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Review

Advances in detection techniques for ion chromatography

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Abstract

The advances in detection techniques for ion chromatography that have been achieved within the last five years are reviewed, with special attention to conductivity, amperometric and potentiometric detection, post-column reaction detection including UV–Vis absorbance, fluorescence and luminescence measurements, atomic spectroscopic detection and combination with mass spectrometry. Typical applications for each detection mode are summarized. © 1997 Elsevier Science B.V.

Keywords: Reviews; Detection, LC; Water analysis; Metal cations

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1. Introduction

When ion chromatography (IC) was introduced in 1975, it was the novel detection approach of eluent conductivity suppression that made this separation technique different from other liquid chromatographic methods and justified the new name. Over the years, improvements in detection have remained an important area of research in IC. The progress made

so far has led to advances in convenience, in sensitivity as well as in detection selectivity. Although universal detection by a bulk property detector based on conductivity measurements is still the preferred mode for routine work, new applications might need detection techniques that also provide some information about the identity, the structure or the elemental composition of the analytes.

Fundamentals of conductivity detection, voltammetric and potentiometric detection, UV–Vis absorbance detection, fluorescence detection and

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atomic spectroscopic detection in IC have been comprehensively covered in two monographs on IC [1,2]. In the present review, advances in detection achieved within the last five years are discussed and typical application areas are outlined.

2. Advances in suppressed conductivity detection

Suppressed conductivity detection for anion separations involves the use of eluents like sodium hydroxide or carbonate–bicarbonate buffers that can be converted into species of low conductance like water or H_2CO_3 after exchanging the cations of the eluent for hydrogen ions by a suitable cation-exchange device (analogous principles can be exploited for cation separations). Originally, suppressors consisted of columns packed with cation-exchange particles in the H^+ form. This type of suppressor is still successfully used in some commercially available instruments [3], although, nowadays, continuously operated devices incorporating ion-exchange membranes are widely preferred. Significant advances with respect to convenience in operation have been made recently by the development of electrolytic suppressors [4,5]. In this case, water is electrolyzed to generate protons (or hydroxide ions) that can cross the ion-exchange membrane and neutralize the eluent. Eluent concentrations up to approximately 100 mM of base or acid can be neutralized in this way. The easiest mode of operation is to use the effluent of the suppressor (which is virtually pure water in the case of NaOH eluents) as the liquid phase for the electrolysis in the regenerant chamber of the suppressor (Fig. 1). Most applica-

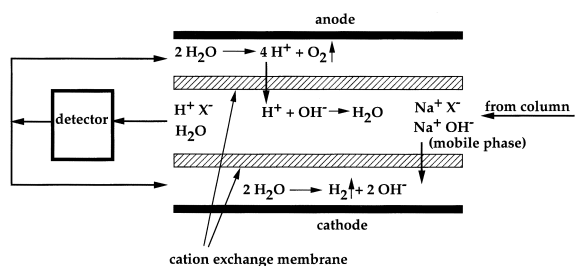


Fig. 1. Schematic diagram of the self-regenerating suppressor (Dionex) in a recycle mode.

tions done in routine analytical work, including concentration gradients, can be run in this mode. If the highest sensitivity must be achieved, an external source of deionized water is recommended for the electrolysis process. One should be aware that electrolytic suppression can lead to undesired by-reactions, such as the oxidation of chloride ions to various chlorine species, if chloride-containing eluents are used for the separation of cations. Oxidation products from chloride (and nitrate) can damage the ion-exchange membrane. Therefore, the preferred eluent for cation chromatography with electrolytic suppression is methanesulfonic acid.

The technique of electrolyzing water to generate protons or hydroxyl ions for suppression has also been employed for regeneration of packed-bed suppressors [6]. A small suppressor column is used in front of the conductivity detector; a second suppressor column that requires regeneration is placed after the detector, where the suppressed eluent undergoes an electrolysis reaction so that protons or hydroxyl ions (depending on the polarity of the electrode in the mobile phase) are generated to regenerate the column. Thereby, a fresh suppressor column is available for each run (Fig. 2).

A significant disadvantage of suppressed conductivity detection is the fact that weak and especially

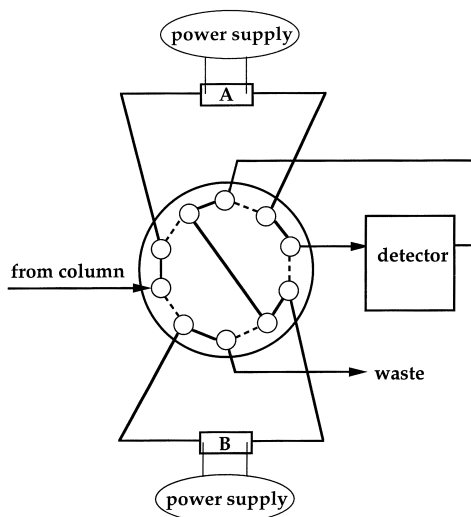


Fig. 2. Schematic diagram of an electrochemically regenerated packed-bed suppressor (Alltech). A, B=suppressor cells (one being used for eluent suppression, the other being regenerated).

