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Review

Detection in ion chromatography

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ABSTRACT

Species determined by ion chromatography are nearly all ionic, so that conductivity detection has become the workhorse detector. However, there are several other important types of detectors which offer major advantages for determining many species by ion chromatography. These include other forms of electrochemical detection, specifically d.c. and pulsed amperometry, as well as optical methods of absorbance and fluorescence. Using these forms of detection, nearly all forms of ionic species can be detected, ranging from inorganic ions to carbohydrates and peptides. In this paper, the factors to be considered when selecting a detection method are reviewed, for example, the properties of different classes of ions which make them amenable to a specific form of detection.

CONTENTS

1. INTRODUCTION

Ion chromatography is a form of high-performance liquid chromatography (HPLC). Its true definition is a matter of debate. A good definition is that ion chromatography is simply the liquid chromatography of ions, implying that any HPLC separation and detection method can be used and still be called ion chromatography. Regardless of which definition one accepts, ion chromatography is

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clearly more than just ion-exchange chromatography with conductimetric detection. All the detectors commonly used in HPLC are now used in ion chromatography. Although the conductivity detector is probably the most popular, other forms of detection each have specific advantages for different types of analytes.

The main detection methods which have proven to be useful can be classified as either electrochemical or optical. They include the following: *Electrochemical*: conductimetric, d.c. amperometric, pulsed and integrated amperometric, and potentiometric. *Optical*: photometric (UV–visible absorbance), photometric following post-column derivatization, indirect photometric, fluorescence, and refractive index. In addition to the expansion of the separation and detection methods considered part of ion chromatography, the original application (the determination of inorganic ions) has expanded to include organic ions as well. Not only are strong acid inorganic anions, such as chloride and sulfate, determined by ion chromatography, but nowadays organic ions such as sulfonates and carboxylic acids are also included. Even carbohydrates (which are only ionic above pH 12) are determined by ion chromatography, although the detection method is pulsed amperometric instead of conductimetric. The increase in the number and types of ions determined has highlighted the need for many detection methods.

This article reviews the advantages of each detection method when applied to the detecton of ionic species.

2. ELECTROCHEMICAL DETECTION METHODS

Of the four types of electrochemical detection listed above, conductimetric detection and the forms of amperometric detection have in common the fact that voltage (or a voltage waveform) is applied to electrodes in a low-volume flow-through cell and that the current is measured. Potentiometric detection is different in that the potential of an ion-specific electrode is measured.

2.1. Conductimetric detection

This detection method is based on the application of an alternating voltage, E, to the cell electrodes and the measurement of the cell current, i, which is directly proportional to the conductance, G, of the solution between the electrodes by Ohm's law:

$$G = \frac{1}{R} = \frac{i}{E}$$

The solution conductivity, κ, is the conductance which would be measured in a cell with 1 cm^2 electrodes placed 1 cm apart and is easily calculated from the cell constant.

The measured conductivity is the sum of the individual contributions to the total conductivity of all the ions in solution. This is called Kohlraush's law of independent migration. It can be stated as:

$$\kappa = \frac{\Sigma_i \lambda_i^0 c_i}{1000}$$

where c_i is the concentration of each ion. λ_i^0 is the limiting equivalent conductivity, which is the contribution of an ion to the total conductivity divided by its concentration, extrapolated to infinite dilution. Kohlraush's law is only valid in dilute solutions, generally 1 m*M* or below. However, the concentrations commonly used in ion chromatography are generally dilute enough for the equation to be valid. For example, the equivalent conductivity of 1 m*M* potassium chloride is 146.9. Extrapolated to infinite dilution, the limiting equivalent conductivity is 149.9, a difference of only 2%.

