks have provided impetus for the development of rapid and sensitive methods of analysis using liquid chromatography, and considerable advances have been made in this area in recent years. This development has been chiefly directed towards inorganic anion analysis; however, the experience gained can often be applied to cation analysis with equal success. The current availability of satisfactory alternative methods for cation analysis (such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and polarography) means that cation analysis by liquid chromatography does not have the same priority as anion analysis.

The most significant factors contributing to the recent advances in chromatographic anion analysis have been the development of specialized columns and improvements in detection systems. The purpose of this article is to outline the modern approaches used, particularly with respect to separation and detection modes.

## Separation methods

The systems used for anion analysis can be broadly divided into two groups. In the first group, a low capacity anion exchange column (called the 'separator' column) is used to separate the sample anions and a secondary column, consisting of a strong cation exchanger, is used to reduce the conductivity of the eluent. The secondary column is generally referred to as the 'suppressor' or 'stripper' column. The second group consists of those systems using only a single column for the analysis: this column may be an ion-exchange, reversed-phase, cyano, amino or polystyrene-divinylbenzene copolymer column. No suppressor column is used.

## Suppressed systems

Different ion-exchange resins are used for the separator and the suppressor columns. The separator column is packed with a specially developed material consisting of an animated latex agglomerated on to an ion-exchange substrate<sup>1</sup>. This material contains a core of styrene-divinylbenzene polymer (S/DVB) which has surface sulfonic acid groups. These groups serve to hold (via electrostatic attraction) small latex particles which have been aminated; the amination process converts the neutral latex particles into an anion exchange material.

Thus the packing material comprises a sulfonated S/DVB core (20-30  $\mu\text{m}$  diameter) covered with a monolayer of anion exchange latex particles (0.1-0.5  $\mu\text{m}$  diameter). On the other hand, the suppressor column is packed with a conventional microporous strong acid cation exchange resin.

The mode of operation of the separator-suppressor combination is typified by the following example involving separation of the inorganic

anions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , using a mobile phase of  $\text{HCO}_3^-/\text{CO}_3^{2-}$ , with conductivity detection. Separation is achieved through conventional ion-exchange competition between the sample and eluent anions for the cationic sites on the aminated resin. When the eluent and sample ions pass into the suppressor, the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  ions are converted to  $\text{H}_2\text{CO}_3$ , thereby greatly reducing the conductivity of the eluent.

This technique, called 'Ion Chromatography', was developed by Small *et al*<sup>1</sup> and has since been extensively developed by the Dionex Corporation; numerous applications are now available<sup>2</sup>. From the chromatographic point of view, the technique has some drawbacks, including band broadening resulting from the suppressor column, the limited lifetime of the suppressor column (which must be periodically regenerated) and a restriction in the choice of eluent buffers to those which give low background conductivity after passage through the suppressor. These disadvantages have been partly offset by introduction of a new type of suppressor column based on a counter-current regenerated shell and tube device incorporating sulfonated polyethylene ion exchange hollow fibres<sup>3</sup>. This hollow fibre suppressor allows continuous use without regeneration; however, it produces greater band broadening than conventional suppressor columns. Recent studies have shown that packing of the hollow fibre suppressor with inert beads leads to a considerable reduction in band broadening<sup>4</sup>.

Ion chromatography is particularly useful for trace analysis where the sample can be concentrated in a small pre-column mounted before the separator column<sup>5</sup>. Using this approach, common anions can be determined at concentrations as low as 2 ppb. In the area of general applications, the use of gradient elution has given improved separations of some anions<sup>6</sup> and some useful information on the effects of major ions on the determination of trace anions has also been reported<sup>7</sup>. A significant advantage of ion

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chromatography is that due to the resin based column packings used, there is no restriction on the pH of the sample or eluent.

