The Use of Chelating Solid Phase Materials in Flow Injection Systems: A Review

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Flow and Sequential Injection—General Approaches

THE USE OF CHELATING SOLID PHASE MATERIALS IN FLOW INJECTION SYSTEMS: A REVIEW

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Flow injection analyses facilitate faster, inexpensive, and more environmentally friendly sample-preparation techniques than many traditional "wet chemistry" methods, and the use of flow injection has, therefore, expanded significantly in recent years. This review focuses on chelating solid phase materials, which have been used in flow injection analyses and also describes important information, such as type of chelating groups, the type of stationary phases, and their efficiency at pre-concentrating metal ions. Discussions of the improvement of the sensitivity and of improving limit of detection, as well as the efficiency with which concomitant ions are removed for the flow injection methods using chelating solid phase materials, are also made.

INTRODUCTION

The application of Lewis' electronic theory of acids and bases to the consideration of coordination compounds is very useful when deciding whether a particular functional group will act as a chelating agent. A metallic cation, being electron-pair deficient, may be considered a polybasic acid capable of reacting with several basic entities, the number of which is related to the coordination number of the metal. According to Lewis' theory, we can anticipate that the stability of a metal coordination complex will depend on: 1) factors related to the acidity of the metal ion; 2) factors related to the basicity of the coordinating ligand such as ligand immobilized chelating solid phase materials (the subject in this review); and, 3) special factors related to the configuration of the resultant complex (Morrison and Freiser 1957). A coordination complex can be non-ionic, cationic, or anionic, depending on the charge of the central ions and the ligands. The selectivity of most chelating materials for metal cations resides predominantly in their ability to form chelates or complexes with certain cations or groups of cations and ionogenic

groups such as iminodiacetate, thiol and thiocarbamide, N-methylglucamine, benzyltriethylammonium, phenol, and phenol-methylenesulfonate have a strong influence. The selectivity behavior of these materials is based on the different stabilities of the metal chelates. These stabilities can be quantified in the form of stability constants, which can be evaluated by application of the law of mass action to the equilibrium involving the complexes. Besides these ionogenic groups the structure of the material used in the flow injection analyses (FIA) manifold influences the properties of the chelating material and several flow injection parameters (e.g., chelation/complexation, flow rate, back pressure, dispersion, etc.). Optimization of each of these parameters can lead to increased retention efficiency and hence, improved performance. Some functional groups interact with certain analytes slowly. Therefore, should the analyst try to increase sample throughput by increasing the sample flow rate, they may discover that the amount of analyte retained actually decreases and hence limit of detection (LOD) are degraded. Elevating the temperature can increase the kinetics of the retention process, but if the temperature is raised excessively, it may lead to problems such as increased back-pressure and boiling of certain solvents leading to gas bubbles forming. In addition, there is also the possibility that the increased temperature may accelerate the degradation of the column packing material.

Chelating solid phase materials have been widely used for the preconcentration and separation of trace metal ions from matrix constituents. Even with increased sensitivity of measurement using techniques such as inductively coupled plasma-mass spectrometry (ICP-MS), the LODs achievable are insufficiently low to be able to determine analytes directly in complex matrices such as seawater. In addition, many atomic spectrometric techniques cannot cope with high dissolved solids loading, e.g., the 3.5% salt found in seawater may block burner heads, nebulizers, ICP torches, or ICP-MS sample interface cones. It is, therefore, often necessary to dilute such samples by a factor of 5 or 10, hence degrading the LOD further. The chelating solid phase materials are used mainly for the selective separation of one (or more) metal ion(s) from the matrix solution leading to improved limits of detection because of the high ratio of preconcentration and, if a suitable wash period is used to remove matrix concomitants from the system, the removal of potentially interfering species. Since sample may be flowed through the resin, which retains the analyte of interest and the ions may be eluted to detection using a very small volume of eluent large pre-concentration factors may be obtained. The lower LOD are limited only by the purity of the chemicals used to buffer the samples and time constraints. Clearly, larger pre-concentration factors may be obtained if sample is flowed through the resin for much longer periods, but the sample throughput is decreased to such an extent that the method becomes no longer viable. A compromise must, therefore, be made between sample throughput and the LOD obtainable. Similarly, the more pure the reagents used to buffer the samples, the lower the LOD obtainable.

From a historical perspective, the first chelating resin containing dipicrylamine groups was originally proposed in 1940 by Skogseid (Hering 1967) for the selective isolation of K^+. The first flow injection analysis methods were proposed in 1975 by Ruzicka and Hansen (Ruzicka and Hansen 1975). However, according to the web of science, the first flow injection method using a chelating resin appeared in 1986 and

was applied to the determination of aluminum in hemodialysis liquids (Hernandez, Hernandez, and Losada 1986).