Limiting equivalent conductivities for common ions are listed in Table I. The value of λ_i^0 is dependent on several atomic and molecular parameters. λ_i^0 increases as the charge on the ion increases, and as the ionic mobility increases. Mobility is largely dependent on the size of the ion, with small ions being more mobile than large ions. Therefore, the magnitude of the signal from a conductivity detector will be greatest for small, high-mobility ions with multiple charges, such as sulfate. Mobility, and therefore sensitivity, can be an order of magnitude less for large ions such as long-chain sulfonic acids. The size of the ion includes not only the atomic or molecular diameter, but also the hydration sphere. This explains why fluoride, which has a larger hydration sphere than chloride, also has a lower equivalent conductivity.

A second factor affecting detector response is the extent of the dissociation of the ion. Protonation of a weak acid has the effect of lowering the net ionic charge. If a monoprotic weak acid is 50% protonated (*i.e.* the eluent pH is the same as the acid's pK_a), then the effective charge on the ion will be one-half, and the conductivity will be about one-half that of the fully dissociated ion. In addition to strong acid inorganic anions such as chloride and sulfate, all sulfonic, phosphonic, and carboxylic acids are sufficiently strong acids to be largely dissociated when they enter the detector cell, making conductivity an excellent choice as a detector for these species. A more extensive presentation of the principles of conductivity can be found in Ch. 4 of ref. 1.

During ion-exchange chromatography, the ionic strength of the column effluent is constant after the column void volume has eluted. In an eluting volume containing analyte ions, there must be an equivalent decrease in the eluent concentration. The

TABLE I

LIMITING EQUIVALENT CONDUCTIVITIES IN AQUEOUS SOLUTIONS AT 25°C

In units of S · cm²/equiv. From ref. 3, p. 19.

Anions	λ_i^0	Cations	λ_i^0
OH^-	198	H^+	350
F^-	54	Li^+	39
Cl^-	76	Na^+	50
Br^-	78	K^+	74
I^-	77	NH_4^+	73
NO_3^-	71	Mg^{2+}	53
HCO_3^-	45	Ca^{2+}	60
SO_4^{2-}	80	Sr^{2+}	59
Acetate	41	$CH_3NH_3^+$	58
Benzoate	32	$N(CH_3CH_2)_4^+$	33

analyte ions can be thought of as displacing an equivalent amount of eluent ions. All ions in the solution contribute to conductivity regardless of whether they are analyte ions or part of the eluent. Therefore, maximum sensitivity is produced by maximizing the difference in equivalent conductivity between the analyte and eluent ions. In chemically suppressed ion chromatography [2], this is accomplished by reducing the eluent conductivity to a very low value, either by removing it completely or by neutralizing it. All analytes then produce conductivities greater than the eluent ions displaced, so sensitivity is directly proportional to the conductivity of the ion.

In non-suppressed ion chromatography [3], sensitivity is directly proportional to the difference in equivalent conductivity between the analyte and the eluent ions. If the eluent contains low-conductivity ions such as benzoate and/or phthalate, then sensitivity will increase as the analyte ion's equivalent conductivity is increased. If the eluent contains a high-conductivity ion such as a hydrogen ion (cation exchange), then sensitivity will be greatest for ions of the lowest conductivity. In this case, the detector response is a decrease in measured conductivity, producing a dip instead of a peak. Although there is no fundamental difference between this form of detection and non-suppressed ion chromatography with the eluent conductivity lower than the analyte, it is commonly referred to as *indirect conductimetric detection.*

Taking the factors discussed above into account, conductivity detection has been found to be the optimum detection method for many small inorganic and organic ions, especially those which do not absorb UV light and are difficult to detect by optical means. This includes all strong acid anions such as chloride, nitrate, sulfate and trifluoroacetate; organic sulfates, sulfonates, phosphates and phosphonates. Carboxylates are also strong enough acids to be detected by conductivity following ion-exchange separation [4]. Using indirect detection or ion-exclusion chromatography with suppression, weaker acids such as silicic, carbonic and boric acids may be detected.