#### **Non-suppressed systems**

The concept of utilizing conventional HPLC instrumentation for the analysis of anions has proved highly attractive to many chromatographers. This approach provides an alternative to the purchase of a dedicated (and relatively costly) ion chromatograph and is particularly appropriate to laboratories which routinely perform HPLC analyses and also have some need for anion analyses. In such cases, it is economically sound to make full use of the capabilities of the HPLC instrument, rather than to outlay further funds on a dedicated ion chromatograph. For these reasons, an intensive search has been made over the past three years for viable systems of anion analysis which do not use a suppressor column. The non-suppressed systems, which are discussed below, are often loosely referred to as 'ion chromatography'; however, strictly speaking, this term applies only to the Dionex system.

#### **Low capacity silica-based ion-exchange columns**

Silica columns with bonded quaternary amine functionalities have been developed as low capacity anion exchangers<sup>8</sup>. This material has an ion exchange capacity of less than 0.1 mequiv/g, which enables dilute eluents such as 5 mM phthalic acid to effectively elute common inorganic anions. These eluents have low conductivity and therefore use of a suppressor column to reduce eluent background conductivity is not required. It is an important point that this ion exchange material was developed specifically for conductivity detection; however, the later discussion in this paper will indicate that alternative detection methods are often superior.

The low exchange capacity of this material necessarily means that eluents of low ionic strength give best results. The most favoured eluent is *o*-phthalic acid (1-10 mM) with pH adjustment within the approximate range 3.5-6.0 being used to vary the ionic strength and hence elution characteristics<sup>9</sup>. Other isomers of phthalic acid have also been studied<sup>10</sup>.

The choice of eluent is clearly severely restricted and this approach has the further disadvantages of a small linear range of sample loadings and a restricted working pH range (pH 2-7) due to the use of a silica-based material. A considerable advantage, however, is the high efficiencies of the silica materials compared with agglomerated latex materials. A commercial silica-based low capacity anion exchange material is marketed under the trade name Vydac 302 IC (The Separations Group, Hesperia, California), and columns used routinely in our laboratory typically have efficiencies of 16,000 plates/metre (for NO<sub>3</sub><sup>-</sup>). The lifetimes of these columns depend strongly on the nature of samples used; however, we have found that a working lifetime of approximately six months can generally be expected.

#### **Surface aminated macroporous ion-exchange materials**

Inorganic anions have been separated on columns containing a macroporous anion exchange resin which has a very low capacity (0.07 mequiv/g); because of the low resin capacity, only a very dilute solution of an aromatic organic acid was needed as eluent<sup>11, 12</sup>. Again, a direct result of the low background conductivity of the eluent was that no suppressor column was required for conductivity detection.

The resins were prepared using macroreticular cross-linked polystyrene beads (XAD-1, supplied by Rohm and Haas, Philadelphia, Pa, USA) as substrate. These beads were ground and sieved, before being chloromethylated, one method for which involved the use of chloromethylmethyl ether, methylene chloride and nitromethane, with ZnCl<sub>2</sub> as catalyst. The reaction time was varied to control the degree of chloromethylation. The treated resin was then aminated with trimethylamine in methanol. The resulting material has excellent chemical and mechanical stabilities and flow properties.

A number of eluents has been studied for use with this surface aminated resin, including benzoate, biphthalate and sulfobenzoate<sup>11, 13</sup>. As with the previously described silica-based ion exchange material, eluents have been studied only for their suitability with conductivity detection. It is likely

that the list of suitable eluents will be considerably enlarged when alternative forms of detection (as discussed later in this article) are considered.

At present low capacity surface aminated macroporous anion exchange resins are not available commercially; however, fairly detailed information is available on their selectivity characteristics and the effect of variation of exchange capacity<sup>11, 14</sup>. Data from published chromatograms indicates that these resins are of fairly low efficiency (approx. 1000 plates/m); however, they have the advantage of utility over the entire pH range.

#### **Other columns**

In addition to ion-exchange, a variety of column types have been employed for the separation of inorganic anions. These include octadecyl, amino and cyano columns, as well as polystyrene divinylbenzene copolymer columns.