An ideal analytical method for routine analysis and quality assurance should be precise and accurate, robust, easily automated, simple and cost-effective, as well as having a high sample analysis frequency. Flow injection techniques are readily automated techniques that offer significant advantages for the determination of one selected analyte and can, therefore, be applied to routine analysis. Furthermore, flow injection (FI) offers a simpler flow manifold, reduced consumption of sample and reagents, and provides an easier, more convenient variation of the experimental parameters and greater potential for fluidic handling (Kara, Fisher, and Hill 2008). Despite the advances in analytical instrumentation, the search for specific analytical reagents and techniques is still far from being completed. Improvements have been attained through the coupling of powerful analytical techniques, which has been fueled by the pursuit towards speciation analysis. Flow injection is a powerful tool to extend the capabilities of analytical techniques. The coupling of a FI system to an atomic spectroscopic detection method is well established and has obvious advantages, such as improvement of the action of the pneumatic nebulizer (i.e., samples with very high dissolved solids loading may be analyzed for longer periods before burner or torch blockage becomes problematic), lower consumption of samples and masking reagents, reduced contamination risk, and increased sample throughput (Burguera 1989; Fang 1995). The applicability of the FI–FAAS coupling is again extended by using mini-columns containing chemical materials for improving selectivity by discarding the matrix and preconcentrating the analyte, thereby improving detection limits. A comprehensive discussion about on-line preconcentration in FI–FAAS systems can be found in the excellent text written by Fang (1993). Most proposed analytical applications have involved the use of selective column materials or at least an enhancement of selectivity by appropriate adjustment of reaction conditions. A schematic diagram of an on-line flow injection system is shown in Figure 1 and is taken from the work by Kara, Fisher, and Hill (2005).
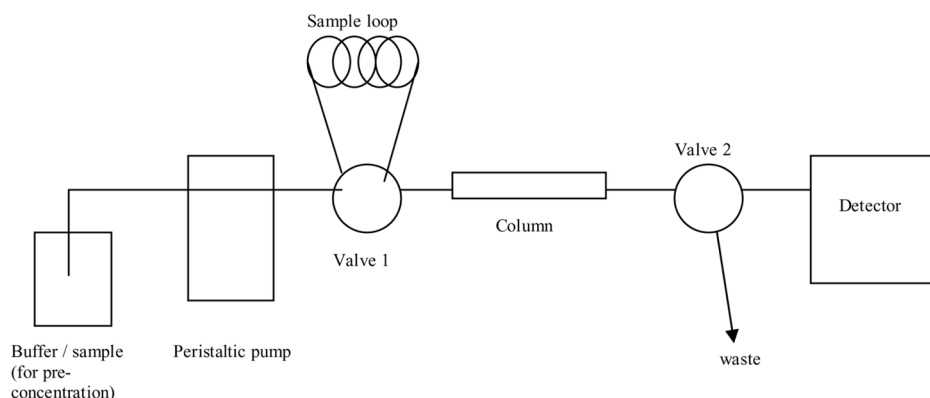

Figure 1. Schematic diagram of the on-line flow injection system (Reproduced by permission of The Royal Society of Chemistry, http://dx.doi.org/10.1039/b508841k, Kara et al. 2005).

Chelating Solid Phase Materials Used in FIAs

Chelating solid phase materials prepared either in-house or available commercially have been widely used in on-line FIAs. Several types of chelating solid phase materials have been used in flow injection systems such as: a) modified inorganic material (e.g., silica, alumina, glass and titanium dioxide) and b) modified organic material (e.g., polymeric resins, chitin, chitosan, Sepharose, cellulose). In most of them, a solid support such as silica gel or divinylbenzene polymer has been modified with organic compounds that have a special structure containing atoms such as N, O, S, or P to bond with metal ions. The following review will be split into the different sections, each describing a different type of support material that may have been modified to form a chelating resin. Three rather elderly, but good reviews that have summarized much of the early work in the area have been produced by Nickson, Hill, and Worsfold (1995), by Bilba, Bejan, and Tofan (1998), and by Torre and Marina (1994).

Modified Silica and Glass

The most frequently modified inorganic solid supports are silica gels and glass, which are inexpensive, easily prepared, and are commercially available in suitable grades. The first stage of the preparation of the modified silica gel is the immobilization on its surface by silanes containing an appropriate functional group such as 3-aminopropyltriethoxysilane or 3-aminopropyltrimethoxysilane. The silane bonded silica gel is then derivatized with a material having chelating functional groups to complex the metal. Silica gels modified with different types of chelating agents have been used in both on-line and off-line flow injection systems for the determination of metal ions in different samples. A good recent review of chelating materials bonded to silica gels has been provided by Zougagh, Pavon, and de Torres (2005). This review contains 148 references and is an excellent starting point for any scientist wanting to revise the earlier work. A comparison of many of the proposed immobilized silica gel resins used in on-line flow injection analyses is given in Table 1. It should be noted that the ''interferences'' column in all of the Tables describes a species that causes interference during any part of the process. This may actually be an interference, with the detection process or with the preconcentration process, or both. If it is a potential problem with the preconcentration process, it could indicate that the species is retained on the resin and so, if it is present in the sample at high concentration, it may swamp the active sites and prevent the analyte of interest from being retained. Such species may have to be ''masked'' or treated chemically to convert them into a form where they are prevented from being retained.

One of the first applications of a flow injection method using an immobilized chelating agent on silica was published by Canada-Rudner and co-workers (1998) who used methylthiosalicylate as the functional group. The resin was used for flow injection cold vapor generation, preconcentration, and determination of mercury in biological samples and sea water with inductively coupled plasma atomic emission spectrometry as a means of detection. The method was very fast, with a typical analytical cycle lasting about 90 seconds. This is substantially faster than the other offline methods proposed for the determination of mercury. A macrocyclic ligand immobilized on a silica gel support, The Superlig® (SL-Cd), a Cd selective material

Table 1. The comparison of the on-line flow injection methods used modified silica gel