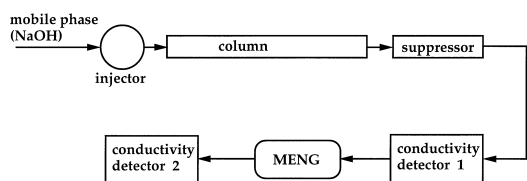


Fig. 3. Experimental set-up for two-dimensional conductivity detection [7]. MENG=microelectrolytic NaOH generator.

very weak acid anions (e.g. silicate, cyanide) yield poor sensitivity and a significant non-linear response. In order to circumvent this problem and also to achieve some confirmation of the identity, two-dimensional conductivity detection has been developed by Berglund et al. [7] and Sjogren and Dasgupta [8]. This approach utilizes NaOH as the mobile phase. The eluent is converted to water in a conventional suppressor and the conductivity is measured, yielding signals primarily for strong acid anions. Afterwards, the mobile phase enters a microscale electrolytic NaOH generator and a second conductivity detector, which records the decrease in the NaOH background signal when acid anions (regardless of the strength of the acid) enter the detector (Fig. 3). Obviously, this technique combines the advantages of both suppressed and non-suppressed conductivity detection in IC. It also provides some information on peak identity, as the signal ratio from the two detectors is characteristic for a certain analyte ion according to its pK_a value.

3. Advances in amperometric and potentiometric detection

Constant-potential amperometric detection at carbon, platinum or silver electrodes has been used as a detection technique complementary to conductometric and photometric detection since the early developments of IC. A pronounced selectivity of amperometric detection can be found for ions like nitrite, bromide, iodide, sulfite, thiosulfate, thiocyanate, cyanide or arsenite. In the analysis of complex samples, an amperometric detector in series with a universal conductivity detector can yield valuable information about the identity of the analytes. Typi-

cal applications reported in recent years are summarized in Table 1.

Deactivation of the electrode surface by products of the electrochemical reaction can sometimes lead to a serious deterioration in the sensitivity from run to run. In such cases, pulsed amperometric detection can be advantageous. Generally, a triple-pulse waveform is applied, which includes the successive application of a measuring potential, a cleaning potential as well as a conditioning potential in a repetitive way. Nowadays, pulsed-amperometric detection is well established for the detection of carbohydrates after separation by anion-exchange chromatography under alkaline conditions. Applications of this detection technique in carbohydrate analysis have been extensively reviewed recently [23] so that this topic will not be discussed further in the present paper.

Considerable efforts have been spent on the development of new electrode materials that allow the detection of otherwise electrochemically inactive analyte ions. An interesting approach is the use of conducting polymers based on polypyrrole or polyaniline films deposited on an inert substrate like platinum. Detection of electroinactive anions is based on the fact that the oxidation of the polymer involves the incorporation of an anionic species to counterbalance the positive sites generated in the oxidation process. Therefore, at a certain constant oxidation potential, current will only flow if anions pass the electrode. This uptake is reversible for hydrophilic anions, whereas some hydrophobic anions are taken up in an irreversible way. In this case, the reduction process of the electrode material can only take place if cations pass the electrode to counterbalance the negative charge generated in the reduction process. Applications in combination with IC have been reported for inorganic anions and cations [24–27], although the whole potential of this technique is not yet fully exploited.

Analyte identification in IC has been suggested by chronoamperometric profiles of the ions [28]. Anions are separated in a mobile phase of NaOH, which is then converted into water by a suppressor device. Afterwards, the analyte ion enters a cell containing two electrodes with a constant voltage applied. The resulting current will decrease according to the mobility of an ion, so that this profile is characteris-

Table 1
Recent applications of amperometric detection in ion chromatography

Analytes	Separation mode	Mobile phase	Electrode material	Voltage reference electrode	Detection limit	References
Iodide in serum	Anion exchange	4 mM Na ₂ CO ₃ –1.5 mM NaHCO ₃	Silver	+0.05 V Ag/AgCl	0.1 µg/l	[9,10]
Iodide in geological materials	Hydrophobic interaction	45 mM HNO ₃	Platinum	+0.8 V Ag/AgCl	0.45 ng	[11]
Bromide in snow samples	Anion exchange	1.7 mM NaHCO ₃ –1.8 mM Na ₂ CO ₃	Silver	+0.2 V Ag/AgCl	1 µg/l	[12]
Bromide, iodide, sulfite, thiosulfate, thiocyanate in water	Anion exchange	20 mM NaNO ₃ –10 mM NaH ₂ BO ₃ (pH 7)	Platinum on glassy carbon	+1 V SCE	1...20 µg/l	[13]
Nitrite, iodide, thio-sulfate, thiocyanate, sulfide in water	Ion interaction	60 mM phosphate buffer (pH 5.5)–3 mM tetrabutylammonium hydroxide–0.1 mM EDTA+ methanol (85:15, v/v)	Glassy carbon	+1 V Ag/AgCl	1...100 µg/l	[14]
Sulfide, cyanide in peatland water	Anion exchange	0.5 M sodium acetate–0.1 M NaOH–0.5% ethylene diamine	Silver	0 V	5 µg/l	[15]
Cyanide released from flaxseed	Anion exchange	10 mM H ₃ BO ₃ –10 mM NaOH–1 mM Na ₂ CO ₃ –0.5% ethylene diamine	Silver	0 V		[16]
Sulfide in waste water	Anion exchange	0.1 M NaH ₂ PO ₄ (pH 2.3)	Glassy carbon	+0.8 V SCE	5 µg/l	[17]
Nitrite in spinach	Anion exchange	2 mM Phthalic acid–10% acetone (pH 5)	Porous graphite	+0.7	10 µg/l	[18]
Sulfite in fruit juices	Ion exclusion	50 mM HClO ₄	Platinum on glassy carbon	+1.4 V Ag/AgCl	250 µg/l	[19]
Sulfite in beer and beverages	Ion exclusion	5 mM H ₂ SO ₄ –1 mM NaCl	Platinum	+0.4 V Ag/AgCl	100 µg/l	[20]
Arsenite in mineral water	Ion exclusion	10 mM H ₃ PO ₃	Platinum	+0.8 V Ag/AgCl	0.4 µg/l	[21]
Arsenite in water	Anion exchange	2 mM NaHCO ₃ –5 mM Na ₂ CO ₃ (pH 10.5)	Platinum	+0.35 V	3 µg/l	[22]

tic for each analyte. Although this approach holds some interesting aspects for future investigations, such as tandem IC–capillary electrophoresis, practical applications are still missing.