Reversed-phase ion-pair chromatography has been successfully applied to the separation of inorganic ions using C<sub>18</sub><sup>15, 16</sup> and CN<sup>17</sup> columns. A considerable number of quaternary ammonium salts have been employed as ion-pairing reagents, including those with C<sub>4</sub>, C<sub>8</sub>, C<sub>16</sub>, C<sub>25</sub>, C<sub>32</sub> or C<sub>37</sub> alkyl chains. Different ion pairing reagents are useful for different groups of anions; for example F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are separable using tetrabutylammonium hydroxide<sup>16</sup>, whereas IO<sub>3</sub><sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and I<sup>-</sup> are separable using tridodecylmethylammonium iodide<sup>15</sup> on C<sub>18</sub> columns. This approach is characterized by the attainment of high column efficiencies, typically 20,000 plates/m. However, as with all ion-pairing methods, the column requires considerable equilibration time and extreme care is necessary for the achievement of precise results. Inert polystyrene divinylbenzene copolymer materials (such as Hamilton PRP-1) have also been employed as substrates for dynamic coating by hydrophobic ion-pairing reagents<sup>15</sup>. The major equilibria contributing to retention of organic anions have been identified<sup>18</sup> and the application of this approach to inorganic anions is currently under study.

Amino columns have found limited use in inorganic anion analysis. NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and Br<sup>-</sup> are separable using pH 3.0 phosphate buffer as mobile phase<sup>19</sup> and separation of a mixture of nine

inorganic and organic anions has been reported using 0.03M phosphate buffer at pH 3.2<sup>20</sup>. Again, high column efficiencies were obtained.

### Detection Methods

The detection of trace quantities of eluted ions has provided a major obstacle to the determination of inorganic ions by HPLC. Numerous detection methods have been developed; the most commonly employed methods, however, are conductivity, uv absorbance and more recently, indirect refractive index or indirect uv absorbance detection.

### Conductivity detection

Since the initial development of ion chromatography, conductivity measurements have been the preferred method of detection. Both the suppressed and non-suppressed separation modes have been designed specifically to operate with conductivity detection. A number of specialized conductivity detectors has been developed in order to improve the detectability of inorganic ions<sup>16,21</sup>. These detectors feature a large electronic offset range for nulling of the background conductivity of the eluent and small cell currents to minimize heat dissipation in the cell and the resulting baseline noise and drift.

Conductivity detection gives best results when used with suppressed separation systems due to the low background conductivity of the eluent. Advantages of this form of detection include its applicability to a wide range of ions and its sensitivity; strict temperature control of the detector cell is essential and the choice of available eluents is somewhat restricted. The use of conductivity detection has also proved successful with reversed-phase ion-pair HPLC of inorganic ions<sup>16</sup>, despite the commonly held belief that solutes elute as neutral ion-pairs in this form of chromatography.

### UV absorbance detection

A considerable number of inorganic anions show uv absorbance in the range 210-220 nm<sup>22</sup>; for example, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup>, SCN<sup>-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. The important anions Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, ClO<sub>4</sub><sup>-</sup> and CN<sup>-</sup> do not absorb uv radiation in the above wavelength range.

Direct uv absorbance detection has been coupled with several of the

previously described separation modes<sup>17, 19, 20, 23, 24</sup> and has been applied to the analysis of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> in a variety of sample matrices. The chief disadvantage of this approach is that the solvents used must be of high purity to minimize background absorbance.

### Indirect detection methods

The widespread use of eluents containing aromatic species such as phthalic or benzoic acids in the non-suppressed ion-exchange separation modes has led to the development of sensitive indirect methods of detection. In these systems separation is achieved by competition between phthalate ions from the eluent and solute anions for the ion exchange sites on the column, and it follows that elution of a solute anion will be accompanied by a localized deficiency of phthalate ions in the eluent. Since

phthalate is highly uv absorbing and its aqueous solutions have a considerable refractive index, the elution of a solute anion can be indirectly detected by the corresponding decrease in uv absorbance or refractive index (RI) of the eluent.