Cations detected by conductivity [5] include the strong base inorganic cations: alkali metals and alkaline earths. Nearly all the other inorganic ions commonly considered to be cations are amphoteric, hydrolyzing water to form oxyanions except in highly acidic conditions. Most transition metals fall into this category. Another reason why conductivity detection is not used for transition metals is that selectivity is poor without the addition of chelating agents to the eluent. These are highly conductive and can not be suppressed to adequately low conductivities, so the addition of chelating agents makes conductimetric detection impractical due to poor signal-to-noise ratios. Organic cations are nearly all amines. Quaternary amines are very strong base cations. Aliphatic primary, secondary and tertiary amines are all sufficiently strong bases to be protonated cations under normal separation and detection conditions. Aromatic and heterocyclic amines (analine, pyridine) are weak bases. They can be detected by indirect conductimetric detection, but not by suppressed conductivity. However, since they absorb UV light, direct UV photometric detection avoids a problem common to indirect detection methods: that of high background noise caused by high baseline levels (see ref. 2, section 7.5 for a discussion of the effect of high baselines on background noise).

Conductimetric detection is one of the most useful forms of detection in ion chromatography, being applicable to a wide variety of small organic and inorganic ions. An example of both organic and inorganic ions detected by conductivity is shown in Fig. 1.

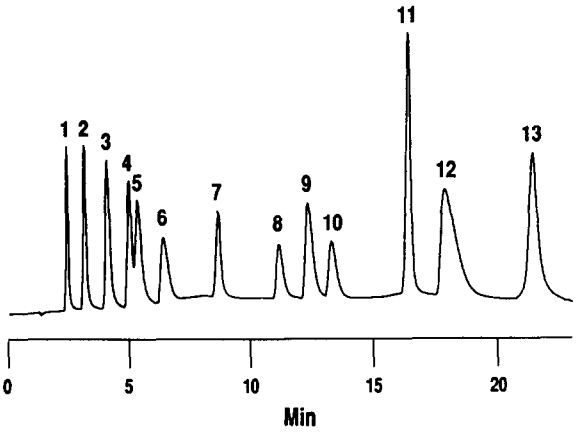

Fig. 1. Alkali metals, alkaline earths and organic amines using gradient elution with suppressed conductivity detection. Peaks: 1 = Li^+; 2 = Na^+; 3 = NH_4^+; 4 = methylammonium$^+$; 5 = K^+; 6 = trimethylammonium$^+$; 7 = diethylammonium$^+$; 8 = triethylammonium$^+$; 9 = piperidinium$^+$; 10 = tetraethylammonium$^+$; 11 = cyclohexylammonium$^+$; 12 = Mg^{2+}; 13 = Ca^{2+}. Column: Dionex IonPac CS-10, 250 × 4 mm cation-exchange column. Eluent: gradient of HCl, 2,3-diaminopropionic acid and CH_3CN at 1 ml/min.

2.2. d.c. Amperometric detection

This detection method is based on the oxidation or reduction (electrolysis) of analyte molecules at the surface of the working electrode in a flow-through cell. A single constant potential is applied to the electrode, and the current is measured directly and reported to the data recording device.

Under the right conditions, any molecule can be oxidized or reduced. However, to be detected by d.c. amperometry, it must be electrolyzed at a lower potential than the components of the mobile phase. If the electrolysis is an oxidation, it must also occur at a lower potential than the oxidation of the working electrode itself. There are several major classes of analytes that fit into this category. The most important are molecules containing aromatic rings substituted with amine or hydroxyl (phenol and catechol) functional groups. Aromatic amines, phenols and catechols have in common the presence of pairs of non-bonding electrons on the nitrogen and oxygen atoms. These are able to shift toward the aromatic ring and stabilize the positive charge resulting from oxidation, making the reaction favorable at a relatively low potential.