IC combined with potentiometric detection techniques using ion-selective electrodes (ISEs) allows the selective quantification of selected analytes even in complex matrices. On the other hand, a high selectivity of the electrode can be a distinct disadvantage, as the information obtained might be just the same as that gained from a flow-injection analysis. Therefore, it may be advisable to use detectors

with ISEs in series with a universal detection technique. This approach has been used recently for the determination of chloride, nitrate and sulfate in extracts of filter-collected airborne particles with a chloride-selective electrode placed in series with a non-suppressed conductivity detector [29].

A different way to more universal detection by ISEs consists of the use of electrode materials with reduced selectivities that respond to a wider range of analytes rather than to a single species. Ion-selective materials of low selectivity are often obtained as by-products in the development of new electrode

materials, especially new ionophores for liquid poly(vinyl chloride) (PVC)-based membranes. Isildak and Covington [30] reported various applications for the combination of IC with PVC membrane electrodes that are selective for univalent cations or univalent anions. De Backer and Nagels [31] employed various macrocyclic amines as well as a lipophilic quaternary ammonium salt in PVC membranes for the potentiometric detection of carboxylic acids in wine and coffee samples. Kwon et al. [32] demonstrated that ion-selective membranes doped with monensin methyl ester yield a comparable response for different alkali metal and ammonium ions.

Another approach to developing a potentiometric detector with similar sensitivity to several ions has been described by Kwon et al. [32] Han et al. [33] Lee et al. [34] and Hong et al. [35]. It is based on the incorporation of several selective ionophores in suitable proportions in a polymer membrane. A PVC or polyurethane membrane with four different ionophores yielded similar sensitivity to ammonium, alkali and alkaline earth metal ions [33,34]. Different monovalent cations could be detected at a membrane doped with a crown ether together with a lithium ionophore [32]. Finally, the simultaneous determination of alkali and alkaline earth metals could be achieved with a membrane doped with a mixture of a

monovalent cation-selective ionophore and a divalent cation-selective ionophore [35], as can be seen from Fig. 4.

Potentiometric detection at metal electrodes like copper has attracted attention for species that react with copper ions by complexation or for species that can oxidize the surface of the metallic copper electrode. Recent applications include the analysis of carboxylic acids and halides [36–38]. Due to the simplicity of its design, this detector has been suggested for use in a portable IC instrument [39].

4. Advances in UV–Vis absorbance detection

Direct UV–Vis detection is a straightforward technique in IC for monitoring analytes of sufficient absorptivity and needs no further discussion within the present review. Indirect UV absorbance detection has become a standard mode for the analysis of inorganic anions with mobile phases that generally consist of benzenepolycarboxylates with strong UV absorption, such as phthalate, trimellitate, trimesite or pyromellitate. Recently, it has been claimed that sulfoisophthalate results in superior sensitivity and detection limits, which are almost as low as those obtained in suppressed conductivity detection [40]. Details of indirect UV detection are comprehensively covered in existing textbooks on IC.

UV–Vis detection in combination with post-column reactions proves to be a versatile technique that combines enhanced sensitivity and selectivity for specific applications. Probably the most widely used reagents for post-column reactions are 4-(pyridylazo)resorcinol (PAR), for the detection of transition metals and lanthanides (sometimes used in combination with Zn(EDTA) to allow the detection of alkaline earth metals, which displaces Zn from the EDTA complex to form the Zn–PAR complex) and Arsenazo III, for the detection of lanthanides. Another post-column reaction that is now well established and has even become an ASTM method is the determination of chromium with diphenylcarbazide [41]. Some of the most recent applications involving these reagents as well as several less common post-column reactions reported within the last few years for UV–Vis absorbance detection can be found in Table 2. The high sensitivity and

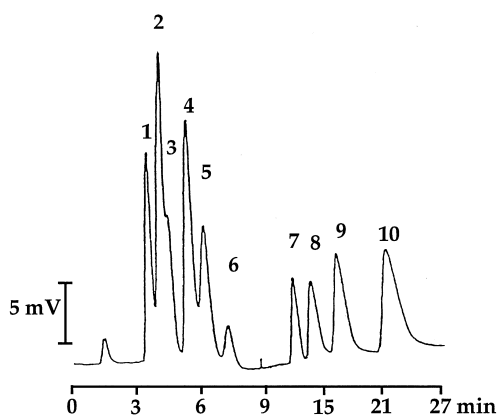


Fig. 4. Separation of mono- and divalent cations with potentiometric detection at a neutral carrier-based electrode containing a mixture of monensin methyl ester and ETH 4030. Peaks: 1= Li^+ , 2= Na^+ , 3= NH_4^+ , 4= K^+ , 5= Rb^+ , 6= Cs^+ , 7= Ca^{2+} , 8= Mg^{2+} , 9= Sr^{2+} and 10= Ba^{2+} . Sample concentration: 0.5 mM for each cation (adapted from [35]).

