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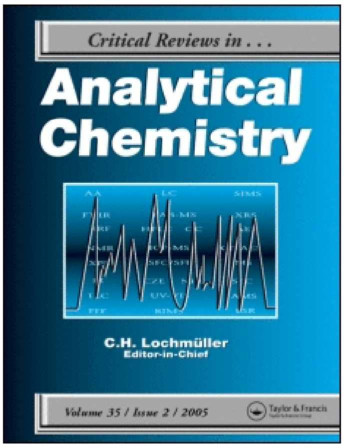

## Critical Reviews in Analytical Chemistry

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# Ion Chromatography

Frank C. Smith Jr; Richard C. Chang; Timothy S. Stevens

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# ION CHROMATOGRAPHY

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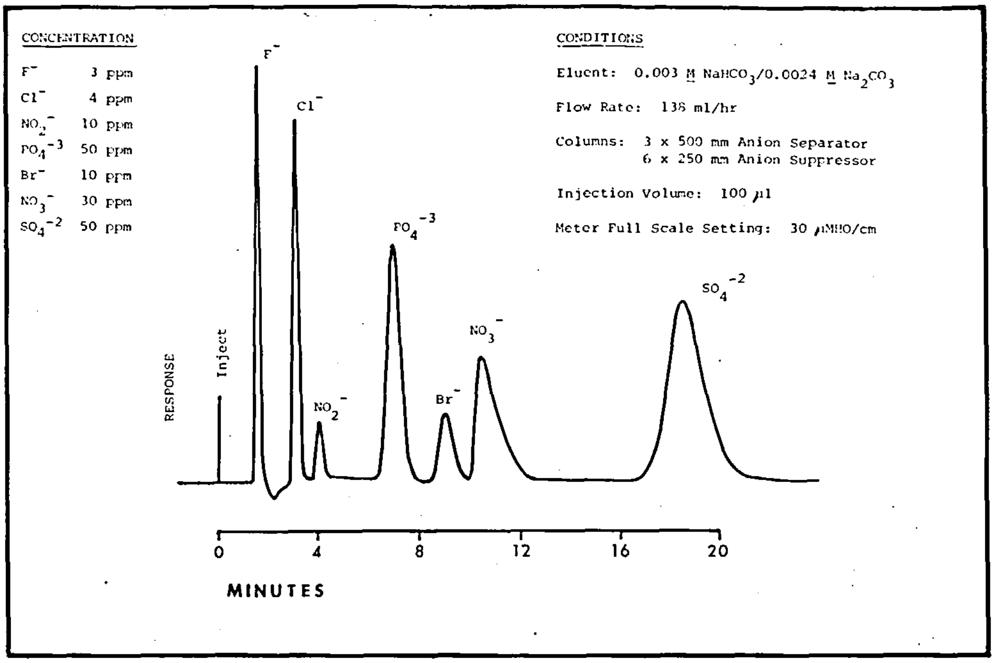


FIGURE 1. Separation of inorganic anions.

# I. INTRODUCTION

## A. Purpose of This Review

This review deals with a new analytical methodology which successfully combines ion-exchange principles with conductimetric detection. This technique, known as ion chromatography (IC), was introduced in 1975 by Small, Stevens, and Bauman.[1] IC has proven to be very useful for the determination of aqueous ionic species with pK less than approximately seven. The technique fills the need for simple, rapid, and reliable determination of the common ions (such as $SO_4^{2-}$, $Cl^-$, $NO^-_3$, etc.) in either simple or complicated matrices. Typical ion chromatograms of anions and cations are shown in Figures 1 and 2. Both organic and inorganic ions have been separated and detected by IC. This review is intended to illustrate IC principles, practice, and instrumentation. The bulk of this work is devoted to the application of IC in air and water pollution, quality control, process sampling, clinical chemistry, microelemental and geochemical analysis, and energy-related areas such as power production.

## B. Relationship of IC to Other Chromatographic Methods

Volatility and polarity can be conveniently used to relate IC to other chromatographic techniques. Figure 3 shows a much simplified comparison of GC (gas chromatography), HPLC, and IC based on volatility and polarity. These three techniques are complementary. There is considerable overlap between techniques, and the indicated divisions should not be viewed as absolute. While GC can be used over an extended range of polarity, the limiting factor for separation is constituent volatility. Increased temperatures or derivitization are commonly used to increase volatility. Liquid chromatography is the preferred technique for nonvolatile compounds. Four major modes of liquid chromatography are practiced: liquid/solid, bonded phase (normal and reverse), exclusion, and ion exchange. These techniques are grouped together un-

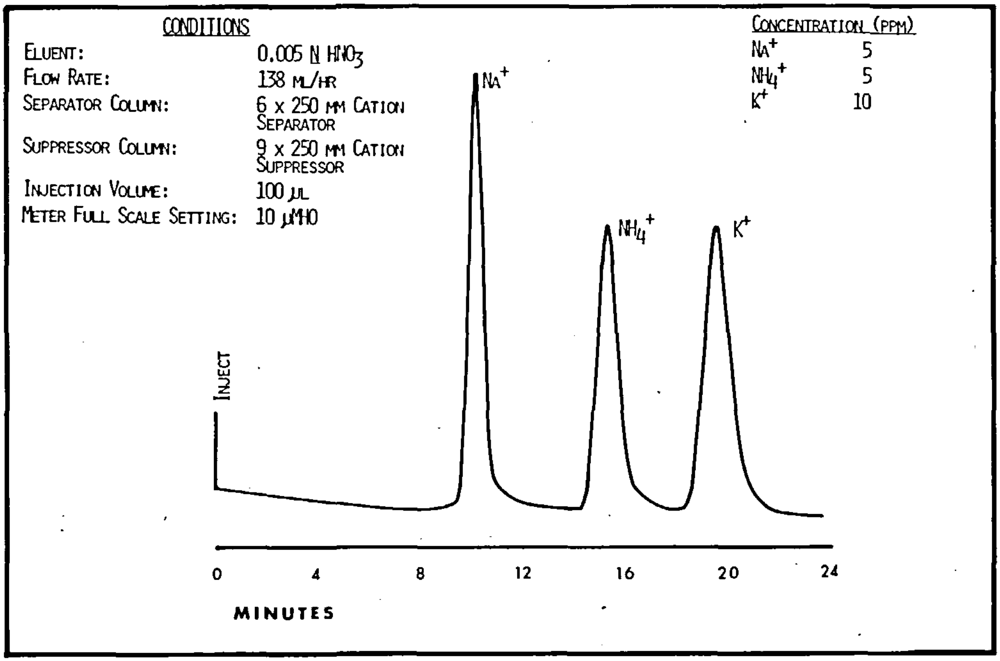


FIGURE 2. Separation of monovalent cations.

der the name HPLC (High Performance Liquid Chromatography). However, many cations and anions (e.g., $NH_4^+$ or $Cl^-$) cannot conveniently be analyzed by normal HPLC methods, chiefly due to column and detector limitations. It is at this extreme end of the polarity scale, where constituent pK values are low, that IC is the most powerful separation and detection method. Types of compounds analyzable by IC range in volatility from small primary amines with very high volatility to inorganic salts with very low volatility.

In recent years liquid chromatography has evolved toward high-speed automated analysis of compounds. This has been accomplished by coupling high-pressure separations systems to continuous-monitoring detectors. Ion exchange chromatography has been used successfully in these systems only if the separated components absorb visible or ultraviolet light or can be detected by refractive index or electrochemical changes. In some cases, species that do not absorb light are chemically combined to form light-absorbing species. One example is the use of ninhydrin in amino acid analysis. But simple ions such as $Cl^-$, $SO^{2-}_4$, and $NH_4^+$ cannot easily be detected with good sensitivity by the conventional detection systems used.