Chelating group	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
1,5-bis(di-2-pyridyl) methylene thiocarbohydrazide	ICP-AES	Hg	1 μg L^{-1}	99	Zn(II), Cr(III), Ni(II) and Pb(II)	Tap Water, Sea Water	Canada Rudner, Garcia-de Torres, et al. 1998
Methylthiosalicylate	ICP-AES	Hg	5 μg L^{-1}	79	Cd(II), Mn(II), Zn(II)	Tap Water, Sea Water	Canada Rudner, Cano-Pavon, et al. 1998
The Superlig® (SL–Cd)	ET-AAS	Cd, Cu and Pb	0.8, 46, 20 ng L^{-1} for Cd, Cu and Pb	52 (Cd), 82 (Cu), 42 (Pb)	–	Sea Water	Hosten and Welz 1999
7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline	ICP-MS	Cd, Cr, Cu, Mn, Ni, Pb, U, V, Zn	ng L^{-1} range	–	–	Sea Water	Ferrarello et al. 2001
1-(di-2-pyridyl) methylene thiocarbonohydrazide	ET-AAS	Ni	0.06 μg L^{-1}	58	Fe(III), Co(II), Cr(III), Sn(II), Mn(II)	Sea Water	Cordero et al. 1999
DPTH-gel and TS-gel	ICP-AES	Cd	1.1 μg L^{-1} for DPTH-gel and 4.3 μg L^{-1} for TS-gel	86 for DPTH gel and 62 for TS gel	Zn(II), Cu(II), Cr(III), Ni(II), and Mn(II)	Sea Water, Waste Water	Zougagh, Garcia-de Torres, and Cano-Pavon 2002
DPTH-gel	ICP-AES	Co	5.7 μg L^{-1}	13	Mn(II), Ni(II), Cd(II), Zn(II), Pb(II), Fe(III)	Biological Samples	Zougagh et al. 2004
8-hydroxyquinoline	Spectrophotometry	Fe	0.01 μg L^{-1}	–	Cr(VI), Cu(II) Co(II), and F	Tap Water, River Water	Feng et al. 2005

(*Continued*)

Table 1. Continued

Chelating group	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
Dy(III) ion-imprinted thenoyltrifluoroacetone	ICP-AES	Dy	$0.2\ \mu g\,L^{-1}$	10	Fe(III)	Soil, Sediment	Zhang, Hu, Huang, 2007
Diphenylcarbazone	Spectrophotometry	Hg	$0.90\ \mu g\,L^{-1}$	500	–	Cigarettes	Fan et al. 2008
TE-05	ICP-AES	Cd, Co, Cu, La, Mn, Ni, Pb, Sc, V, Y, Zn	0.22(Cd), 0.23(Co), 0.85(Cu), 0.81(La), 0.18(Mn), 1.99(Ni), 1.85(Pb), 0.15(Sc), 0.80(V), 0.20(Y), 0.83(Zn) $ng\,g^{-1}$	–	–	Concrete Samples	Noguchi, Oshima, and Motomizu 2009
Analig Pb-01	ICP-AES	Pb	$30\ pg\,ml^{-1}$	19	Ag	River Water	Sabarudin et al. 2006

that is manufactured commercially by IBC Advanced Technologies (American Fork, Utah, USA), has been used to determine trace amounts of Cd, Cu and Pb in riverine, estuarine and sea water as well as in urine samples using a flow injection on-line preconcentration procedure coupled with electrothermal atomic absorption spectrometry (Hosten and Welz 1999). Other manufactured silica gel-based modified chelating materials such as TE-05 and Analig Pb-01 have also been used in on-line flow injection analysis. The TE-05 resin has been used for multi-element analysis in concrete samples with detection using ICP-OES by Noguchi, Oshima, and Motomizu (2009). Analig Pb-01 is a Pb selective resin and has been used by Sabarudin et al. (2006) for lead determination in river waters by on-line flow injection systems using ICP-OES as a detector. A paper by Zhang, Hu, and Huang (2007) described the use of a dysprosium(III)-imprinted thenoyltrifluoroacetone (TTA) modified silica gel sorbent that was obtained by a surface imprinting technique. The resin was employed as a selective solid-phase extraction material using flow injection coupled on-line with inductively coupled plasma atomic emission spectrometry (ICP-AES) for the determination of Dy(III). The selectivity of the method for Dy(III) in the presence of competitive ions such as La(III), Nd(III), and Gd(III) was very good with a factor of above 350 obtained, compared with the other non-imprinted modified silica gels.

The modification of controlled glass is achieved in a similar way to silica gel. The chelating agent modified controlled glasses have also been used for the flow injection analysis of metal ions. The 8-hyroxyquinoline modified controlled glass pores were used for the on-line preconcentration of V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U from seawater with ICP-MS being used as a means of detection (Hirata et al. 2003). It has also been used for the preconcentration of Cr(III) and Mn(II) from milk and mussel samples with detection using FAAS (Bruhn et al. 2002). [1,5-bis(2 pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide] functionalized aminopropyl-controlled pore glass was used for the on-line separation, preconcentration and determination of inorganic and organo-mercury species using cold vapor atomic absorption spectrometry (CV-AAS or CV-ETAAS) (Vereda Alonso et al. 2008).

Modified Divinylbenzene

Polystyrene cross-linked with divinylbenzene solid supports are modified by covalent bonding of a ligand to the copolymer backbone. These materials tend to be more chemically stable to acidic eluents than those resins prepared by impregnation. The most modified commercially available Polystyrene Divinylbenzene supports are Amberlite XAD-2 and Amberlite XAD-4. The most important features of these resins are the content and accessibility of the vinyl group. The XAD resins have a copolymer backbone onto which assorted chelating ligands may be immobilized. The advantages of such resins include the uniform pore size distribution, the high surface area, and their chemical stability towards acids, bases, and to oxidizing agents (Hubbard, Finch, and Darling, 1999). A review of the synthesis, characterization, and the role of these materials in inorganic analysis has been presented by Rao, Praveen, and Daniel (2004). The review contains 93 references and gives a good account of the earlier literature. Many chelating exchange resins have been prepared from several different XAD resins. Those that have been used in flow injection analysis of trace elements with different detection methods are shown in Table 2. As stated previously,