Table 2
Recent applications of UV–Vis post-column reaction detection in ion chromatography

Analytes	Sample matrix	Post-column reagent	Detection wavelength (nm)	References
Thorium and uranium	Mineral sands	0.13 mM arsenazo III–10 mM urea–62 mM acetic acid	658	[42]
Thorium and uranium	Sea water	0.13 mM arsenazo III–10 mM urea–62 mM acetic acid	658	[43]
Thorium and uranium	Fertilizer solutions	0.3 mM arsenazo III–0.5 M acetic acid	660	[44]
Lanthanides	Silicate rocks	0.1 mM arsenazo III, pH 2.5	650	[45]
Lanthanides	Fertilizer solutions	0.1 mM arsenazo III–0.5 M acetic acid	658	[46]
Lanthanides	Magnesium alloys	50 mg/l arsenazo III in 0.5 M acetic acid	658	[47]
Lanthanides	Water	0.1 mM chlorophosphonazo III–50 mM HCl	700	[48]
Lanthanides	Water	50 mg/l chlorophosphonazo III in 20 mM HNO ₃	660	[49]
Lanthanides	Ytterbium fluoride	0.2 mM PAR–1 M acetic acid–3 M NH ₃	520	[50]
Transition metals	ppt levels in water	0.1 mM PAR–3 M ammonia–1 M acetic acid (pH 9.7)	520	[51]
Transition metals	Plant materials	0.3 mM PAR–1 M 2-dimethylaminoethanol–0.5 M NH ₃ –0.5 M NaHCO ₃	520	[52]
Transition metals	Coral skeletons	0.5 mM PAR	520	[53]
Pb, Zn, Fe, Cu	High-purity CdTe	0.3 mM PAR–1 M 2-dimethylaminoethanol–0.5 M NH ₃ –0.5 M NaHCO ₃	520	[54]
Transition metals	Irradiated nuclear reactor materials	0.4 mM PAR–3 M NH ₃ –1 M acetic acid	520	[55]
Cr(III), Cr(VI)	River water	(1) 0.5 g/l Ce(IV)sulfate in 0.8 M H ₂ SO ₄ (2) 0.05% diphenylcarbazide–0.8 M H ₂ SO ₄	540	[56]
Chromium(III) fluoride complexes	Water	8 mM pyridine-2,6-dicarboxylic acid–100 mM sodium acetate	335	[57]
Al and its fluoro complexes	Water	0.3 mM tiron–3 M ammonium acetate	310	[58]
As(V)	Waste water	(1) 0.94 g of ammonium molybdate in 150 ml of concentrated HNO ₃ , mixed with 2.81 g of ascorbic acid, 15 ml of NH ₃ –10% bismuth nitrate (2:1), 0.014 g EDTA and diluted to 250 ml with H ₂ O (2) 1.2% Triton X-100	700	[22]

Table 2 (Continued)

Analytes	Sample matrix	Post-column reagent	Detection wavelength (nm)	References
Ge, Sn	Alloys, food	0.75 mM Phenylfluorone–0.5% cetyltrimethylammonium bromide–20 mM oxalic acid–8% H ₂ SO ₄	520	[59]
Aluminium	Sea water	0.004% pyrocatechol violet–2 M hexamine (pH 6)	580	[60]
Ca and Mg	Sea water	0.4 mM <i>o</i> -Cresolphthalein complexone (in the mobile phase)	572	[61]
Cyanide, Cu(I)cyanide, thiocyanate	Gold cyanidation process liquors	(1) 0.15% <i>N</i> -Chlorosuccinimide–3% succinimide–0.1 M succinate buffer (pH 5.6) (2) 0.23 M isonicotinic acid–15.6 mM barbituric acid–2% Na ₂ EDTA (pH 7.8)	436	[62]
Iodide	ppb levels in sea water	(1) 0.8 g/l 4,4'-Bis(dimethylamino)diphenylmethane in the mobile phase (2) 1.5 g/l <i>N</i> -chlorosuccinimide–15 g/l succinimide–11.8 g/l succinic acid (pH 4)	605	[63]
Nitrite, nitrate		(1) Column filled with copper-plated cadmium (2) 0.05% naphthylethylenediamine dihydrochloride–0.5% sulfanilamide–5% phosphoric acid	540	[64]
Borate		0.5% azomethine H–1% ascorbic acid–1% diammonium EDTA–1.5 M ammonium acetate	420	[65]
Sulfide, sulfite, thiosulfate		25 μM iodine–10 mM iodide–0.8 M acetic acid	330	[66]

selectivity of post-column reaction detection is demonstrated in Fig. 5, which shows the analysis of inorganic iodide at the ppb level in sea water [63].

In cases where more than one reagent is needed for post-column addition, the instrumentation can be kept simple if one of the reagents can be a component of the mobile phase. It must be kept in mind that post-column reagents in the mobile phase can gradually coat the stationary phase, thereby altering the chromatographic performance. Sometimes, such an effect can be deliberately used for specific applications, such as the determination of calcium

and magnesium in sea-water using a hydrophobic stationary phase that has been dynamically coated with a metallochromic ligand in the mobile phase; at the same time, this ligand also allows the selective detection of the analytes [61].

5. Advances in fluorescence and luminescence detection

Apart from straightforward applications for analytes with native fluorescence properties or for

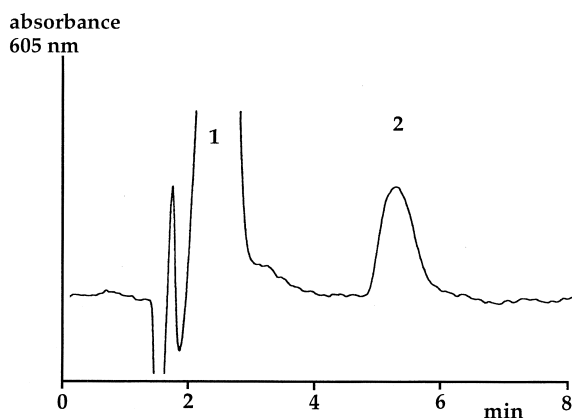


Fig. 5. Chromatogram for the determination of 5 ppb iodide in seawater with post-column reaction detection. Post-column reagent: 0.8 g/l 4,4'-bis(dimethylamino)diphenylmethane (in the mobile phase); 1.5 g/l N-chlorosuccinimide–15 g/l succinimide–11.8 g/l succinic acid (pH 4). Detection wavelength: 605 nm. Peaks: 1=bromide and 2=iodide (reproduced from [63] with permission).