Ions in solution exhibit electrical conductance; thus a good universal ion detector could be based on conductivity. Unfortunately, eluents used in ion exchange separations contain strong electrolytes and exhibit high conductivity. The classical problem in using conductimetric detection with ion-exchange chromatography is the presence of this high background conductivity signal. This detector limitation is one main reason why the use of ion exchange resins has not expanded in modern HPLC. Suppressor-type IC is a technique which has been developed to cope with the high background signal problem. A second ion-exchange column, called the suppressor, is used in series with the separator column. This second column converts the eluent to a low conductivity species after separation of the sample constituents has taken place. Eluent suppression is discussed in more detail in Section II. A second IC method, utilizing electronic

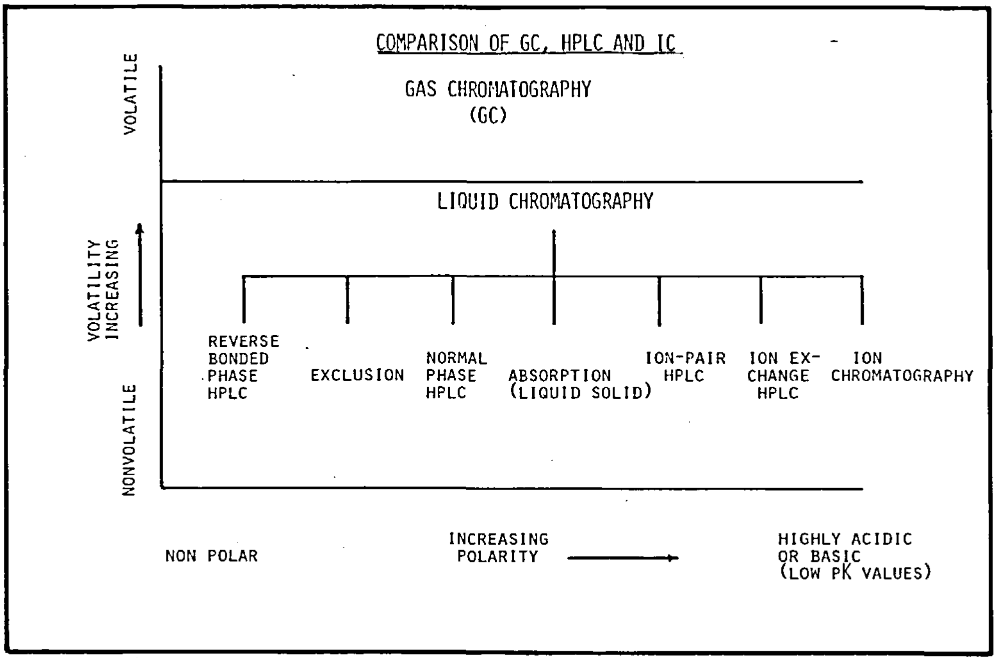


FIGURE 3. Comparison of GC, HPLC, and IC.

method, utilizing electronic background suppression and no suppressor column, has recently been demonstrated. Since this is a very new technique, most of this review article will cover suppressor-type IC.

### C. Advantages and Current Limitations of IC

Ion chromatography is uniquely powerful in solving problems in ion analysis. IC has many of the same advantages as HPLC:

1. High sensitivity
2. Freedom from matrix interferences
3. Specificity in analyzing similar types of ions
4. Multiple ion determinations in a single chromatographic run

One of the main advantages of IC is the ability to detect ions at microgram to nanogram levels. Actual sensitivity is determined by the sharpness of the eluted peaks, the magnitude of these peaks above background, and freedom from artifacts in the chromatogram. IC is routinely capable of accurately determining many ions at sub-part per million (ppm) levels. Analysis at one part in $10^8$ has been achieved by Stevens for $Na^+$, $K^+$, $Cl^-$, and $SO_4^{2-}$.[2] Injection of samples as large as 1 mℓ allows sub-ppm detection because the peaks do not broaden significantly with large-volume injections. In addition, use of concentrator columns allows detection of ions at part per billion (ppb) levels, with calculated detection limits considerably below 1 ppb.[3] These columns are made of resins similar to the separator columns, and samples as large as 50 to 100 mℓ can be passed through the column and thus concentrated.

Two other major features of IC are the specific determination of closely related ions and the sequential determination of several ionic species in a single isocratic run, even in very complex matrices. IC is remarkably specific for ions. For example, fluoride,

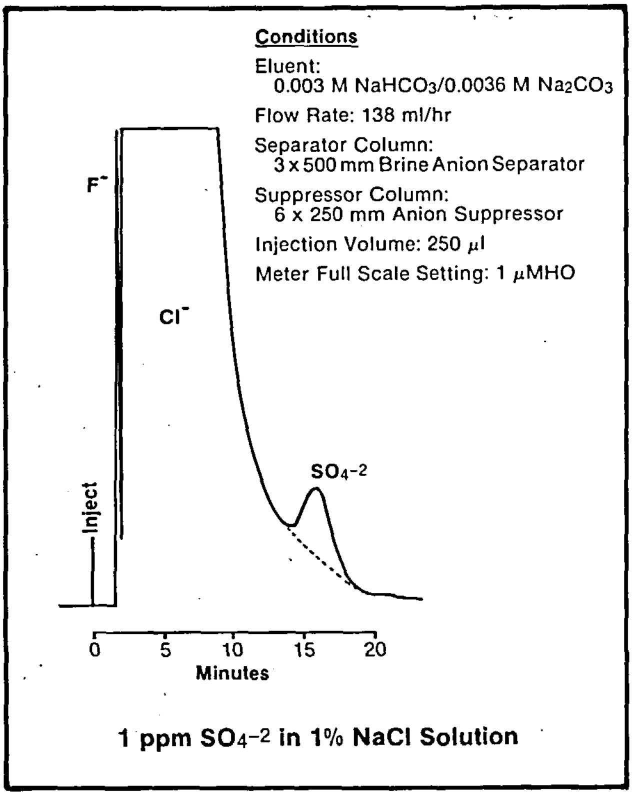


FIGURE 4. Trace sulfate in 1% brine.

chloride, and bromide are all quite well separated, as shown in Figure 1. Iodide elutes much later with the stated instrument conditions since it has a greater affinity for the column packing. Also, ammonia is totally separated from even the small, very volatile primary amines such as methylamine. Some of the more interesting ion speciations are nitrite-nitrate, sulfite-sulfate, and hexavalent chromium and other anionic metal oxides. The ion profile of the samples often provides interesting additional information about the sample, such as other ions that are present and were previously unidentified. Although individual ion analysis by other methods is faster for single ions, increased equipment costs or time necessary to make instrument changes and recalibrations with other methods more than compensate for the seeming "slowness" of the IC. Specialized techniques can be developed to decrease analysis time for specific ions if the samples are all similar. Complex matrices such as brine and caustic solutions present little problem to ion chromatographic analysis. Dilution is usually the only pretreatment necessary. Figures 4 and 5 show the determination of trace $SO_4^{2-}$ in 1% NaCl and $Cl^-$, $ClO_3^-$, and $SO_4^{2-}$ in 50% NaOH, respectively.

Present limitations of the ion chromatographic technique come from three sources. First, ions with pK values higher than seven have poor detection limits, even though they may be separated by IC. Cyanide, borate, silicate, and phenates are among the anions presently not detectable by IC at trace levels. The second major limitation comes from irreversible reactions of the separated ions with the suppressor resin. Transition and heavy metal ions precipitate as hydroxides in the suppressor used in routine cation analysis. The third limitation is the amount of organic materials that can be present in the sample. Alcohol content above 10% in the sample, for example, can cause channeling in the separator column, and ruin the resin bed.