Table 2. The comparison of the on-line flow injection methods used modified divinylbenzene resins

Chelating group	Detection method	Analyte	LODs	Preconcentration factor	Interferences	Samples	Reference
N-hydroxyethylethylene diamine (Amberlite XAD-4)	Chemiluminescence	Fe(II) and Total Fe	0.80 for Fe(II) and 0.36 for total Fe n mol L^{-1}	–	Mn(II), Co(II), Ni(II), Pb(II), Cd(II), Cr(III), Cu(II), and Fe(III)	Water samples	Hirata, Yoshi-hara, and Aihara 1999
Chromotrope 2R coated Amberlite XAD-1180	FAAS	Cr	2.59 µg L^{-1}	20	–	Drinking water, sea water	Saracoglu, Soylak, and Elci 2002
Nitroso **R** salt (Amberlite XAD-2)	FAAS	Co	0.39 µg L^{-1}	223	Cu(II), Fe(III) Ni(II)	Natural water samples, biological samples	Lemos et al. 2003
(S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester (styrene-divinylbenzene)	FAAS	Cu	1.1 µg L^{-1}	21	Fe(III), Zn(II)	Tap water, Sea water, mineral water	Cassella et al. 2005

Sorbent	Technique	Analytes	Detection limit	Enrichment factor	Interference	Sample	Reference
Salicylic acid (Amberlite XAD-4)	FAAS	Al(III) and Fe(III)	4.9 (Al) 5.6 (Fe) $\mu g\,L^{-1}$	2.5	—	Drinking water	Vanloot et al. 2007
3,4-dihydroxybenzoic acid (Amberlite XAD-4)	TS-FF-AAS	Cd(II), Cu(II), and Zn(II)	28 (Cd), 100 (Cu) and 77 ng L^{-1} (Zn)	102 (Cd), 91 (Cu), and 62 (Zn)	—	Biological standard reference materials	Lemos, Bezerra, Amorim 2008
2-aminothiophenol (Amberlite XAD-4)	FAAS	Cd(II) and Ni(II)	0.3 (Cd) and 0.8 $\mu g\,L^{-1}$ (Ni)	99 (cadmium) and 43 (nickel	—	Tobacco samples.	Lemos, Novaes, et al. 2008
Cu(II)-imprinted polymer, based on salen–OMe (styrene–divinylbenzene)	FAAS	Cu(II)	1.07 $\mu g\,L^{-1}$	12	Zn(II), Cd(II), Ag(I), and Ni(II)	Water samples	Tobiasz et al. 2009
2,6-diacetylpyridine (Amberlite XAD-4)	ICP-MS	Cd, Co, Cu, Mn, Ni, Pb, U, and Zn	0.33 (Cd) 0.094(Co) (0.34) Cu, (0.32) Mn, (0.30) Ni, (0.43) Pb, (0.067) U and (0.20) Zn $\mu g\,L^{-1}$	13	—	Natural Water samples	Kara, Fisher, and Hill 2005
4-phenylthiosemicarbazide 2,3-dihydroxybenzaldehyde, 2-thiophenecarboxaldeyde (Amberlite XAD-4)	ICP-MS	Cd, Co, Cu, Mn, Ni, Pb, U, and Zn	–	13	—	Natural Water samples	Kara, Fisher, and Hill 2006

in general, the resins prepared by covalent bonding of a ligand to the copolymer backbone tend to be more chemically stable to acidic eluents than those resins prepared by impregnation. Several reaction schemes have been proposed for the bonding of ligands to the copolymer backbone. These include intermediary functional groups such as $-N=N-$ produced as the diazotization product of the polymer. Alternatively, $-CH_2-$ formed from the reaction of chlorine +formaldehyde or methylene chloride may be used (Filik 2002). The formation of Schiff bases (produced by condensation of aldehydes with amines) has been used to bond ligands to the copolymer through the formation of a $-C=N-$ bond (Kara et al. 2005).The reaction schemes for the latter two reactions are given in Figure 2.

Most methods developed that used modified Amberlite XAD-4 have been used for single element determination using a FAAS detector. Using preconcentration, the limits of detection were very much improved for these on-line flow injection systems (Kara, Fisher, and Hill 2009). Kara and co-workers have proposed multi-element detection using ICP-MS as a detector (Kara et al. 2005, 2006). These methods supplied not only an improvement in the limit of detection of the ICP-MS instrument but enabled multi-element detection in one analysis. As discussed previously, interferences can occur during the preconcentration process, the detection system, or both. The work by Kara et al. (2009) that utilized resins to preconcentrate analytes from acid digests of soils and sediments observed that iron had some affinity for the resin at certain pH values and also precipitated at the pH necessary for the retention of the analytes. There was, therefore, a possibility that analyte ions may co-precipitate and hence lead to experimental error. These authors, therefore, used sodium fluoride to react with the Fe(III), which prevented it from both precipitating
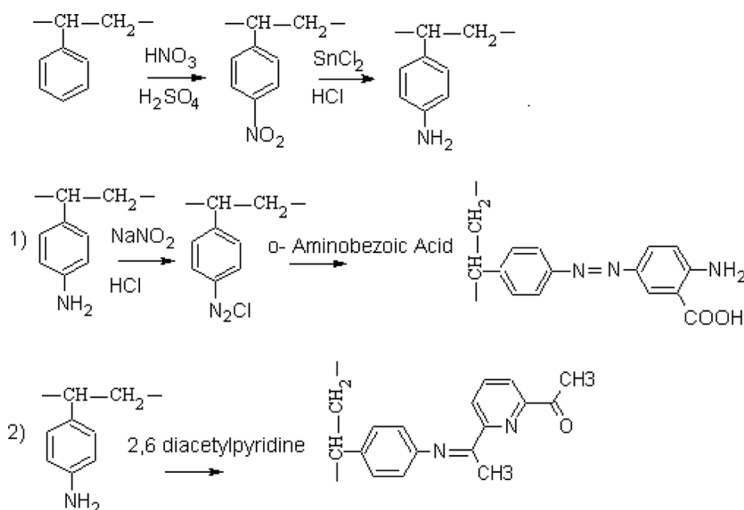