analytes after suitable pre-column derivatization, considerable work has been spent on post-column reactions for fluorescence or chemiluminescence detection. 8-Hydroxyquinoline-5-sulfonic acid (HQS) is a preferred post-column reagent for fluorescence detection that responds selectively to metal ions like Mg(II) and Ca(II) [67], Zn(II) and Cd(II) [68], Al(III) [68,69], Ga(III) [70] and In(III) [68,70]. A more universal response with HQS can be obtained if various displacement equilibria are involved in the post-column reaction. Metal ions can displace magnesium ions from $\text{Mg}(\text{EDTA})^{2-}$ or $\text{Mg}(\text{CDTA})^{2-}$ added to the column effluent (CDTA=*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid); subsequently, liberated Mg(II) reacts with HQS to form a fluorescent complex [71,72]. Whether a simultaneous or a sequential addition of the two reagents is preferable depends on the stabilities of the EDTA (CDTA) and HQS complexes of magnesium and the displacing metal. HQS can also be used for the detection of chelating agents (aminopolycarboxylic acids) and metal–EDTA complexes after formation of ternary fluorescent complexes [73–75]. Generally, HQS forms a fluorescent complex with lutetium and a hexadentate aminopolycarboxylate. This reaction not only allows the selective detection of lutetium, but also of

hexadentate ligands after their separation as lutetium complexes. Metal–EDTA complexes can be detected if a post-column reagent of HQS and lutetium is used, such that lutetium displaces the metals from their EDTA complexes. Finally, ligands with dentation other than six can be detected after separation as lutetium complexes with a post-column reagent consisting of HQS and CDTA, which displaces the ligand in the complex. Various recent post-column reactions for fluorescence detection are summarized in Table 3.

A large part of chemiluminescence detection in IC is based on the luminol reaction that involves the aqueous alkaline oxidation of luminol in the presence of a catalyst [80]. The excited state produced in this reaction decays to the ground state, thereby emitting light with a maximum at 425 nm. Trace analysis of metals like Cr(III), Co, Cu or Ag is possible due to their catalytic effect on the oxidation of luminol, by e.g. hydrogen peroxide. A chromatogram for the determination of traces of Co in nuclear power reactor coolants is shown in Fig. 6. Indirect detection can be applied for species that complex copper or cobalt ions. Ions like silicate, arsenate, phosphate or germanate (especially when present in the form of heteropolyacids) can lead to luminol chemiluminescence even in the absence of an oxidant. A specific application of chemiluminescence detection is the analysis of oxalate in biological and industrial samples with tris(2,2'-bipyridyl)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{3+}$) as the post-column reagent [81–83]. As $\text{Ru}(\text{bpy})_3^{3+}$ is not stable, it should be generated in situ from $\text{Ru}(\text{bpy})_3^{2+}$ by chemical or electrochemical oxidation. Recent applications of chemiluminescence detection in IC are listed in Table 4.

6. Advances in atomic spectroscopic detection

Atomic spectroscopic techniques in use for IC detection include both atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES). Although much current research in this field is focused on atomic emission, atomic absorption has still found a range of applications for IC in recent years. Generally, all common modes of atomic absorption, such as flame AAS, graphite furnace

Table 3
Recent applications of fluorescence post-column reaction detection

Analytes	Post-column reagent	Excitation/emission wavelength (nm)	Detection limit	References	Comments
Magnesium and calcium	2 mM HQS–50 mM Tris (pH 9.2)	390/510	0.6 µg/l (Mg) 40 µg/l (Ca)	[67]	
Ga, Al, Zn, Cd, In	1 mM HQS–4 mM hexadecyltrimethylammonium chloride–10 mM MOPS (pH 9)	400/520	5...16 µg/l	[68]	
Al in pharmaceutical products	4 mM HQS–2 mM cetyltrimethylammonium bromide in 1 M acetate buffer (pH 4.4)	395/500	0.5 µg/l	[69]	
Gallium and indium in aerosol samples	1 mM HQS–1.2 mM cetyltrimethylammonium bromide	389/529	0.10...0.15 ng	[70]	
Metal ions	(1) 0.05 mM MgEDTA (pH 10) (2) 0.44 g/l HQS (pH 10)	390/510	0.3...1.4 µM	[71]	
Metal ions	(1) 1 mM Mg(CDTA) in 0.25 M MOPSO (pH 6.3) (2) 1 mM HQS (pH 12.17)	360/500	5 ng	[72]	
Hexadentate chelating agents	1 mM HQS in 0.3 M bicine (pH 12)	360/500	0.5 pmol	[73]	Separation of analytes in the form of lutetium complexes
Metal–EDTA complexes	(1) 0.1 mM Lu ³⁺ –1 mM HQS in 50 mM acetate buffer (pH 4) (2) 1 M 2-amino-2-methyl-1-propanol (pH 13)	360/500	2 ng	[74]	
Chelating agents	(1) 1 mM HQS–1 mM CDTA (pH adjusted to 2.8 by acetic acid) (2) 1 M NaOH	360/500	0.5...1 ng	[75]	Separation of the analytes in the form of lutetium complexes
Fluoride in water	2 mM HQS in 10 mM acetate buffer (pH 4.1)	360/512	0.2 µg/l	[76]	Separation of the analyte in the form of AlF ²⁺
Butyltin ion species in water	0.005% Morin–0.6% Brij-35 (pH 3.5)	408/534	5 ng	[77]	
Aluminium speciation in water	0.5 M Lumogallion in 0.2 M acetate buffer (pH 5.2)	500/595	7 nM	[78]	
Cyanide in waste water	54 mM <i>o</i> -Phthalaldehyde–0.5 M sodium borate buffer (pH 9.5)	328/370	0.1 µg/l	[79]	