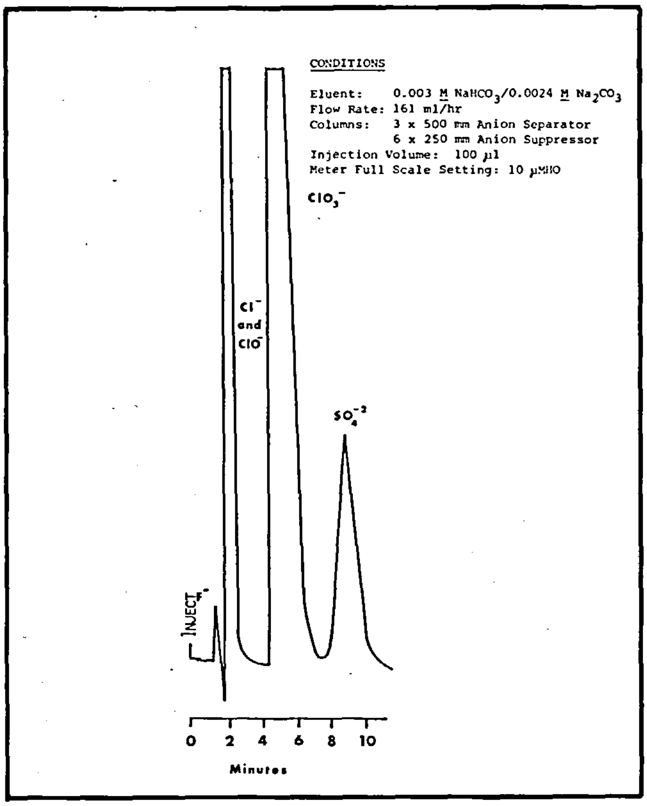


FIGURE 5. Anions in 50% caustic after sample dilution.

## II. PRINCIPLES AND PRACTICE OF IC

### A. Principles of Operation

Suppressor-type ion chromatography is a combination of ion exchange, eluent suppression, and conductimetric detection. The basic principles will be illustrated for a system configured to do anion determinations (the most common use). Figure 6 shows the basic components of an ion chromatograph needed to do anion separations.

The low-capacity, pellicular separator column provides high efficiency separation of the anionic species. The anions in the sample and those in the eluent compete for the fixed active sites of the resin. Differential migration of the sample species is the result of differences in relative affinities of the anions for the active sites. Higher affinity species will be retained longer on the column; the resultant peaks will elute later and will be broader than species with lower affinity. The most commonly used eluents for anion separations are mixtures of NaOH, $NaHCO_3$, and $Na_2CO_3$. The hydroxide, bicarbonate, and carbonate anions are the eluting ions (the species which compete with the sample ions for the active site).

The suppressor column is involved in a number of important chemical reactions. One reaction is the conversion of the highly conductive eluent to a form which has low conductivity. Equations 1, 2, and 3 illustrate these reactions for the eluent constituents commonly used in anion analysis. The parentheses around some of the reactants indicate the ions at the fixed active site of the resin in the suppressor column. The underlined species represent the slightly conductive suppressor effluent.

$$(SO_3^- - H^+) + NaOH \rightleftarrows (SO_3^- - Na^+) + H_2O \quad (1)$$

$$(SO_3^- - H^+) + NaHCO_3 \rightleftarrows (SO_3^- - Na^+) + H_2CO_3 \quad (2)$$

$$2(SO_3^- - H^+) + Na_2CO_3 \rightleftarrows 2(SO_3^- - Na^+) + H_2CO_3 \quad (3)$$

In each case, the sodium cation associated with the eluting anion is stoichometrically exchanged for the protons of the suppressor resin. The resulting protonation of the eluting anion results in species with low conductance, either $H_2O$ or $H_2CO_3$. A second reaction of the suppressor is conversion of the anion species to a single, highly conductive form

$$Na^+ - Anion^- + (SO_3^- - H^+) \rightleftarrows (SO_3^- - Na^+) + H^+ - Anion \quad (4)$$

The conversion of the anions to their acid analogs enhances their detectability and eliminates the need for individual calibrations plots for every cation-anion combination.

Electrical conductance is generally a simple function of ionic species concentration. This is particularly applicable in the low concentrations best handled by IC (10 $\mu g/l$ to 1 $g/l$). Quantitation can be accomplished by the usual external or internal or standard addition techniques.

Another effect of the suppressor is separation of species by ion exclusion chromatography. This form of chromatography is based on Donnan exclusion, reverse phase partition, adsorption, and other mechanisms. The high-charge density of the interior of the resin bead is caused by the high capacity of the suppressor resin. Species which are completely dissociated are prevented from entering the bead. Strong acids are not retained, while weaker acids are allowed to enter the bead and are therefore retarded and separated from the strong acid species. This method has recently been applied to the separation of some organic acids.

### B. Choice of Eluents

A variety of low concentration eluents have been used to obtain IC separations. These eluents and the associated suppressor reactions are summarized in Table 1 for anion analysis and in Table 2 for cation analysis. The sodium phenoxide/sodium hydroxide eluent mixtures first used for anion separations have been replaced by mixtures of $Na_2CO_3$, NaOH, and $NaHCO_3$. For most separations the millimolar carbonate eluents offer equivalent separations without the eluent degradation and column poisoning problems of the phenate eluents. Recently, $Na_2B_4O_7$ mixtures have been used to separate short-chain aliphatic carboxylic acids from inorganic anions. These acids elute rapidly and are poorly separated from inorganic anions by the $NaHCO_3/Na_2CO_3$ mixtures. Greatly increased separation is seen with the highly selective borate eluents. Water and $Na_2B_4O_7$ have also been used for separation of some acids by ion exclusion chromatography (Figure 7). Millimolar concentrations of $HNO_3$ are used with cation column sets to obtain separations of the Group IA metal ions ($Na^+$, $K^+$ etc.), ammonium ion, aliphatic amines, and some quaternary ammonium ions. Group IIA ions ($Ca^{+2}$, $Mg^{+2}$, etc.) are usually eluted with phenylenediamine dihydrochloride on a different set of cation columns. Although this eluent shows many of the problems associated with phenate type eluents, it is considerably superior to $HNO_3$ for elution of these species. The lower concentration of the phenylenediamine dihydrochloride allows more samples to be run before the suppressor is exhausted. The other listed cation eluents show few advantages and are not widely used in IC at this time.