Figure 2. The reaction schemes for the divinylbenzene 1) the modification by diazotization reaction (Çekiç, Filik, and Apak 2004) Reprinted from Analytica Chimica Acta, 505/1, 15–24, with permission from Elsevier) 2) modification by Schiff base reaction (Kara et al. 2005), Reproduced by permission of The Royal Society of Chemistry, http://dx.doi.org/10.1039/b508841k,).

and being retained on the resin. Other workers have adopted similar approaches to removing the possibility of interference effects.

In a separate piece of work, *N*-hydroxyethylethylene diamine modified Amberlite XAD-4 was used for iron speciation in water samples using chemiluminescence detection (Hirata, Yoshihara, and Aihara 1999). The Fe(II) was adsorbed onto the modified Amberlite XAD-4 in an on-line flow injection system and then eluted using HCl. The eluted Fe(II) was reacted with the brilliant sulfoflavin and H_2O_2 in a flow system, and the chemiluminescence signal was measured. Total iron was determined with the same procedure after the addition of hydroxylamine hydrochloride solution that reduced any Fe(III) present to Fe(II).

Iminodiacetate Resin

It can be seen from the literature that chelating solid phase materials containing iminodiacetate groups have frequently been widely used to separate transition elements from alkaline earth ions in natural water samples especially from saline matrices. The chelating solid phase materials with iminodiacetate groups have been widely studied since Riley and Taylor (1968) first reported on a batch preconcentration procedure using Chelex 100 followed by atomic absorption detection. Chelex-100 has been widely used to concentrate trace metals from aqueous samples although there are two major drawbacks to its performance. These are: (1) the chelating resin undergoes a drastic volume change from the NH_4^+ to the H^+ form (Olsen et al. 1983; Kingston et al. 1978), and (2) the resin has an affinity for alkali and alkaline earth elements that cause matrix problems during atomic absorption spectrometry of trace metals (Culberson et al. 1982; Ikeda 1985; Kumamaru et al. 1986; Hirata, Umezaki, and Ikeda 1986). Muromac A-1 and Chelex-100 both contain iminodiacetic acid $[-CH_2-N(CH_2COOH)_2]$ functional groups, but they differ in their chelating properties. As reported by Hirata et al. (1986), the Muromac A-1 chelating resin is better purified and does not swell or shrink. For Chelex-100, the swelling and contraction that is dependent upon the pH and the solvent may cause difficulty in maintaining a reasonable flow rate through the column, as, in its swollen form, it can cause increases in back-pressure. In the shrunken form, it is possible that voids may occur at the beginning of columns and this may lead to unwanted sample dilution effects, etc. Muromac A-1 does not show significant volume change in the pH range 1.0–9.0 and maintains an approximately constant flow rate (Hirata et al. 2001). This has been attributed to its increased cross-linking. Many of the methods using iminodiacetate resins have been performed off-line with open columns and large amounts of sample. This has the obvious disadvantage of potentially introducing contamination. On-line separations using micro-columns and flow injection (FI) methods using these resins are, however, more successfully used, especially when coupled to inductively coupled plasma mass spectrometry (ICP-MS) detectors. Some example on-line flow injection methods using different iminodiacetate resins are given in Table 3. In addition to the most commonly used iminodiacetate resins in flow injection systems (Chelex 100 and Muromac A-1), others have also been used, and these include Metpac CC-1, Chelite Che, 3 M Empore, IDA–Novarose, and Toyopearl AF-Chelate-650 M. Again, these have been used with different detectors including ICP-AES and ICP-MS and for different

Table 3. The comparison of the on-line flow injection methods used iminodiacetate-based resins

Chelating resin	Detection method	Analyte	LOD	Samples	Reference
Dionex Metpac CC-1	ICP-MS	Mn, Co, Cu. Zn, and Pb	$0.09\,\mu g\,L^{-1}$(Cu)	Sea water	Bloxham, Hill, and Worsfold, (1994)
Dionex Metpac CC-1	ICP-MS	Cu, Mo, Ni, U, Zn	Unspecified	Sea water, brines	Ebdon, Fisher, Handley et al. 1993
Dionex Metpac CC-1	ICP-MS	Pb, Cu, Cd, Ni, U, Cr, Mn, Al, Co, Ga, In, Zn, V, Tl, Bi, Ag, and Sn	0.2 (Bi) 0.5 (U) 1.0 (In) 2.0 (Co) 3.0 (Ga) 4.0 Cd 15.0 (Pb) $ng\,L^{-1}$	Estuarine water, seawater	Nicolai et al. 1999
Muromac A-1	GF-AAS	Cu and Mo	0.05 (Cu) and 0.25 (Mo) $\mu g\,L^{-1}$	Sea water	Sung, Liu, and Huan 1997
Muromac A-1	ICP-MS	Cr(III) and total Cr	$0.020\,\mu g\,L^{-1}$	Sea water	Hirata et al. 2000
Muromac A-1	ICP-MS	Al, V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U	0.007 (Al), 0.011 (V), 0.007 (Mn), 0.014 (Co), 0.029 (Ni), 0.099 (Cu), 0.076 (Zn), 0.007 (Mo), 0.010 (Cd), 0.007 (Pb) 0.001 (U) $\mu g\,L^{-1}$	Sea water	Hirata et al. 2001
Muromac A-1	ETAAS	Bi, Cd and Pb	1.3×10^{-2} (Bi), 2×10^{-3}(Cd), and 4.5×10^{-3} (Pb) $\mu g\,L^{-1}$	Urine	Sung and Huang 2003
Muromac A-1	ICP-AES	Al, Bi, Cd, Co, Cu, Fe, Ga, Hg, In. Mn, Mo, Ni, Pb, Pd, Sn, Sc, Ti, V, Tl, Y, W, Zn, Zr	0.005 (Al), 0.001 (Cd), 0.003(Co), 0.007(Cu), 0.008 (Fe), 0.02(Hg), 0.001(In), 0.001(Mn), 0.009(Mo), 0.006(Ni), 0.01(Pb), 0.002(Ti), 0.006(V), 0.006(Y),0.006(Zn) $\mu g\,L^{-1}$	Sea water, River water	Vassileva and Furuta 2003