Only a small amount of systematic study has been devoted to these detection methods<sup>25-27</sup>. Nevertheless it is clear that they hold significant promise. Both uv and RI methods are more sensitive than conductivity detection<sup>26</sup> and they give less baseline noise. Moreover, they provide a highly convenient approach for chromatographers wishing to adapt an existing HPLC instrument for inorganic anion analyses. The uv detector is optimally operated in the region 285-300 nm and the only departure from normal procedure is that the reference cell of the detector must be filled with eluent to enable the small changes in absorbance to be measured. This procedure is routine for refractive index detectors.

Some examples of the results obtained with these indirect detection methods using injection of large sample volumes of trace concentrations of

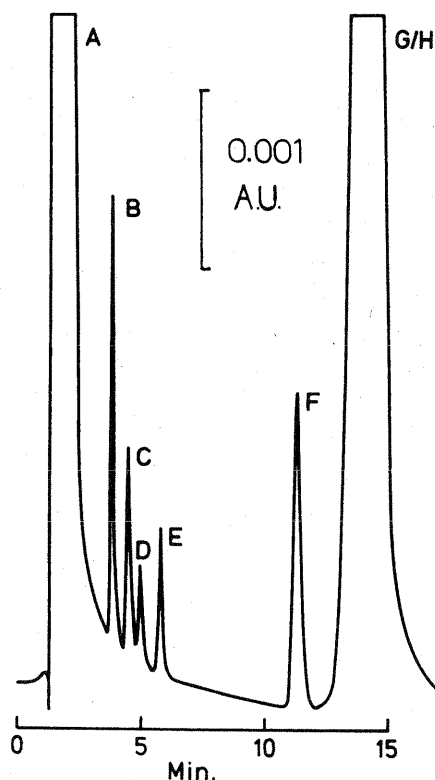


Figure 1. Separation of inorganic anions; indirect uv detection. Conditions: column, Vydac Anion column 3021C, 250 mm x 4.6 mm I.D. column temperature 35.0°C (Bioanalytical system inc. Model LC-22A and LC-23A); mobile phase, 5 mM. Potassium hydrogen phthalate pH 4.0, flow rate 2 ml/min; chart speed 0.5 cm/min. Detector, Waters Assoc. model M480 uv spectrophotometer, 285 nm, 0.005 a.u.f.s. reference cell filled with mobile phase.

Peak Identities: A = solvent; B = Cl<sup>-</sup> (424 ppb); C = NO<sub>2</sub><sup>-</sup> (920 ppb); D = Br<sup>-</sup> (400 ppb); E = NO<sub>3</sub><sup>-</sup> (440 ppb); F = I<sup>-</sup> (720 ppb); G = SO<sub>4</sub><sup>2-</sup> (456 ppb); H = system peak; injection volume 750 μl.

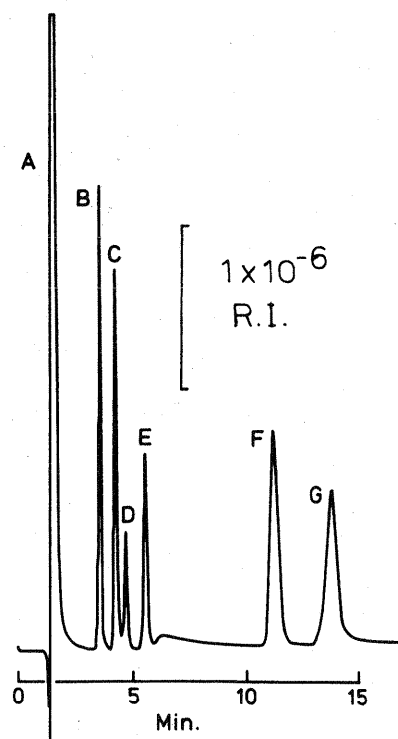


Figure 2. Separation of inorganic anions; indirect R.I. detection. Detector Erma 7510 R.I. detector at x 1/2, 35°C detector temperature. Peak Identities: A = solvent, B = Cl<sup>-</sup> (10.6 ppm), C = NO<sub>2</sub><sup>-</sup> (23.0 ppm), D = Br<sup>-</sup> (10.0 ppm), E = NO<sub>3</sub><sup>-</sup> (11.0 ppm), F = I<sup>-</sup> (18.0 ppm), G = SO<sub>4</sub><sup>2-</sup> (11.4 ppm). Injection volume 100 μl. Other conditions as per Figure 1.