The major application of d.c. amperometry is the determination of catecholamine and other biogenic amine neurotransmitters [6–8]. These molecules are cations at both physiological and commonly used mobile phase pH values and are separated by either reversed-phase ion pair or by cation exchange. The amino acid tyrosine is a phenol and can be detected by d.c. amperometry. Also, peptides [9] containing either tyrosine or phenylalanine can be detected. The neurotransmitter serotonin is based on the tyrosine structure and can also be detected. There are other oxidizable organic species. Aromatic amines are easily oxidized [10]. Thiols can be oxidized to disulfides [6]. Examples are glutathione and peptides containing cystein. Ascorbate (vitamin C) [11] and fumarate can also be oxidized. Aromatic nitro compounds [12] are detected by reduction. The electron-withdrawing nitro group stabilizes the negative charge on the aromatic ring.

The mechanism of oxidation for organic molecules is simply the transfer of electrons from the molecules to the electrode. The electrode is otherwise not involved in the reaction and acts as an inert electron sink. Although metal electrodes such as platinum can be used, carbon electrodes have been found to provide the greatest freedom from fouling and the largest resistance to electrode oxidation; *i.e.* the positive potential limit is greatest on carbon. In contrast, most oxidizable inorganic species require more direct involvement of the electrode either as a catalyst or as part of the reaction mechanism. For example, sulfite is oxidized to sulfate at a platinum electrode [13]. The platinum oxide surface of the electrode acts as a catalyst, providing a mechanism for the transfer of an oxygen atom to the sulfite. An example of the electrode being involved in the reaction is the oxidation of iodide at a platinum electrode [14]. The electrode is first dipped into an iodide solution before placing it inside the cell. Iodide becomes adsorbed onto the surface, and is available to form iodine or triiodide during the oxidation of analyte iodide ions.

An important use of an electrode involved in the oxidation reaction is the detection of cyanide [15,16], sulfide [16] and the halides [16] at a silver electrode. In this reaction, it is the electrode itself which is actually oxidized in the presence of these complex or precipitate forming anions, as shown in the reactions below.

$$\begin{aligned} Ag + 2CN^- &\rightarrow Ag(CN)_2^- + e^- \\ 2Ag + S^{2-} &\rightarrow Ag_2S + 2e^- \\ Ag + X^- &\rightarrow AgX + e^- \end{aligned}$$

The chromatogram shown in Fig. 2 was produced using an amperometric detector with a silver working electrode.

Because of the excellent sensitivity and selectivity of d.c. amperometric detection, it is usually the optimum detection method for the analytes discussed above.

Fig. 2. Sulfide (peak 1, 50 ng/ml) and cyanide (peak 2, 100 ng/ml) separated on a Dionex IonPac AS4A 250 × 4 mm anion-exchange column using d.c. amperometric detection at a silver working electrode, E_{app} = 0 V *vs.* Ag/AgCl. (Reprinted with permission from Dionex).

2.3. Pulsed and integrated amperometric detection

These detection methods are similar to d.c. amperometric detection in that current resulting from the electrolysis of analyte molecules is measured. They are different from d.c. amperometry in that a repeating sequence of potentials is applied to the working electrode and the current is only measured during a portion of the potential *vs.* time waveform (for a recent discussion of the difference between pulsed and integrated amperometry, see ref. 17). The purpose of using a repeating potential waveform is to clean the surface of the working electrode electrochemically, thereby providing a reproducible surface for the detection of analytes. This is only necessary for those analytes whose oxidation products coat and poison the surface of the electrode, preventing further detection. These analytes are carbohydrates [18–21], alcohols [22], glycols and aldehydes [23]; amines (primary, secondary and tertiary) [17]; and most sulfur species [17] such as thiols, the exception being fully oxidized sulfur species such as sulfate, organic sulfates, sulfonates, and sulfones.

It is interesting that carbohydrates, which are not usually considered ionic species, are anionic at the high pH used for detection, while amines, which are cations at neutral pH, must be deprotonated, neutral molecules to be detected. However, all of the species detected by pulsed and integrated amperometry are separated using ion-exchange resins, so this detection method should be considered an ion chromatographic method.