AAS, hydride generation AAS and cold vapour AAS, have been employed for element-specific detection in IC. Flame AAS is a well established technique but suffers from a drawback when coupled to IC; for optimal operation, common nebulizers require flow-rates that are higher by a factor of two to three than the chromatographic flow-rates. This mismatch can lead to poorer detection limits. Nevertheless, flame AAS has been successfully employed

for the detection of selenite and selenate in animal food [92,93] or for copper speciation in jet fuel [94]. Graphite furnace AAS cannot be used in a truly on-line combination with IC but needs discrete sampling of small fractions from the effluent. In this way, selenium species like selenite, selenate, selenocystine and selenomethionine have been detected [92,95,96]. On-line hydride generation is a suitable alternative for the detection of arsenic

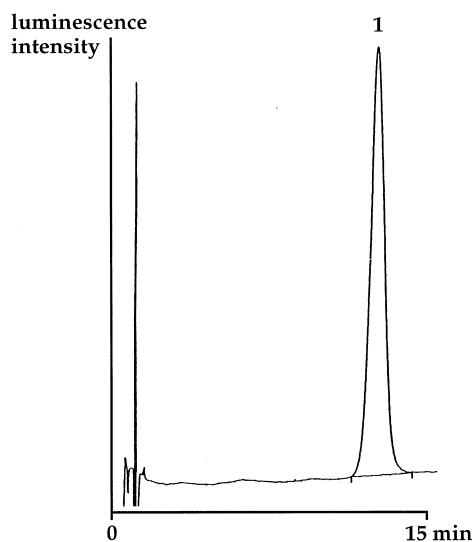


Fig. 6. Chromatogram for the determination of cobalt in a pressurised water reactor coolant sample with post-column reaction luminescence detection. 1=15 pg Co injected (reproduced from [90] with permission).

species (arsenite, arsenate, monomethylarsonic acid, dimethylarsonic acid and arsenobetaine in urine [97]) and tin species (tributyltin, dibutyltin and monobutyltin in water [98]). On-line cold vapour AAS has been used for the determination of methylmercury, ethylmercury and inorganic mercury [99].

Among atomic emission spectroscopic detection techniques, simple flame emission spectroscopy has occasionally been used, such as in series with conductivity detection for the simultaneous determination of anions and cations [100]. The majority of atomic emission techniques for detection in IC are based on an inductively coupled plasma (ICP) source. Typical flow-rates of IC are within the range required for conventional interfaces with the ICP, such as a pneumatic nebulizer and a spray chamber. Transport efficiency at the interface can be increased by the use of an ultrasonic nebulizer or by direct injection nebulization, which is compatible with microbore columns [101].

In ICP-AES, the combination with IC may be desirable for two reasons. On the one hand, spectral interferences from matrix elements can be avoided when a separation step is included. On the other hand, successful speciation analysis of metals like

As, Hg, Pb, Sn, Se or Cr by ICP-AES depends on combination with an efficient separation technique.

When IC coupled with ICP-AES is used for the separation of metals from interfering matrix components, short columns of low chromatographic efficiency may be sufficient. At the same time, the columns may also be used for preconcentration of the analytes. This approach has been used for the determination of trace impurities in samples such as high-purity refractory metals and silicides of Mo and W [102–107]. In this case, it seems to be a matter of philosophy whether one considers ICP-AES as a detector for IC or IC as an on-line sample-pretreatment device for ICP-AES.

Applications of IC in combination with ICP-AES in the field of speciation analysis are listed in Table 5. Instead of ICP-AES, ICP-mass spectrometry is becoming increasingly important for these applications, as is outlined below; the drawback of more sophisticated instrumentation is often outweighed by the ten- to hundred-fold increase in sensitivity.

7. Advances in mass spectrometric detection

There are two major fields where mass spectrometry (MS) plays an important role as a detection technique for IC. On the one hand, MS with ICP ionization serves as an element-selective detector that is similar to ICP-AES but with considerably lower detection limits. On the other hand, ionization techniques and interfaces developed for combining MS with high-performance liquid chromatography (HPLC) in organic analysis, like particle beam or electrospray, can also be used in IC to obtain structural information on the analytes.

Reasons for employing ICP-MS in combination with IC are similar to those in ICP-AES. Matrix elements may form polyatomic ions that interfere with the analyte's signal. Furthermore, different analytes can interfere with each other due to isobaric isotopes. Although these types of interferences can sometimes be overcome by using sophisticated high-resolution mass spectrometers, it may be more convenient to employ less expensive quadrupole instruments in combination with an IC separation step that can also serve for preconcentration of the analytes (e.g. metal ions on chelating resins). Apart

Table 4
Recent applications of chemiluminescence post-column reaction detection in ion chromatography