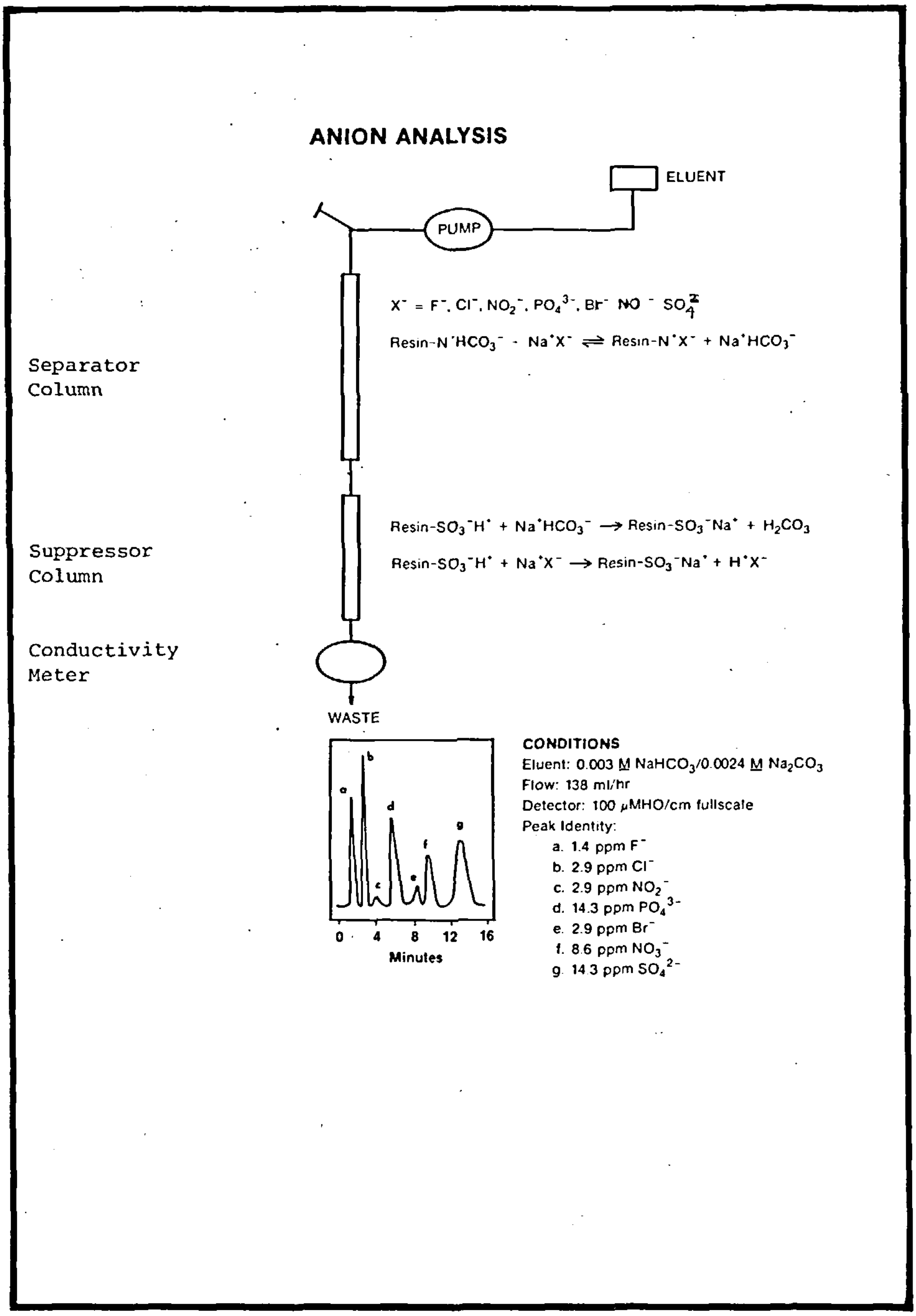


FIGURE 6. Basic components necessary for anion determinations.

## C. Hardware

The IC is a low pressure, high performance liquid chromatograph. Since the IC technique is closely related to conventional HPLC, many similarities exist between the instrumentation of the two techniques. Both instruments contain liquid eluents, an adjustable "constant volume" pump, a separation column, a liquid switching system, and on-line detectors.

## Table 1
## ELUENTS USED IN ANION ANALYSIS

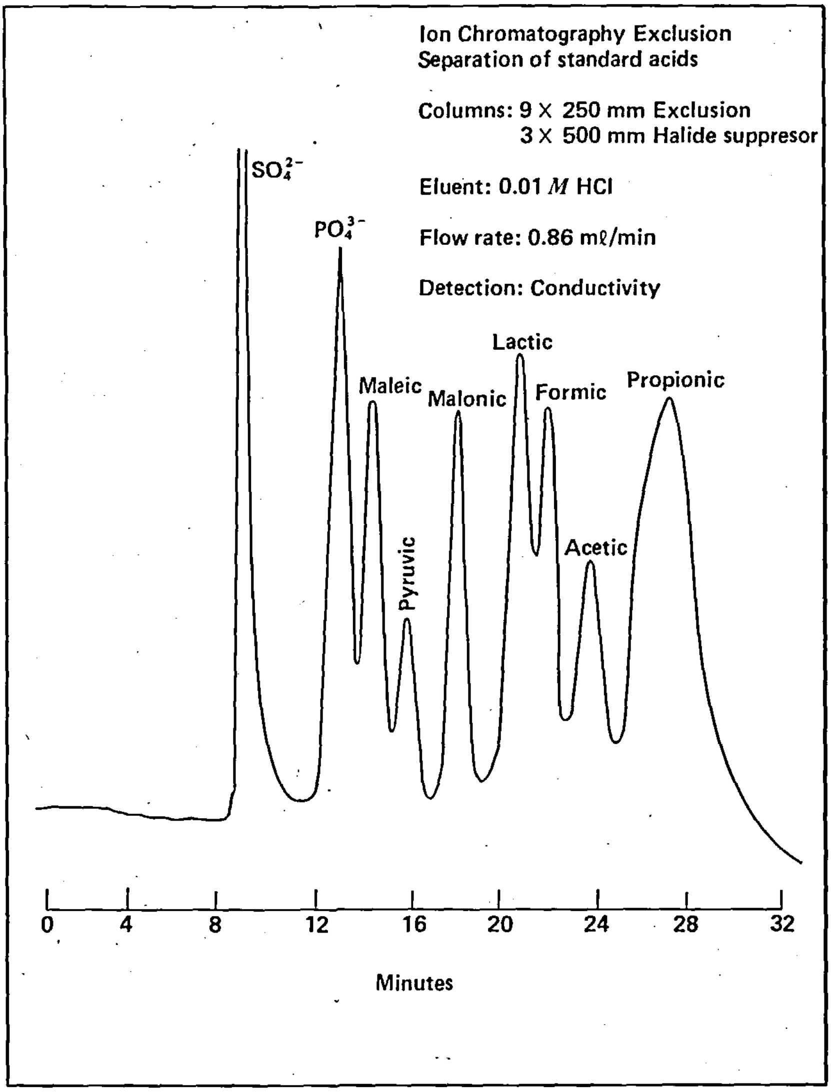
| Eluent | Eluting ion | Relative strength | Suppressor form | Column effluent | Comments |
|---|---|---|---|---|---|
| NaOH | $OH^-$ | Weak | $H^+$ | $H_2O$ | Mixed with $Na_2CO_3$ or $NaHCO_3$ |
| $C_6H_5ONa$ | $C_6H_5O^-$ | Medium-strong | $H^+$ | $C_6H_5OH$ | Not frequently used |
| $NaHCO_3$ | $HCO_3^-$ | Weak | $H^+$ | $H_2CO_3$ | General use |
| $Na_2CO_3$ | $CO_3^{-2}$ | Strong | $H^+$ | $H_2CO_3$ | General use |
| $Na_2B_4O_7$ | $B_4O_7^{-2}$ | Very weak | $H^+$ | $H_2B_4O_7$ | Works with carboxylic acids |
| $Na_4EDTA$ | $Na_4EDTA$ (depends on pH) | Strong | $H^+$ | EDTA | pH adjusted with NaOH |

## Table 2
## ELUENTS USED IN CATION ANALYSIS

| Eluent | Eluting ion | Suppressor form | Suppressor reaction |
|---|---|---|---|
| $HNO_3$ | $H^+$ | $OH^-$ | Neutralization |
| $AgNO_3$ | $Ag^+$ | $Cl^-$ | Precipitation |
| $Cu(NO_3)_2$ | $Cu^{+2}$ | $NH_3$ | Complexation |
| $Hg(NO_3)_2$ | $Hg^{+2}$ | $Cl^-$ | Complexation |
| Pyridine · HCl | Pyridine + $H^+$ | $OH^-$ | Neutralization |
| Analine · HCl | Analine + $H^+$ | $OH^-$ | Neutralization |
| Phenylenediamine dihydrochloride | Phenylenediamine and $H^+$ | $OH^-$ | Neutralization |

Of more interest are the differences between the two types of instruments. Chemically inert liquid tubing, columns, and valves are necessary in IC because the eluents and regenerating solutions are strongly acidic or basic. Present IC instrumentation uses Teflon® tubing, glass columns, and Kel-F® and Teflon® valves. These components limit the IC to 700 psig maximum system pressure. While conventional HPLC instruments are largely constructed of stainless steel, the IC has only two very small stainless steel parts — the pumping chamber itself and the electrodes of the conductivity cell. Another unique feature of the IC is the suppressor column regeneration system. Since the suppressor column is periodically completely exhausted (converted from the active form to a nonsuppressing form), another pump, a valving system, and a timer are needed to control resin regeneration (reconversion to active form). The regeneration sequence is fully automatic and is initiated by the IC operator when the suppressor is exhausted. First, a strong electrolyte regenerating solution is pumped through the suppressor to convert the resin to the active form. In the case of anions, 1N $H_2SO_4$ converts the expended $Na^+$– form of the suppressor resin to the active $H^+$– form. Sodium hydroxide is used to convert the cation suppressor to the $OH^-$– form. The excess regenerant is then flushed out with water and the regenerant pump stopped when the water wash is complete. Typical cycle time is ½ to 1 hr. Two suppressor columns used in parallel allow almost uninterrupted operation because one suppressor can be regenerated while the second is being used for sample analysis.