The major purpose of pulsed and integrated amperometry is to provide a sensitive and selective detection method for certain aliphatic organic molecules which do not absorb UV light and are therefore difficult to detect by other means. Aliphatic amines can also be detected by conductivity, with comparable sensitivity. However, the only other direct detection methods for carbohydrates are refractive index and low-wavelength UV absorbance. Both methods are very non-selective and have only moderate sensitivity. With pulsed amperometric detection, sensitivity and selectivity are excellent, as seen in the chromatogram shown in Fig. 3.

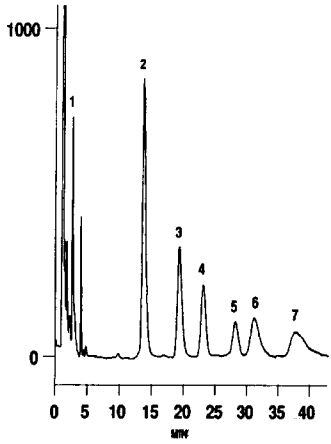

Fig. 3. Carbohydrates in instant coffee with pulsed amperometric detection at a gold working electrode. Peaks and concentrations in ppm: 1 = mannitol 21; 2 = arabinose 140; 3 = galactose 76; 4 = glucose 44; 5 = xylose 26; 6 = mannose 51; 7 = fructose 93. The eluent was 15 m*M* NaOH from 0–1 min, deionized water after that, flowing at 1 ml/min. Post-column addition of NaOH to 0.15 *M* enabled detection. The column was a Dionex CarboPac PA1 250 × 4 mm anion-exchange column.

2.4. Potentiometric detection

This detection method is based on the measurement of the concentration dependent potential which develops at a metal or ion-selective electrode. When ion-selective electrodes are used without chromatography to measure concentration, the highest degree of ion specificity is desired. When the detection is preceded by chromatography, the separation provides selectivity and a more general degree of detector specificity is useful. A potentiometric detector with wide applicability is that based on a metallic copper electrode [23]. For this detector, the measured electrode potential is dependent on the concentration of cuprous and cupric ions in the solution immediately next to the electrode surface; the dependence being described by the Nernst equation. These concentrations are affected by analytes in solution by several mechanisms:

(1) Complexing agents will consume copper ions. These include amines, the halides, cyanide, and many sulfur species.

(2) Analytes can be reduced at the copper electrode, causing copper itself to be oxidized, increasing the concentration of copper ions in the solution. Reducible ions include iodate, bromate, and chlorate. For these ions, the detector response will be opposite to that of the copper ion-consuming analytes.

(3) If a dilute copper-complexing agent (such as tartrate) is added to the eluent, eluting non-complexing analytes will displace the complexing agent. Non-complexing analytes include nitrate and sulfate. These analytes will also produce inverse peaks.

In addition to the metallic copper electrode, a silver electrode has also been used [24]. The principles of the two electrodes are the same.

Although there has been research published on potentiometric detection in ion chromatography, it has generally not been used as a routinc analytical method. Potentiometric detection has the disadvantages of having a somewhat lower sensitivity than conductimetric detection, a slower response time, and a less stable baseline. Perhaps the major reasons why potentiometric detection is not used more commonly is that it possesses no major advantages over other forms of detection, and that there are also no commercial detectors available.

3. OPTICAL DETECTION METHODS

3.1. Photometric detection

This detection method is based on direct measurement of the visible or ultra-violet light absorbance by the analytes (photometric detection following post-column derivatization will be discussed separately). Although all ions absorb light at some wavelength, photometric detection is only useful for those ions with appreciable absorbance above the solvent cutoff wavelength, approximately 200 nm. Although "appreciable absorbance" is a relative term, ions with an extinction coefficient above 1000 can be detected with good or excellent sensitivity. Not all ions fit into this category. In fact, the important ions chloride, sulfate, and the alkali metals and alkaline earths can not be detected by direct absorbance. This was of course the driving force for the development of conductimetric detection. However, many other important ions such as nitrate, iodide, and sulfide can be detected by direct UV absorbance.