solute are given in Figs 1 and 2. The instrument used consisted of a Waters Associates M6000A pump, U6K injector and M480 variable wavelength uv detector; the refractive index detector was an Erma Optical Co., Model 7510 R.I.

### Conclusions

Many separation and detection

methods have been proposed for the chromatographic determination of inorganic ions. The most established of these is ion chromatography, with the use of a suppressor column, but the non-suppressed systems are more readily adaptable for use with existing HPLC instrumentation, particularly when indirect uv or refractive index detection is used. Greater diversity in commercially available column types

should lead to wider acceptance of the non-suppressed separation systems. The current intense research activity in the areas of new eluents and alternative modes of separation and detection will undoubtedly result in the development of a new generation of chromatographic techniques which will offer improved selectivity and sensitivity compared with existing methods.

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## Polymer Division 14APS Overseas Speakers Virginian Polymer Experts for 14APS and Polymer Courses

It is unusual for three people from the one overseas laboratory to be invited to Australia at the one time. The Polymer Division has just done this by inviting Professors James E. McGrath, Thomas C. Ward and Garth L. Wilkes from the Virginia Polytechnic Institute and State University, Blacksburg Va, USA.

The expertise of these three covers the major areas of polymer chemistry—synthetic chemistry (Jim McGrath), physical chemistry (Tom Ward) and chemical engineering (Garth Wilkes). They will be presenting plenary lectures at the **14th Australian Polymer Symposium** (14APS) in Ballarat on 12-16 February 1984. In addition these three will team up to present courses entitled *Polymers as Materials; Relating Chemistry to Properties* to be held in Sydney on 8-10 February and repeated in Melbourne on 20-22 February.

Jim McGrath, after completing his PhD at the University of Akron, worked in R&D with Union Carbide before joining VPI&SU. He is currently Professor of Chemistry and co-director of the Polymer Materials and Interfaces Laboratory. His research interests include organosiloxane copolymers, ion containing polymers and anionic polymerizations. His plenary lecture at 14APS will be titled 'Synthesis and Transformations of Engineering Polymers'.

Tom Ward, after graduating from Princeton and postdoctoral

research at Strathclyde and Essex, joined VPI&SU in 1968. His main research interests are in the field of spectroscopic characterization of polymers and the fundamentals of adhesion. At 14APS his plenary lecture will be on 'Solid State NMR of Multicomponent Polymer Systems'.

The last of the Virginian trio, Garth Wilkes, did his doctoral work at Massachusetts before moving to Princeton. In 1978 he joined the Chemical Engineering Dept at VPI&SU. His current research interests include biomaterials, structure property relationships in block and segmented copolymers. The title of his plenary lecture at 14APS will be 'Olefinic Elastomeric Ionomers Based on Polyisobutylene-Structure Property Behaviour'.

While in Australia Professors McGrath, Ward and Wilkes will be visiting Sydney, Melbourne and Brisbane and they will be in Australia for all of February. If you would like to meet them or have one of them visit your laboratory, contact without delay the chairman of the Polymer Division, Bruce Guise on 052 47 2695.

For more information on 14APS or the courses on Polymers as Materials contact the Polymer Division PO Box 224, Belmont, Vic. 3216. Please note registration brochures for these will not be included in *ChemAust*.

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### MS in Life Sciences

Fifth International Symposium on Mass Spectrometry in Life Sciences. 15-18 May 1984, Rijksuniversiteit Ghent. Information: Prof. A. De Leenheer, Symposium Chairman, Laboratoria voor Medische Biochemie en voor Klinische Analyse, Harelbekestraat 72, B-9000 Ghent, Belgium.