The IC detector system is also quite different from conventional HPLC detectors. The IC detector can be thought of as having two parts, the suppressor column and the conductimetric detector. Without the suppressor column the eluent conductivity



Acid Standards by ICE

FIGURE 7. Weak acid determination by ion exclusion.

would be too high for trace ion analysis by conductance detection The suppressor column is required to provide a constant low conductivity background on which the separated peaks are detected. A flow conductivity cell with a 6 $\mu\ell$ volume is connected to a high sensitivity conductivity meter. Since conductivity varies with temperature, the cell and meter electronics are temperature compensated. System output is 0 to 1 V with linear scaling of $10^4$ $\mu$MHO/cm or $\mu$S/cm. Scale ranges run from 0.1 to 1000 in both decades and factors of 3.33. Chromatograms are normally recorded on a two-channel strip chart recorder, with one channel set at 0 to 1 V input and the second channel set at lower input to enhance detection of small peaks. Peak height from these chromatograms is used to calculate species concentration. Until very recently, little success has been achieved with automatic data handling of IC peaks. Peak height determination appears to be adequate.

Dionex Corporation (Sunnyvale, Calif.) is the only company licensed to manufacture and to sell suppressor-type ion chromatographs. There are currently four Ion Chromatograph models available. The Model 10 IC is a complete single system to do either anion or cation separations. A dual pumping system, single detector Model 14 Ion Chromatograph can be used to do both anions and cations without changing eluents, regenerants, and columns. Only anions or cations can be configurated at any one time, although the changeover time is very short. An automatic operation Model 12 AutoIon$^{TM}$ has been introduced recently. The Model 16IC has two pumping systems and two detectors. This system can be used for anion/cation determinations or for coupled chromatography.

An instrument for doing nonsuppressed anion chromatography is available from Wescan Instruments (Santa Clara, Calif.). This instrument utilizes a silica-based separations column and a specially developed conductivity cell to electronically suppress the eluent background. No separation column is available for cation determinations.

### D. Resins Used in IC

The IC is unique in using two columns in series for entirely different purposes — one for species separation and the other as part of the detector system. High-performance liquid chromatographic systems normally use a single column for separation. The two IC columns are packed with quite different ion-exchange resins.

The separator columns for both cation and anion determinations are packed with pellicular styrene-divinylbenzene resins.[4] Precolumns are used in front of the separator columns in either anion or cation analysis. These short columns are filled with resins similar to the separator resins. The precolumn protects the separator column by trapping particulate materials, sorbing organic species, and exchanging ions that can irreversibly attach to the resin active sites. The resins used for both precolumns and separators have exchange capacities in the range of .02 to .05 meq/g of resin. They also have excellent mass transfer characteristics and are stable over wide pH ranges. Silica-based pellicular resins have been tried for anion analysis, but these are not stable at the pH levels normally employed in suppressor-type IC. Cation separator resins are surface-sulfonated styrene-divinylbenzene resins with sulfonic acid (i.e., $SO_3^-$) active sites. Large diameter particles yield low system pressures and excellent separations. A resin similar to that used for cation separations is used as the substrate for the anion separator resin. In this two-part resin, aminated latex particles are bonded in a monolayer to the sulfonic acid active sites of the substrate. This creates a two-part pellicular aminated resin, with relatively little degradation and low pressure. The ion exchange capacity of this resin is controlled by both the capacity of the substrate and the amount and size of the latex particles.

The very low eluent strengths used for separation allow a large number of samples to be injected before the suppressor is completely expended. Typically, 40 to 60 anion samples and 20 to 30 cation samples can be run before suppressor resin beds require regeneration. Separator columns can be used for 1000 or more samples before replacement. Of course, this depends on the nature of the samples and the care the analyst takes to limit potential problems. More complex samples often require dilution prior to injection. In case of simple samples like rainwater, 5000 or more samples have been injected before separator column replacement. Use of precolumns greatly prolongs separator lifetimes. The precolumn requires weekly cleaning and periodic replacement when the system is in continuous operation. Suppressor columns should last for 5000 or more samples before a replacement column is needed.

### Table 3
### IONS SEPARATED BY IC

| ANIONS | | CATIONS | |
|---|---|---|---|
| Inorganic | Organic | Inorganic | Organic |
| Fluoride | Formate | Lithium | Mono-, di, and tri-methylamine |
| Chloride | Acetate | Sodium | Tetramethyl ammonium bromide |
| Chlorate | Propionate | Ammonium | Mono-, di-, and tri-ethyl amine |
| Bromide | Butyrate | Potassium | Tetraethyl ammonium bromide |
| Bromate | Mono-, di-, and tri-chloroacetate | Rubidium | *n*-Butylamine |
| Iodide | Glycolate | Cesium | Di-*n*-propylamine |
| Iodate | Oxalate | Calcium | Cyclohexylamine |
| Nitrite | Maleate | Magnesium | Tri- *n*-butylamine |
| Nitrate | Fumarate | Barium | Mono-, di-, and tri-ethanolamine[•] |
| Azide | Succinate | Strontium | Mono-, di-, and tri-isopropanolamine[•] |
| Sulfite | Malonate | | |
| Sulfate | Itaconate | | |
| Thiosulfate | Lactate | | |
| Ortho-phosphate | Acrylate | | |
| Pyro-phosphate | Methacrylate | | |
| Tripoly-phosphate | Tartrate | | |
| Sulfide[•] | Benzoate | | |
| Chromate | Citrate | | |
| Arsenate | Hydroxycitrate | | |
| Thiocyanate | Methyl phosphonate | | |
| Carbonate | Ethyl methyl phosphonate | | |
| Tetrafluoroborate | Mon- and di-butyl phosphate | | |
| Dithionate | Sarcosinate | | |
| Rhenate | Cyclamate | | |
| Hypochlorite | Thioacetate | | |
| Cyanide[•] | Thiolactate | | |
| | Thioglycolate | | |
| | Methyl sulfate | | |
| | Dibutoxyethylphthalate[•] | | |
| | Pyruvate | | |

This species may not be separable with existing columns and recommended eluents or without special instrument modifications.

## III. APPLICATIONS

### A. Scope of IC

Ion chromatography has found widespread use in applied research, trace and ultratrace analysis, quality control, and many other areas where analytical chemistry is used. A wide variety of samples, ranging in complexity from rainwater to Kraft black liquors, have been analyzed by IC. Table 3 is a summary of the ions that have been separated and detected by IC. This tabulation is intended to show feasibility of possible IC separations. Not all the ions can be detected at trace levels nor can all the ions be separated from every other listed ion. Indeed, some of the listed species may not be separable with existing columns and recommended eluents or without special instrument modifications. These ions are indicated in Table 3. An Analytical Methodology Guide is available from Dionex Corporation.[5] The Guide is a detailed compilation covering most of the ions listed in Table 3. Approximate elution time with standard

Table 4
COMPARISON OF ION CHROMATOGRAPHIC (IC) METHOD WITH COLORIMETRIC METHODS FOR SULFATE AND NITRATE IN ACTUAL AMBIENT AEROSOLS

| | $SO_4^=$ (μg/mℓ) | | $NO_3^-$ (μg/mℓ) | |
|---|---|---|---|---|
| Sample number | Ion chromatography | Methyl thymol blue | Ion chromatography | Cadmium reduction |
| 1 | 65.1 | 66.2 | 9.23 | 14.8 |
| 3 | 79.4 | 72.9 | 21.2 | 20.4 |
| 5 | 29.2 | 30.9 | 6.4 | 7.0 |
| 7 | 52.9 | 53.2 | 23.6 | 23.5 |
| 9 | 35.5 | 35.3 | 9.3 | 9.6 |
| 11 | 88.8 | 82.1 | 4.3 | 4.5 |
| 13 | 23.6 | 25.1 | 5.2 | 5.9 |
| 15 | 35.9 | 36.5 | 17.5 | 18.2 |
| 17 | 47.6 | 48.7 | 12.3 | 12.4 |

From Mulik, J., Puckett, R., Williams, D., and Sawicki, E., *Anal. Lett.*, 9(7), 653 (1976). With permission.

instrument configurations, known interferences, and estimated minimum detection limits are listed for a great many of these anions and cations.