The major category of UV-light absorbing ions are aromatic and heterocyclic

acids and amines. These include benzoic acid, benzenesulfonic acid, analine, pyridine, pyrrole, and the numerous *o*-, *m*-, and *p*-substituted derivatives of these molecules. Most have one or more wavelengths of maximum absorbance in the ultraviolet with extinction coefficients between 1000 and 10 000. An example of the use of direct UV absorbance detection for aromatic anions is shown in Fig. 4. UV-light-absorbing inorganic anions and the best wavelengths for detecting them are listed in Table II.

For analytes with strong UV absorbance, direct UV photometric detection provides several advantages compared to conductivity detection. High concentrations of salts from either the sample matrix or the eluent do not interfere with detection. Highly conductive eluents can be used, expanding the list of permissible eluents and thereby increasing the control the user has over the chromatography. Also, a suppressor is not needed.

An example of the use of UV-absorbance detection is the determination of nitrite and nitrate in potassium chloride soil extracts (Fig. 5) [25]. The diluted extracts contain 1% potassium chloride, which greatly overloads both the column and the detector when standard carbonate–bicarbonate eluent is used with conductivity detection. Using UV-absorbance detection allows potassium chloride to be used as the eluent. This matching of the eluent to the sample matrix greatly increases the amount of potassium chloride which may be loaded onto the column, since the form of the resin (chloride) does not need to be converted back to carbonate from the eluent. The same technique can also be used to determine UV-light-absorbing anions in seawater, using sodium chloride as the eluent. Another example is the detection of precious metal cyanides, usually contained in high ionic-strength sample matricies such as mining leachates (Fig. 6).

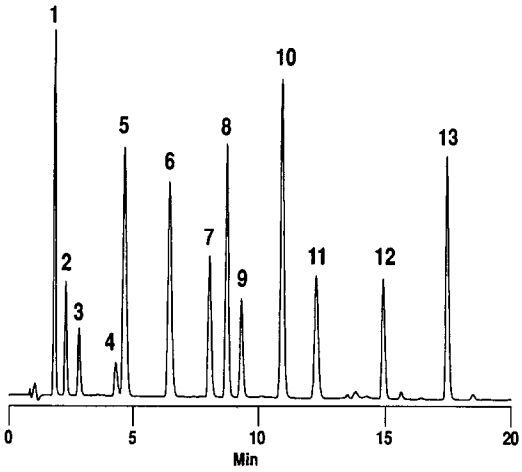

Fig. 4. Anion exchange separation of aromatic anions with direct UV detection at 254 nm. Peaks and concentrations in ppm: 1 = benzoate 40; 2 = benzenesulfonate 40; 3 = *p*-toluenesulfonate 40; 4 = *p*-chlorobenzenesulfonate 40; 5 = *p*-bromobenzoate 20; 6 = 3,4-dinitrobenzoate 10; 7 = phthalate 20; 8 = terephthalate 6; 9 = *p*-hydroxybenzoate 2; 10 = *p*-hydroxybenzenesulfonate 2; 11 = gentisate 10; 12 = trimesate 20; 13 pyromellitate 10 ppm. Column: Dionex OmniPac PAX-100, 250 × 4 mm. Eluent: constant 20% CH_3CN, 1 m*M* NaOH, 0.05–0.4 *M* NaCl gradient in 20 min; 1 ml/min flow-rate. (From ref. 36).