Sorbent	Technique	Analytes	Detection limits	Sample	Reference
Muromac A-1	ICP-AES	Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sc, V, and Zn	0.02 (Ba), 0.001(Be), 0.018 (Cd), 0.10(Co), 0.09(Cr), 0.08(Cu), 0.05(Fe), 0.008 (Mn),0.16(Ni), 0.18(Pb), 0.01(Sc), 0.09(V), 0.02(Zn) $\mu g\,L^{-1}$	Tap, river water	Katarine, Lenghor, and Motomizu 2007
Chelite Che	FAAS	Cu, Fe, Mn, and Ni	0.5 (Cu), 1.1 (Fe), 0.8 (Mn), and 0.8 (Ni) $\mu g\,L^{-1}$	Urine	Cespon-Romero and Yebra-Biurrun 2008
Chelex 100	ETAAS	Cd and Pb	1 (Cd) and 8 (Pb) $ng\,L^{-1}$	Sea water	Fernandez et al. 1997
Chelex 100	ETAAS	Cu, Cd, Mn, and Pb	—	Estuarine samples	Ellis and Roberts 1998
Chelex 100	ICP-MS	Cd, Cu, Mn, Pb, V, and Zn	$\mu g\,L^{-1}$ range	Biological materials	Ebdon, Fisher, Worsfold, et al. 1993
Chelex 100	EcHG-QT-AAS	Sb	$4.3\,n g\,mL^{-1}$	Sediment	Bolea et al. 2006
Chelex 100 and NTA Superflow	Spectrophotometric	Fe	$0.05\,\mu g\,L^{-1}$	River water	Pascoa, Toth, and Rangel 2009
IDA–Novarose	ICP-AES	Mn, Fe, Co, Ni, Cu, Zn, and Cd	0.5 (Mn), 50(Fe), 3.5(Co), 10 (Ni), 10 (Cu), 2.5 (Zn), 3 (Cd) $\mu g\,L^{-1}$	Natural waters	Hashemi, Noresson, and Olin 1999
Toyopearl AF-Chelate-650 M	ICP-MS	Cu, Ni, Zn, Co, Pb, Cd, and Fe	3.0 (Cu), 11 (Ni), 12 (Zn), 0.1 (Co), 1.0 (Pb), 5.5(Cd), and 11 (Fe) $ng\,L^{-1}$	Sea water, Fish otoliths	Willie et al. 2001
3 M Empore	ICP-MS	V, Mn, Co, Ni, Cu, Mo, Cd, and U	0.006 (Co) 0.4 (Mo), 1.3 (Cr), 1.2 (As) 0.12 (Ba), 0.8(Al), 0.35(Zn), and 0.31(Pb) $\mu g\,L^{-1}$	Sea Water	Lee, Oshima, and Motomizu 2002
3 M Empore	Spectrophotometric	Fe speciation	19 ng	Sea water	Pons, Forteza, and Cerda 2004

sample types including natural water samples especially sea waters. From Table 3, it can be seen that these methods lead to improved sensitivity and very low limit of detections can be obtained, even down to the ng L^{-1} level. As with many resins, IDA chelating solid phase materials may retain significant amounts of unwanted concomitant ions. The IDA resins, in particular, have affinity for the alkaline earth metals such as Ca and Mg which are present in natural waters in appreciable amounts. These could, therefore, potentially occupy sufficiently high numbers of active sites on the resin to prevent the analytes of interest becoming retained. The analytes could, therefore, break through the resin bed and be lost analytically, leading to errors. Many workers have managed to prevent the retention of the alkaline earth metals by careful optimization of the pH using buffer solutions such as ammonium acetate (Ebdon, Fisher, Handley et al. 1993).

Chitosan Modified Resin

Chitosan (CTS), obtained by deacetylation of chitin, is a natural polysaccharide. It is the most abundant polysaccharide after cellulose on Earth. Chitosan has been found to be an excellent base material compared with other natural polymers, activated sludge, synthetic polymers, etc. The use of chitosan as solid support for an ion exchange and as a chelating resin is increasing because of its advantages, which include the ease of derivatization of its amino groups and because it is more hydrophilic than synthetic base materials such as polystyrene-divinylbenzene, polyethylene, and polyurethane (Oshita et al. 2002; Gao et al. 2002). These advantages provide a fast reaction rate, as well as rapid sorption kinetics of analyte species. However, chitosan can easily dissolve in acidic solutions through the protonation of its amino groups. Therefore, cross-linking agents such as ethyleneglycol-diglycidylether (EGDE) and glutaraldehyde (Hsien and Rorrer 1997) were used for improving its chemical stability and mechanical strength.