At the time of this review, publications on IC are few in number — 25 published papers and 2 books covering the papers presented at the Symposia on Ion Chromatographic Analysis of Environmental Pollutants. Numerous papers have been presented at technical conferences and are presently in preparation for publication; these works will be referenced where applicable. However, a survey of only these works would not cover many of the interesting applications of IC. A paper such as this is intended to be a widescope review. Since great emphasis is on applications, unpublished works will necessarily be referenced if these are pertinent and important. Thus, many private communication references will be used in this paper. To facilitate communication with people who are experts in particular application areas, the scientist's employer and geographic location will be included. The uses of IC will be detailed by applications area.

## B. Air Pollution Analysis

One of the first areas where IC was recognized as a useful analytical method was in air pollution analysis. Mulik recognized the potential of IC for analysis of air pollution samples, particularly ambient aerosols. Aqueous extractions of particulates collected on high-volume glass fiber filters were analyzed for $NO_3^-$ and $SO_4^{2-}$. Table 4 shows comparisons for field-collected samples analyzed for $NO_3^-$ and $SO_4^{2-}$ by established methods and by IC.[6] Use of the IC subsequently spread rapidly to many other air pollution analyses.

In April 1977, the first Symposium on the Application of Ion Chromatographic Analysis to Environmental Pollutants was held. The proceedings of this symposium have been compiled into the first book on IC.[7] Mulik presented results for ammonium ion from ambient aerosol analysis.[8] Other papers reported similar results for ambient aerosols analysis. In one paper, IC analysis of aqueous extracts of high-volume filters were compared to fluoride ion analysis by thorin nitrate titration, nitrate ion analysis by brucine colorimetric analysis, and sulfate ion analysis by barium perchlorate-thorin

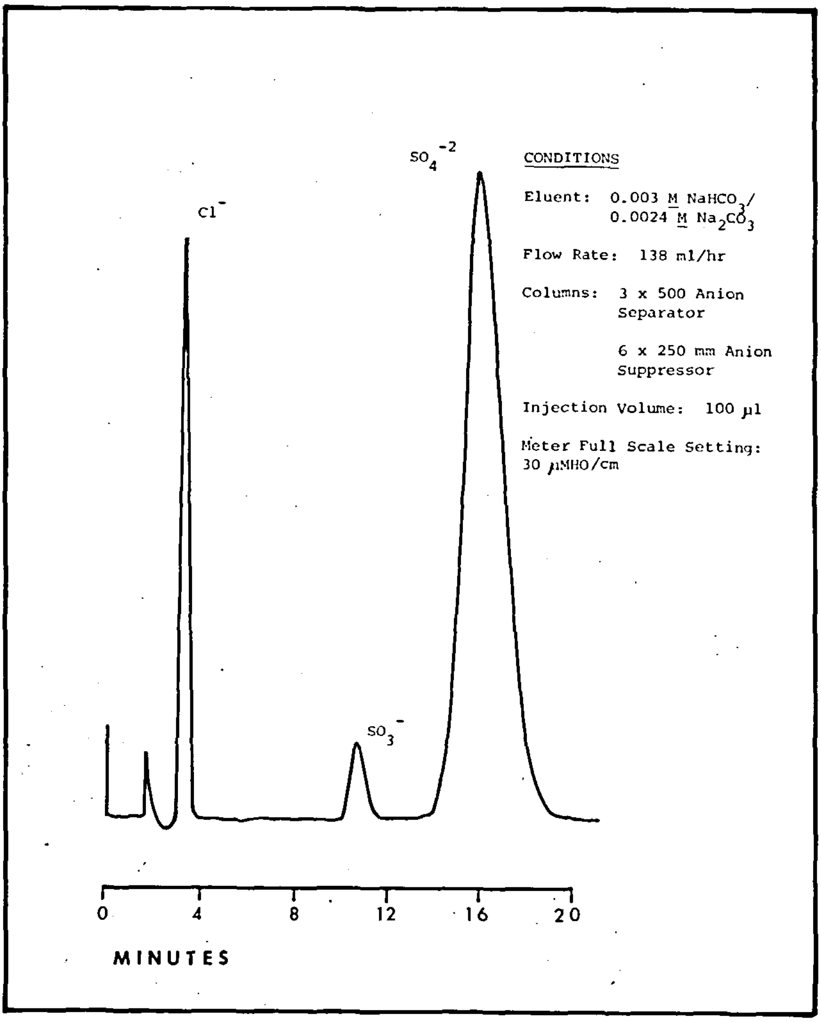


FIGURE 8. Separation of sulfite and sulfate.

titration.[9] Other papers reported quantitative IC analyses of $NO_3^-$ and $SO_4^{2-}$ ions on filter samples taken in southern California[10] and a comparison of IC analysis to analyses by fluoride selective electrode determinations and automated wet chemical analyses for nitrate, sulfate, chloride, and ammonium ions.[11] All of these papers indicated good agreement between IC and established methods. The high sensitivity and specificity of IC were noted by other scientists at the symposium. A large number of blank high-volume filter papers were analyzed by IC and automated wet chemistry for trace levels of ions.[12] Results by both methods were quite comparable. The author noted that the sum of the IC concentrations of widely separated $NO_2^-$ and $NO_3^-$ were found to agree quite well with the total ($NO_3^-$ + $NO_2^-$) value of the nonspecific automated cadmium reduction method. IC studies were also reported for particulates collected at high altitudes and on interfering reactions between glassware and dibutoxyethylphthalate.[13,14] The unique ability of the IC to separate $SO_3^{2-}$ and $SO_4^{2-}$ (Figure 8) has been exploited in the analysis of flue gas desulfurization samples taken from coal-fired power plants with limestone scrubbers,[15] and from sulfuric acid mists in gas streams.[16] A second symposium was held in October 1978. The second book on IG, published in

Table 5
TYPICAL ANALYSIS PERFORMED BY IC IN THE PULP AND PAPER INDUSTRY

| Sample type | Analyzed for | Concentration range |
|---|---|---|
| Hatchery water | $NO_3$–N | 20—60 ppb |
| | $PO_4$–P | 5—20 ppb |
| Paper mill effluent | $SO_4$–S | 10—100 ppm |
| Biopond water | $NO_3$–N | 10—50 ppb |
| | $PO_4$–P | 100—175 ppb |
| KCl soil extract | $SO_4^{-2}$ | 100—300 ppm |
| Acetate soil extract | $SO_4^{-2}$ | 10—100 ppm |
| Ammonium fluoride soil extract | $PO_4^{-3}$ | 1—10 ppm |
| Sulfuric acid soil extract | $PO_4^{-3}$ | 10—50 ppm |
| Bicarbonate soil extract | $SO_4^{-2}$ | 1—5 ppm |
| Pulping liquid (green) | $S^{-2}$ | Very high |
| | $SO_4^{-2}$ | Very high |

late 1979, covered the papers presented at this meeting.[17]

Ambient $SO_2$ gas was analyzed by IC after trapping the gas in scrubbers.[18] The scrubbing solution converts the $SO_2$ gas to sulfate ion. Sensitivity, linearity, interferences, and agreement between the IC and the modified West-Gaeke Federal Reference Method were reported. The IC method gave results comparable to the Reference Method without exhibiting the well-known temperature dependence of the Reference Method.

The authors are aware of other unpublished air pollution applications of IC. One of these is the analysis of particulate materials collected in low altitude fly-by samples.[19] Extractable anion species from coal fly ash[20] and arsenic compounds in samples collected near coal-burning power plants have been studied.[21] Several industrial hygiene applications related to air pollution have been reported. These include analysis of formic acid vapor,[22] acetylchloride vapor,[23] and $SO_4^{2-}$ in industrial plants.[24] One final area where IC has been extensively used is in the analysis of rainwaters. Numerous scientists have analyzed the ionic content of rain and snow. Chloride, nitrate, sulfate, phosphate, potassium, sodium, ammonium, calcium, and magnesium ion analyses have been reported.[25,26] Maximum information on even trace concentrations of these ions is possible because of the sensitivity of the ion chromatograph.