TABLE II

IONS DETECTED BY ABSORBANCE

Wavelengths of maximum absorbance (λ_{max}, nm) and extinction coefficients, ε, for UV-light-absorbing inorganic anions with extinction coefficients greater than 1000. For each anion, approximately 0.1 m*M* of the sodium salt was dissolved in deionized water. For some anions, λ_{max} is below 200 nm. Detection below that wavelength is impractical because of the absorbance of the eluent. However, absorbance above 200 nm is substantial for many of these anions, although absorbance decreases rapidly as wavelength increases. For these anions the optimum detection wavelength is determined by measuring both signal and noise. Extinction coefficients at 200 and 210 nm are listed for those ions with substantial absorbances at those wavelengths. For anions with multiple peaks in the absorbance spectrum, maximum sensitivity is obtained at the wavelength with the greatest extinction coefficient. However, freedom from interferences may be better using a longer wavelength.

Ion	$\varepsilon \times 10^3$ (200 nm)	$\varepsilon \times 10^3$ (210 nm)	$\lambda_{max\ 1}$	$\varepsilon \times 10^3$ ($\lambda_{max\ 1}$)	$\lambda_{max\ 2}$	$\varepsilon \times 10^3$ ($\lambda_{max\ 2}$)	$\lambda_{max\ 3}$	$\varepsilon \times 10^3$ ($\lambda_{max\ 3}$)
AsO_2^-	9.5	5.0						
$AuCl_4^-$ [a]			227	38	313	5.5		
Br^-	8.9	1.9						
BrO_3^-	2.0	1.1						
CrO_4^{2-}			273	3.6	372	4.7		
$Fe(CN)_6^{3-}$	12.3	10.0	260	1.0	303	1.6	420	1.0
I^-			226	12.1				
IO_3^-	17	3.9						
MoO_4^{2-}			207	10.0	227[c]	5.1		
N_3^-	6.0	1.7						
NO_2^-		5.2	209	5.2				
NO_3^-	9.3	7.8						
HS^- [b]			230	8.0				
SCN^-	5.1	3.2	215	3.1				
$S_2O_3^{2-}$	2.8	3.5	215	3.8				
SeO_3^{2-}	5.1	2.3						
VO_3^-	6.6	4.3	266	3.4				
WO_4^{2-}	6.7	2.7						

[a] In 100 m*M* HCl.
[b] In 1 m*M* NaOH.
[c] Shoulder.

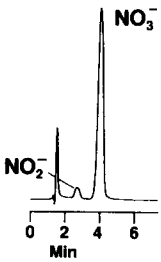

Fig. 5. Determination of 2 ppm nitrite and 38 ppm nitrate in a 10% KCl soil extract using direct UV-absorbance detection at 215 nm. Sample was diluted 1:10, filtered, and injected. Column: Dionex IonPac CS5, 250 × 4 mm. Eluent: 35 m*M* KCl at 1 ml/min. (Reprinted with permission from ref. 25, © 1987, Dionex, Sunnyvale, CA.)

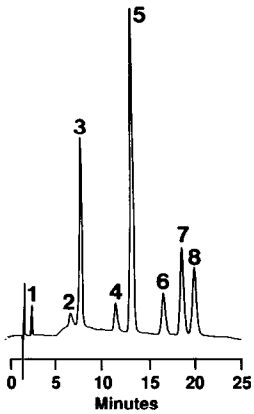

Fig. 6. Separation of metal cyanide complexes with direct UV detection at 215 nm. Peaks (10 ppm each): 1 = Ag(I); 2 = Au(I); 3 = Cu(I); 4 = Ni(II); 5 = Fe(II); 6 = Pd(II); 7 = Co(III); 8 = Pt(II). Gradient of 30–135 m*M* $NaClO_4$ in 18 min with constant 20 m*M* NaCN and 20 m*M* NaOH at 1 ml/min. Column is an IonPac AS5 250 × 4 mm anion-exchange column.