Modified chitosan with different chelating agents have been used in on-line flow injection determination of metal ions (Table 4). The 8-hydroxyquinoline modified chitosan has been used to determine Cu and Cd (Martins, Silva, Carasek, Laranjeira, and Favere 2004), Pb (Martins et al. 2005) and Al (Carletto et al. 2008) in water samples using FAAS in on-line flow injection systems. Chitosan modified with 2-amino-5-hydroxy benzoic acid has been used to determine 24 elements using an on-line flow injection system and ICP-AES detection leading to very low detection limits being obtained (Sabarudin, Lenghor et al. 2007). Chen, Hu, and Huang (2009) have chemically modified aminopropyl, modified ordered mesoporous silica through the $-NH_2$ functional group found on the chitosan surface in formaldehyde media, and used this modified chitosan resin for V, Cu, Pb, Cd, and Hg determination in water samples by ICP-AES using on-line flow injection analysis.

Modified Anion Exchange Resin

Anion exchange resins have been modified with chelating agents to preconcentrate metal ions from different samples and have been used in both off-line and on-line systems. These ligands mainly immobilize analytes using electrostatic attraction between the positive charge on the anion exchange resin and negative charge on the

Table 4. The comparison of the on-line flow injection methods using Chitosan modified resins

Chelating group	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
5-sulphonic acid 8-hydroxyquinoline	FAAS	Cu and Cd	0.2 (Cd) 0.3 (Cu) $\mu g\,L^{-1}$	19.1 (Cu) 13.9 (Cd)	NA	Water samples	Martins, Silva, Carasek, Laranjeira, et al. 2004
8-hydroxyquinoline	FAAS	Cu and Cd	0.1 (Cd) 0.4 (Cu) $\mu g\,L^{-1}$	—	NA	Water samples, oyster tissue	Martins, Silva, Carasek, Gonçalves, et al. 2004
8-Hydroxyquinoline	FAAS	Pb	$1.7\,\mu g\,L^{-1}$	26.5	Zn	Water samples	Martins et al. 2005
3,4-dihydroxy benzoic acid	ICP-AES	Ag, Bi, Cu, Ga, In, Mo, Ni, U, V	0.08 (Ag), 0.9 (Bi), 0.07 (Cu), 0.9 (Ga), 0.9 (In), 0.08 (Mo), 0.09 (Ni), 0.9 (U), 0.08 (V) $\mu g\,L^{-1}$	8–12	NA	River water, sea water	Sabarudin, Noguchi, et al. 2007
2-amino-5-hydroxybenzoic acid	ICP-AES	Ag, Be, Cd, Ce Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Ni, Pb, Pr, Sm, Tb, Tm, U, V, Y, Yb	0.006(Ag), 0.001(Be) 0.006(Cd), 0.22(Ce) 0.023(Co), 0.006(Cu) 0.009(Dy), 0.018(Er) 0.008(Eu), 0.007(Gd) 0.005(Ho), 0.006(La) 0.004(Lu), 0.020(Nd) 0.028(Ni), 0.022(Pb) 0.015(Pr), 0.008(Sm) 0.018(Tb), 0.002(Tm) 0.93(U), 0.007(V) 0.002(Y), 0.001(Yb) $\mu g\,L^{-1}$	20–36	—	River water	Sabarudin, Lenghor, et al. 2007
8-hydroxyquinoline	FAAS	Zn	$0.8\,\mu g\,L^{-1}$	7.6	Al(III)	Mineral waters	Carletto et al. 2008
Mesoporous silica.	ICP-AES	V, Cu, Pb, Cd and Hg	0.33(V), 0.30(Cu), 0.96(Pb), 0.05(Cd) 0.93(Hg) $\mu g\,L^{-1}$	20	—	Water samples	Chen, Hu and Huang 2009

chelating agent. Examples of such methods for on-line flow injection analysis are given in Table 5. Sanchez-Rojas and co-workers (Sanchez-Rojas, Bosch-Ojeda, and Cano-Pavon 2004; 2007) have used 1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide as a chelating agent to modify Dowex 1×8 anion exchange resin to determine different metals. Some of these papers are given in Table 5, whereas others can be found in the reference list of these papers. The advantages of using anion exchange resin as a solid support are that they are cheap and are readily available.

Phosphorus-Based Chelating Solid Phase Materials

Phosphorus-based chelating solid phase materials made either in-house or commercially available have been used for the on-line flow injection determination of metal ions by different detection systems (Table 6). A lab made aminophosphonic–carboxylic acid resin has been used to adsorb rare earth elements (REEs) and, after elution with HCl, total REE were determined using the chromogenic reagent Arsenazo II in an on-line flow injection system with spectrophotometric detection(Pu et al. 2002). The authors applied their method to the analysis of alloys but suffered interferences from Fe, Al, Be, Zn, W, V, Mo, Si, and As. Another lab made the phosphorus-based resin Poly(aminophosphonic acid) and used it for the determination of Cd(II) in mussels (Enriquez-Dominguez, Yebra-Biurrun, and Bermejo-Barrera 1998) and for chromium speciation in water samples (Cesph-Romero, Yebra-Biurrun, and Bermejo-Barrera 1996). The methods used on-line flow injection systems with FAAS detection and yielded sub ppb level detection limits. Lewatit TP807'84 is a commercially available resin and two mini-columns containing this resin have been used for the determination of Cd, Cu and Pb in water samples (Castillo et al. 2001). One mini-column was kept at pH 3.2 for the removal of interferences, such as Zn(II) and Fe(III), and the other at pH 5.5 for the selective preconcentration of the target analytes. After elution with HCl the target elements underwent spectrophotometric determination using sulfarsazene as a chromogenic reagent and partial least-squares multivariate calibration. The resin TRU has been used for the determination of U in ground water samples by Aldstadt et al. (1996) and for the determination of U and Th in urine samples (Benkhedda, Epov, and Evans 2005). Both sets of workers used on-line flow injection systems with ICP-MS detection. Benkhedda, Epov and Evans (2005) succeeded in decreasing the LOD for U by a factor of 10. Chelite P has also been used for the determination of Cd in vegetable samples (Yebra, Cancela, and Moreno-Cid 2005) and for the determination of Zn in seawater (Yebra-Biurrun and Cespon-Romero 2006) using FI- FAAS. The Ln-resin has been used in on-line flow injection systems with ICP-MS detection for the determination of Ra at the pg per liter level in natural waters. The authors noted that the method suffered interferences from Ba and Sr (Benkhedda, Lariviere, et al. 2005).