### C. Water Pollution Analysis

One area where IC is naturally applicable is water analysis. Although not yet EPA approved, the IC has found considerable use in individual water labs. Water analysis samples range from the very simple samples for trace determination of micronutrients ($NO_3^-$, $NH_4^+$, $PO_4^{3-}$) in biopond waters to the analysis of very complex high concentration green and Kraft-black pulping liquors for oxalate and sulfate anions.[27] Table 5 shows the range of concentrations for water samples obtained from the pulp and paper industry. Typical common anion determinations in natural ground waters are illustrated by three U.S. Geological Survey Reference Samples Numbers 54, 58, and 60. Results for the IC analysis and for USGS values are compared in Table 6. It should be noted that the USGS values are the result of a long-term interlaboratory study using a variety of analytical methods. A more thorough study showed excellent IC recoveries

Table 6
COMPARISON OF IC VALUES TO REPORTED VALUES FOR USGS REFERENCE SAMPLES

| Sample number | $F^-$ - ppm | | $Cl^-$ - ppm | | $NO_3^-$ - ppm | | $SO_4^{-2}$ - ppm | |
|---|---|---|---|---|---|---|---|---|
| | USGS | IC | USGS | IC | USGS | IC | USGS | IC |
| 54[a] | 1.03 | 0.9 | 186 | 200 | 7.2 | 6.5 | 537 | 540 |
| 58[b] | 0.92 | 0.5 | 1.7 | 1.4 | — | 0.4 | 43.5 | 43 |
| 60[c] | 0.9 | 0.8 | 57 | 55 | — | 20.7 | 140 | 165 |

[a] $Br^-$ 0.4 ppm.
[b] $NO_2$ 0.07 ppm.
[c] $Br^-$ — USGS 0.3 ppm/IC 0.3 ppm; $PO_4$ — USGS 4.6/IC 3.8 ppm; $NO_2$ — 0.02 IC.

for a variety of anions.[28] Many applications in the analysis of industrial wastewaters have been found for IC. Azide anion in air bag deployments and water effluents have been investigated.[29] Electronic component wash waters[30] and industrial plant effluents[31,32] have been analyzed by IC. The growth of IC uses in water pollution analysis should continue.

### D. Quality Control

The complex matrices of samples analyzed in quality control applications are not usually a problem for ion chromatography. The most common treatment prior to injection into the ion chromatograph is dilution. Routine quantitative analysis of plating bath solutions for $F^-$, $Cl^-$, and $SO_4^{2-}$ have been performed.[33] Hexavalent chromium ion has also been separated in these solutions. The $Cr^{+6}$ behaves as an anionic species while the $Cr^{+3}$ appears to be retained on the anion suppressor and cannot be currently estimated. Brine and caustic samples are often directly analyzable on the IC. Separation of acetate, nitrate, bromide, sulfate, and phosphate ions in geothermal brines have been done by IC.[34,35] Determination of $I^-$ and $SCN^-$ anions used as oil field tracers[36,37] and direct analysis of $Ca^{+2}$ and $Mg^{+2}$ in high concentration brines[38] have also been reported. Improved separation and detection of trace levels of $SO_4^{2-}$, $PO_4^{3-}$, $I^-$, and $SCN^-$ in 1% NaCl solutions have been obtained with brine anion separator columns.[39] Chloride removal by using a silver form pretreatment column has been performed.[40] Caustic solutions have been injected into the IC for analysis of $Cl^-$, $ClO^-$, $ClO_3^-$, and $SO_4^{2-}$ ions.[41] The $Cl^-$ and $ClO^-$ were not separated with the particular eluent used for this work. Ion exclusion chromatography has been applied to total carbonate analysis in caustic samples, waters, and soft drinks (Figure 9).[42] The $H^+$-form ion exclusion column is also an effective pretreatment for the caustics. The hydroxide ion is neutralized and the overlap of the $Cl^-$ and $CO_3^{2-}$ peaks is eliminated with this column. The large void volume peak in this separation method contains the unseparated strong acid species. This peak is trapped on a concentrator column on the second pumping system of a Model 16IC. The later eluting carbonate peak is diverted to waste after detection. This allows subsequent quantitative determination of the $Cl^-$, $ClO_3^-$, and $SO_4^{2-}$ in caustics.

Commercial formulation and food analysis are important applications of IC. The following list summarizes some of these uses:

1. Assay of dimethylformamide and determination of trace levels of volatile amines, ammonia, and inorganic cations[43]

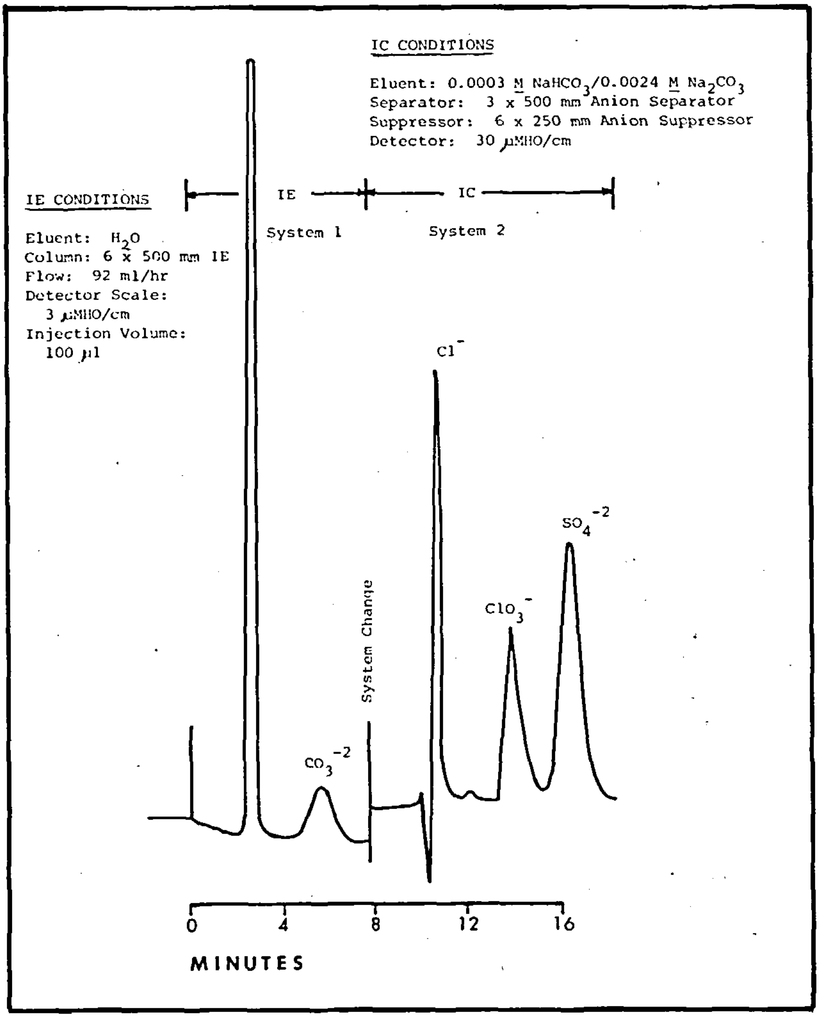
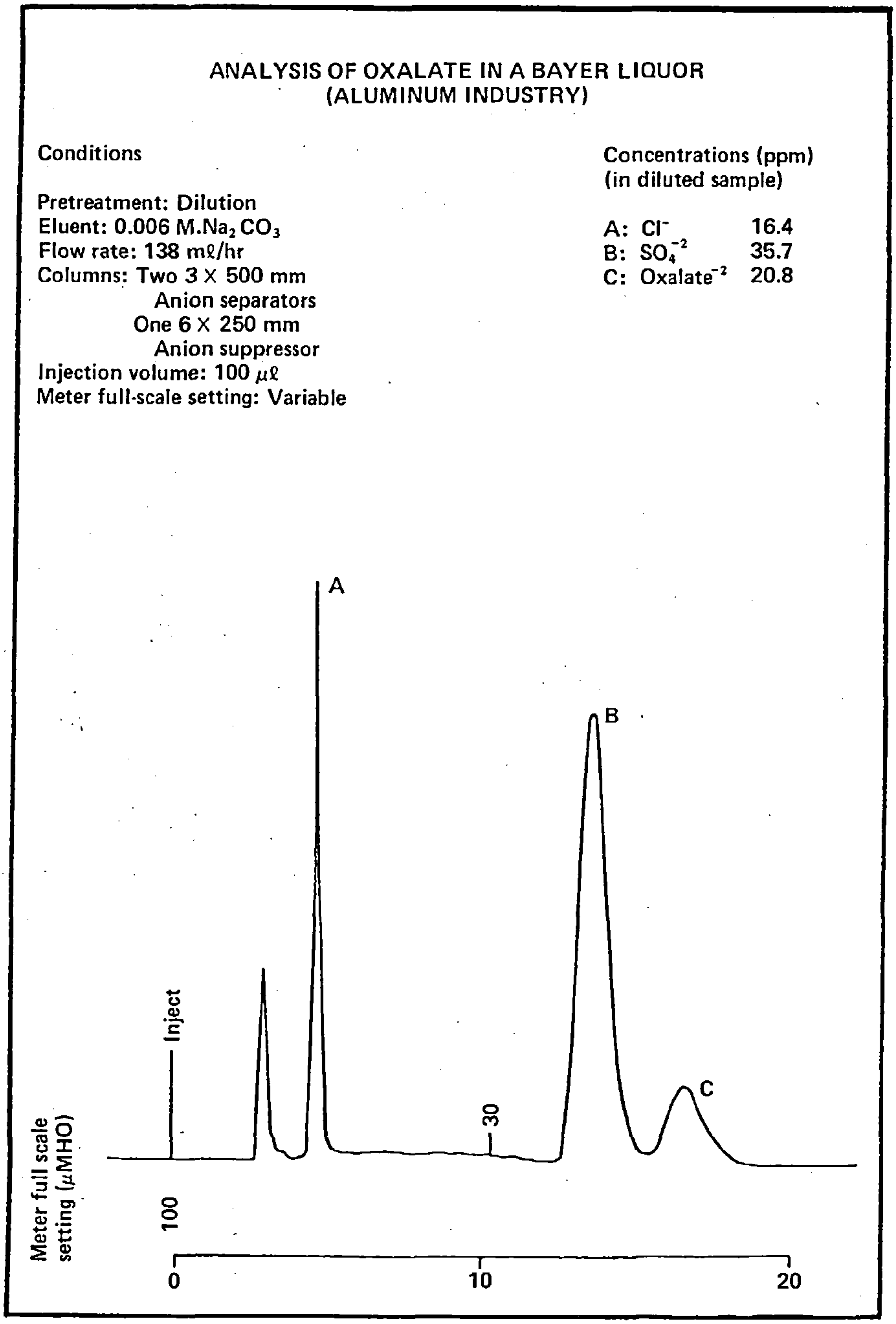