Analytes	Post-column reagent	Detection limit	References	Comments
Oxalate in alumina process liquors	(1) 2 mM Tris(2,2'-bipyridyl)-ruthenium(II) (2) 4 mM Ce(IV)	0.1 $\mu\text{mol}/1$	[81]	
Oxalate in urine and plasma	2 mM Tris(2,2'-bipyridyl)-ruthenium(II)	1 μM	[82]	Electrochemical chemiluminescence flow cell
Oxalate in biological fluids	Tris(2,2'-bipyridyl)ruthenium(III)	0.1 μM	[83]	Electrogeneration of the reagent from 0.25 mM tris(2,2'-bipyridyl)-ruthenium(II) in the mobile phase
Silicate in water	0.1...0.6 mM luminol–5...16 mM KOH	50 $\mu\text{g}/1$	[84,85]	Separation by ion-exclusion chromatography
Arsenate, germanate, phosphate, silicate in seaweed, wine, water	(1) 7...23 mM ammonium molybdate–0.5...1 mM ammonium metavanadate–3.2...20 mM sulfuric acid (2) 0.6...3 mM luminol–0.15...0.2 M NaOH	1...50 $\mu\text{g}/1$	[86]	
Chromium(III) and chromium(VI) in water	0.06 g Luminol, 1 ml 30% H ₂ O ₂ and 5 g of sodium borate per liter (pH adjusted to 11 using NaOH)	0.5 $\mu\text{g}/1$	[87]	Post-column reduction of Cr(VI) by potassium sulfite
Chromium(III) and chromium(VI) in water	0.34 mM Luminol–0.1 M orthoboric acid–0.01 M H ₂ O ₂ (pH 11.5)	0.05...0.1 $\mu\text{g}/1$	[88]	Post-column reduction of Cr(VI) by 15 mM sulfur dioxide
Cobalt and chromium in glass analysis	(1) 0.05 M H ₂ O ₂ (2) Borate buffer, pH 11.5 (3) 0.42 mM Luminol	0.05...15 $\mu\text{g}/1$	[89]	
Cobalt in nuclear power reactor coolants	0.1 g Luminol, 3 g of boric acid and 5 ml of H ₂ O ₂ per 500 ml (pH adjusted to 12 using KOH)	0.3 pg	[90]	
Silver	(1) 1 mM Potassium peroxodisulfate (in the mobile phase) (2) 0.05 mM Luminol–0.1 M orthoboric acid (pH adjusted to 10.5 using KOH)	0.5 $\mu\text{g}/1$	[91]	

Table 5
Recent application of ICP–AES and ICP–MS for speciation analysis

Element	Analytes	Separation mode	Detection mode	Detection limits	References
As	Arsenite, arsenate in food	Anion exchange	AES, 193.7 nm	150 µg/l	[113]
	Arsenite, arsenate, dimethylarsinic acid	Anion exchange	AES, 228.8 nm hydride generation	17...640 µg/l	[114]
	Arsenite, arsenate	Anion exchange	AES, 193.76 nm hydride generation	70...170 µg/l	[115]
	Arsenite, monomethylarsonic acid, dimethylarsinic acid, trimethylarsine oxide, arsenobetaine in urine	Anion exchange	MS, m/z 75	0.2...0.4 µg/l	[116]
	Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine in urine	Anion exchange, ion interaction	MS hydride generation		[97]
	Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, arsenocholine in water	Anion exchange, cation exchange	MS, m/z 75	0.04...0.16 µg/l	[117]
Br	Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, trimethylarsine oxide, arsenocholine, trimethylarsonium iodide in urine		MS, m/z 75	0.8...3.8 µg/l	[118]
	Bromide, bromate in bakery products	Anion exchange	MS, m/z 79	1 µg/l	[113]
	Bromate in drinking water	Anion exchange	MS, m/z 79	0.05 µg/l	[119]
Cr	Bromide, bromate in water	Anion exchange	MS, m/z 79	0.08 µg/l	[120]
	Cr(III), Cr(VI) in waste water	Anion exchange	AES, 267.7 nm	0.25 mg/l	[121]
	Cr(III), Cr(VI)	Anion exchange, cation exchange	MS, m/z 52, 53	1 µg/l	[122]
	Cr(III), Cr(VI) in water	Anion exchange	MS, m/z 52	0.15 µg/l	[123]
Hg	Cr(III), Cr(VI) in waste water	Anion exchange, cation exchange	MS, m/z 52	0.5 µg/l	[124–126]
	Hg(II), methylmercury, ethylmercury, phenylmercury in urine	Ion interaction	MS, m/z 202	4...9 µg/l	[127]
P	Polyphosphates in shrimp	Anion exchange	AES, 214.9 nm		[113]
Pb	Pb(II), trimethyllead, triethyllead	Ion interaction	MS, m/z 208	0.1 µg/l	[127]
Se	Selenite	Anion exchange	AES, 196.0 nm hydride generation	57...230 µg/l	[114,115]
	Selenite, selenate, selenocysteine, methyl selenocysteine, selenomethionine, allyl selenocysteine in vegetables	Anion exchange	MS, m/z 82		[128]
Sn	Sn(II), trimethyltin, tributyltin, triphenyltin in fish tissue	Ion interaction	MS, m/z 120	2 pg	[129,130]
	Monobutyltin, dibutyltin, tributyltin in water	Cation exchange	MS, m/z 120	0.2 ng	[77]
V	Vanadium(IV), vanadium(V)	Anion exchange, cation exchange	MS, m/z 51	0.5...2.5 µg/l	[122]

from this, IC separation prior to ICP-MS is of considerable importance for speciation analysis in the same way as for ICP-AES.

Elimination of the matrix by IC has been applied to the ICP-MS analysis of trace impurities in Mo, W, Re and silicides of Mo and W [105–107] and of fission products, lanthanides and actinides in uranium materials [108,109]. Chelation ion chromatography allows the analysis of rare earth and transition metal ions in sea water, with detection limits in the low ppb range [110–112]. Again, IC might look more like a sample pretreatment technique for ICP-MS than a separation method with a MS detector.

Due to its high sensitivity, ICP-MS coupled to IC has become the most powerful technique for speciation analysis in biological fluids, food, environmental samples and some other matrices. Fig. 7 shows a typical chromatogram for arsenic speciation. A summary of recent applications is given in Table 5.