3.2. Photometric detection following post-column derivatization

The most common application of photometric detection following post-column derivatization is the detection of metal ions derivatized with 4-(2-pyridylazo)resorcinol (PAR) [26,27]. The post-column reagent usually contains less than 1 m*M* PAR dissolved in a high pH buffer, such as ammonia–ammonium acetate. The PAR forms a visible-light-absorbing complex with most transition metals with a λ_{max} at 520 nm. This method also works for the detection of lanthanides [28]. Other ions which may be detected in this manner and the post-column reagents used include aluminum derivatized by 4,5-dihydroxy-*m*-benzyenedisulfonic acid (Tiron) [29], Cr(VI) (chromate/dichromate) derivatized by 1,5-diphenylcarbohydrazide [30], and silicate and phosphate derivatized by molybdate [31]. Another application is the detection of polyphosphonate-based sequestering agents using post-column addition of ferric ion [32].

The major advantage of post-column derivatization is that ions may be detected which cannot be detected by any other means. This far outweighs the disadvantages of requiring the addition of a post-column pump and the minor difficulty of ensuring the correct operation of the post-column system.

3.3. Indirect photometric detection

This detection method is based on the decrease in absorbance of eluent ions during elution of analyte ions in ion-exchange chromatography [33]. Any ions which *do not* absorb UV light at the detection wavelength may be detected. As described earlier in regards to inverse conductimetric chromatography, the ionic strength of the column effluent is constant following elution of the column void volume. Therefore, the eluent concentration must decrease in an amount equivalent to the eluting analyte concentration, so eluting analytes cause a decrease in the absorbance background and are recorded as dips instead of peaks. This technique is called *indirect photometric chromatography*. It is nearly as sensitive as conductimetric detection. The major disadvantage is that detection is accomplished against a high background. Any factors

affecting the background absorbance, such as pump pulsations and temperature fluctuations, will produce noise at the detector. Another disadvantage, common to non-suppressed conductimetric detection, is the presence of system peaks (see ref. 2, section 4.4.5).

For anion exchange, useful UV-light-absorbing eluents include low millimolar concentrations of nitrate, benzoate and phthalate. For cation exchange, cupric ion may be used.

3.4. Fluorescence detection

In ion chromatography, fluorescence detection is rarely used as a direct detection method since very few ions fluoresce (exceptions include Ce^{IV} and U^{VI}). If one stretches the definition of ion chromatography, then the fluorescence detection of proteins separated on ion-exchange columns could be considered. However, for small ions, fluorescence detection is only used following post-column derivatization. The major application is the detection of primary amines following derivatization with *o*-phthalaldehyde and 2-mercaptoethanol. This is an extremely sensitive method, and has been used for many years to detect amino acids [34]. Since the reaction is specific to primary amines, selectivity is exceptional. Although it is not commonly used for other primary amines, there is no reason why it should not be. There are many other organic molecules containing primary amines that are difficult to detect by other means, such as direct UV absorbance. These include numerous pharmaceutical compounds such as aminoglycoside antibiotics.

3.5. Refractive index detection

A general, non-selective detection method commonly used in HPLC is refractive index detection. Because of its only moderate sensitivity, poor selectivity, and sensitivity to baseline fluctuations, it is rarely used in ion chromatography. Also, nearly all ions can be detected by one or more of the methods discussed above. One report in the literature of refractive index (RI) detection used in ion chromatography is the detection of polyphosphonate sequestering agents [35].

4. CONCLUSIONS

Of the many forms of detection used in ion chromatography, conductimetric detection is still the most useful. However, all of the detection methods commonly used in HPLC are also applicable to ion chromatography. In particular, amperometric and photometric detection methods are especially important. New detection methods, some first developed for HPLC, are being used in ion chromatography. For example, a powerful method now being developed is ion chromatography–mass spectroscopy. Ion chromatographic separation may also be coupled with atomic spectroscopy, providing exceptional selectivity for metals. Detection methods used in ion chromatography have come a long way since the days of the first publications.

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