FIGURE 9. Analysis of caustic by ion exclusion combined with ion chromatography.

2. Assay of percentage levels of glycolate, chloroacetate, and chloride anions in surfactants[44]
3. Assay of $F^-$, $PO_4^{3-}$, and $SO_4^{2-}$ ions in fertilizer samples[45]
4. Determination of oxalate and sulfate impurities in Bayer liquors (Figure 10)[46]
5. $NO_2^- - NO_3^-$ ions in sulfuric acid from a nitration process[47]
6. Determination of $C_1 - C_{10}$ carboxylic acids[48]
7. Analysis of ethylene glycol decomposition products[49]
8. Fluoride determination on tobacco products[50] and digested milk substitutes[51]
9. Nitrate determination in extracted barley[52]
10. Toothpaste additives[53]
11. Trace chloride and sulfate in food dyes[54]

## E. Clinical Chemistry

Clinical chemistry applications of IC are not extensive. Those first reported were cation and anion determinations in urine, tissue extracts, cerebral spinal fluid, and



ANALYSIS OF OXALATE IN A BAYER LIQUOR
(ALUMINUM INDUSTRY)

Conditions

Pretreatment: Dilution
Eluent: 0.006 M.$Na_2CO_3$
Flow rate: 138 mℓ/hr
Columns: Two 3 X 500 mm
Anion separators
One 6 X 250 mm
Anion suppressor
Injection volume: 100 μℓ
Meter full-scale setting: Variable

Concentrations (ppm)
(in diluted sample)

| | |
|---|---|
| A: $Cl^-$ | 16.4 |
| B: $SO_4^{-2}$ | 35.7 |
| C: Oxalate$^{-2}$ | 20.8 |

FIGURE 10. Analysis of oxalate in a Bayer liquor.

blood serum.[55] A few other analyses related to clinical chemistry have been developed. These include acetate, lactate, and chloride anion determinations in Ringer's lactate solutions, determination of $SO_4^{2-}$ in isethionic acid, determination of oxalate in urine,

### F. Microelemental Analysis

Heteroatoms in organic compounds can be quantitatively measured by IC after the sample has been decomposed by combustion. Scrubber solutions are used to trap the gaseous combustion products and to convert these species to single ionic forms for analysis. Hydrogen peroxide in anion eluent is the scrubber solution most often used in conjunction with subsequent IC analysis. When hydrazine was used to scrub combustion gases, formation of the reduced $NO_2^-$ species rather than the mixture of $NO_2^-$ – $NO_3^-$ seen with $H_2O_2$ scrubbers was observed.[57] The determination of chlorine, bromine, phosphorus, and sulfur in pure compounds after Schöniger flask combustion[58] and of chlorine and sulfur in a variety of samples[59] have been reported. Use of the IC in the analysis of flame retardant polymers,[60] in anion determinations in combusted polymers,[61] and in the determination of iodide in combusted volatile samples[62] have been investigated. Multiheteroatom standards have been synthesized to take advantage of ICs multiple ion capability.[63]

### G. Energy-Related and Geological Analyses

Energy and power production uses of the IC are quite numerous. Heteroatoms in coal and crude oil after degradation in a Parr bomb have been reported.[64] Oil shale extracts[65] and coal gasification producer waters[66] have been examined for anion and cation content. Boiler blowdown waters have been routinely monitored for $PO_4^{3-}$, $Cl^-$, $SO_4^{2-}$, $SO_3^{2-}$, and glycolate.[67] Ultra-trace analysis of anions and cations at part per billion ($\mu g/\ell$) levels have been done on the deionized waters used in steam turbine electricity generating plants;[68] 10 to 50 m$\ell$ of sample are stripped on concentrator columns, which are then installed in the IC for analysis. Nuclear reactor waters have also been analyzed for anion content.[69]

Insoluble radioactive sludges have been analyzed after hydroxide, metaborate, and carbonate fusions.[70] The fused samples are dissolved in acid and injected onto a modified Model 10 Ion Chromatograph. Radioactive waste solutions and dissolved salt cakes have also been analyzed. Soil samples extracted with high concentration chloride, bicarbonate, sulfuric acid, fluoride, and acetate solutions have been analyzed on IC for $NO_3^-$ and $SO_4^{2-}$.[71] Mining exploration samples have been analyzed for anion content by IC.[72]

## IV. CONCLUSION

Ion chromatography is a powerful analytical tool, capable of separating many chemically similar species. A rapid increase has been seen in the number of anions separable by IC. Over 60 anions are now separable, whereas only 29 anions were listed in the initial publication. Cation species separable by IC have remained relatively constant at fewer than 30 because most application emphasis has been on anion separations. This area should see increases similar to the anions when more applications effort is placed there. IC has found use in many areas of analytical chemistry including air and water pollution, quality control, energy and power production related analysis, and clinical and general analysis areas. The list of analyzable ions and applications should continue to grow in the following years as more innovative scientists with ion analysis problems begin utilizing the technique.

## V. SUMMARY

Ion chromatography (IC) is a major new analytical technique for the determination of anions and cations. This method employs ion exchange resins to separate the ions

and uses a second ion exchange column coupled with a conductivity cell for detection of ions in a variety of matrices. Since its introduction, both the types of ions and the applications of IC have increased rapidly. This article is intended to illustrate the principles and practice of this separations technique. Emphasis is placed on a review of the numerous successful applications in the fields of air and water pollution, commercial formulation, clinical chemistry, elemental analysis, energy and power production, and geological analysis.

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