Besides the availability of the ICP ion source for elemental MS analysis, structural information can be

provided by interfaces and ion sources like particle beam or electrospray. Although the combination of HPLC and MS has become a routinely applicable analytical tool [131,132], there are not yet many investigations on the use of these interfaces with IC. One of the major problems is the possible incompatibility of the electrolyte of the mobile phase with the interface and the ion source of the MS. To circumvent this problem, a micromembrane suppressor, identical to that for conductivity suppression, can be incorporated into the system between the IC column outlet and the mass spectrometer. In this way, ion-exchange chromatography has successfully been coupled to MS by a particle beam interface for the analysis of aromatic sulfonic acids [133,134] and by an electrospray interface for organic ammonium and sulfate compounds [135], organic acids [136] and inorganic anions [136,137]. Some ion-exchange separations have been reported that worked without a membrane suppressor but used volatile buffers (such as in the analysis of aromatic sulfonic acids with a particle beam interface [133]) or introduced just a small portion of the column's effluent into the mass spectrometer, as has been described for the analysis of cationic organoarsenic species [138] and for bromate in drinking water with an electrospray interface [139]. Another approach to improving the compatibility of ion exchange chromatography with MS is the use of microcolumns with flow-rates in the $\mu\text{l}/\text{min}$ range [140]. Ion-exclusion chromatography with HCl as the mobile phase can also be coupled to MS without a membrane suppressor and has been employed for the analysis of organic acids in combination with a particle beam interface [141]. Details of recent applications of IC-MS with particle-beam or thermospray interface are listed in Table 6.

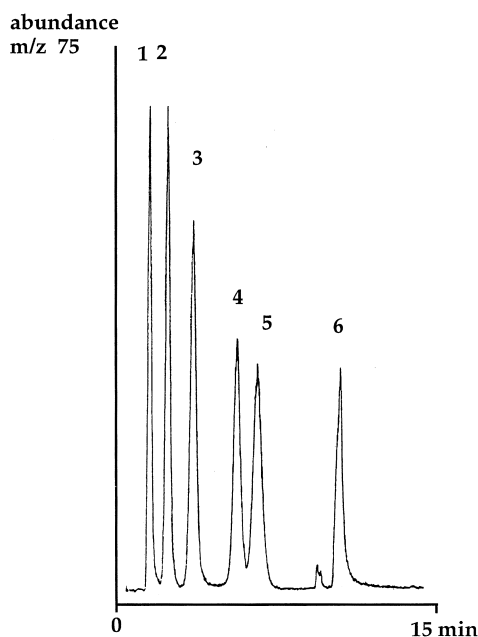


Fig. 7. Chromatogram of a river water sample spiked with 10 ppb (as arsenic) of each arsenic species. Detection: ICP-MS, m/z 75. Peaks: 1=arsenobetaine, 2=dimethylarsinic acid; 3=As(III); 4=monomethylarsonic acid; 5=As(V) and 6=arsenocholine (reproduced from [117] with permission).

8. Conclusions

The performance of ion chromatographic detectors has increased considerably over the last five years. Progress in conductometric detection has resulted in virtually maintenance-free suppressors that are suitable for unattended routine work. Post-column reaction detectors involving UV-Vis absorbance and fluorescence/luminescence measurements allow the development of procedures that are tailor-made for

Table 6
Applications of mass spectrometric detection in ion chromatography

Analytes	Separation mode	Mobile phase	Interface	Comments	References
Bromate at sub-ppb levels in water	Anion exchange	27.5 mg/l (NH ₄) ₂ SO ₄ in water–methanol (10:90, v/v)	Electrospray 50 µl/min (effluent splitting)	Tandem MS mode	[139]
Inorganic anions	Anion exchange	Carbonate–bicarbonate buffer	Electrospray 5.5 µl/min (effluent splitting)	Eluent suppression	[137]
Inorganic anions and organic acids in pharmaceuticals	Anion exchange	NaOH gradient	Electrospray 500 µl/min (effluent splitting)	Eluent suppression	[136]
Organoarsenic species	Ion interaction	1 mM Sodium octanesulfonate–10 mM ammonium citrate in water–methanol (70:30, v/v)	Electrospray 50 µl/min (effluent splitting)		[138]
Organic ammonium compounds	Ion interaction	5 mM Methanesulfonic acid in water–acetonitrile (50:40, v/v)	Electrospray 10–20 µl/min (effluent splitting)	Eluent suppression MS and tandem MS mode	[135]
Organic sulfate and sulfonate compounds	Ion interaction	2 mM Tetrapropylammonium hydroxide in acetonitrile–water (gradient)	Electrospray 10–20 µl/min (effluent splitting)	Eluent suppression MS and tandem MS mode	[135,142]
Aromatic sulfonic acids	Anion exchange	Aqueous ammonium acetate or sodium hydroxide–acetonitrile gradients	Particle beam	Eluent suppression optional	[133]
Organic acids in juices	Ion exclusion	1 mM HCl	Particle beam		[141]
Aromatic sulfonic acids	Reversed-phase, anion exchange	Aqueous NaCl- or NaOH–acetonitrile gradients	Particle beam	Eluent suppression	[134]
Inorganic anions and aminopolycarboxylic acids	Anion exchange	Aqueous ammonium formate–acetonitrile–methanol gradients	Particle beam	Packed capillary columns	[140]
Quaternary ammonium compounds in water waste	Cation exchange		Electrospray	Eluent suppression	[143]

the trace analysis of selected analytes; further research on new or improved reagents can be expected in the future. Amperometric and potentiometric detectors still play a minor role for routine applications, although they might be a low-cost alternative, yielding information that is complementary to that obtained with commonly used detectors. The most powerful detection technique for trace analysis in complex matrices seems to be mass spectrometry with an inductively coupled plasma source or an electrospray source. The high costs of this instrumentation have limited its use in routine work; on the other hand, the trend to small and less expensive bench-top mass spectrometers will result in significantly increased availability in the analytical laboratory.

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