Other Resins Used in On-Line Flow Injection Systems

There are some other chelating solid phase materials used in on-line flow injection systems and some of these are listed in Table 7. There are relatively fewer of these resins, but they still offer some advantages and have been used for some interesting

Table 5. The comparison of the on-line flow injection methods that used modified anion exchange resins

Chelating group	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
Luminol and hexacyanoferrate (II)	Chemi-luminescence	V	$5.4 \times 10^{-3}\ \mu g\ ml^{-1}$	–	CrO_4^{2-}	Geochemical samples, human hair	Qin, Zhang, and Zhang 1997
1,5-bis[(2-pyridyl)-3-sulphophenyl-methylene]-thiocarbonohydrazide	ICP-AES	Pt	$7.4\ \mu g\ L^{-1}$	85	Co(II), Cu(II), and Cr (III)	Water samples	Ramos-Martos et al. 2004
1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide	ETAAS	Rh	$0.3\ \mu g\ L^{-1}$	18.3	Fe(III), Fe(II), Pt(IV), Sn(II), Zr(IV), Ce(IV), and Pd(II)	Vegetable, soil, water samples	Sanchez-Rojas., Bosch-Ojeda, and Cano-Pavon 2004
1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide	ETAAS	Sb	$2\ \mu g\ L^{-1}$	12	Pd(II), Pt(IV), and Rh(III)	Water, biological, vegetation, soil	Sanchez-Rojas, Bosch-Ojeda, and Cano-Pavon 2007
5,10,15,20-tetrakis (4- carboxyphenyl) porphyrin	FAAS	Mn	$16\ \mu g\ L^{-1}$	30	Fe(III), Cu(II), Ni(II), Co(II)	Water samples	Knap, Kilian, and Pyrzynska 2007

Table 6. The comparison of the on-line flow injection methods using Phosphorous-based resins

Chelating Group	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
Aminophosphonic-carboxylic acid	Spectrophotometric	Total REE	$4.0\,\mu g\,L^{-1}$ La	7	Fe, Al, Be, Zn, W, V, Mo, Si and As	Alloy	Pu et al. 2002
Poly(aminophosphonic acid)	FAAS	Cd(II)	$0.56\,\mu g\,L^{-1}$	16–47	Cu(II), Cr(III), Mn(II), Pb(II)	Mussel	Enriquez-Dominguez, Yebra-Biurrun, and Bermejo-Barrera 1998
Poly(aminophosphonic acid)	FAAS	Cr speciation	$0.2\,\mu g\,L^{-1}$	35	–	River, mineral, tap water	Cespon-Romero, Yebra-Biurrun, Bermejo-Barrera 1996
Lewatit TP807'84, (di(2,4,4-trimethylpentyl) phosphinic acid)	Spectrophotometric	Cd(II), Cu(II) and Pb(II)	0.09(Cu), 0.27(Pb) and 0.12 (Cd) $mg\,L^{-1}$	50	Zn(II) and Fe(III)	River, and ground water	Castillo et al. 2001
TRU (octyl(phenyl)-N,N-diisobutyl carbamoyl methylphosphine oxide and tri-n-butyl phosphate)	ICP-MS	U	$0.3\,ng\,L^{-1}$	30	Th and Pu	Ground water	Aldstadt et al. 1996
TRU (octylphenyl-N,N-diisobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate	ICP-MS	U and Th	0.02(U) and 0.03 (Th) $ng\,L^{-1}$	4	–	Urine	Benkhedda, Epov, and Evans 2005
CHELITE P (Aminomethyl-phosphoric acid groups)	FAAS	Cd	$0.014\,\mu g/g$	20.5	–	Vegetables	Yebra, Cancela, and Moreno-Cid 2005
CHELITE P (Aminomethyl-phosphoric acid groups)	FAAS	Zn	$0.02\,\mu g\,L^{-1}$	211	–	Sea water	Yebra-Biurrun and Cespon-Romero 2006
Ln resin (di(2-ethylhexyl)orthophosphoric acid)	ICP-MS	Ra	$0.46\,pg\,L^{-1}$	6.66	Ba, Sr	Natural waters	Benkhedda, Lariviere, et al. 2005

Table 7. Comparison of the on-line flow injection methods using other resins

Chelating solid phase materials	Detection method	Analyte	LOD	Preconcentration factor	Interferences	Samples	Reference
3-(8-quinolinylazo)-4-hydroxybenzoic acid modified Alumina	ICP-OES	Ag, Pd, Au, Ga, In and Nb	0.12(Ag), 0.44(Pd)., 0.27(Au), 0.19(Ga), 0.54 (In) and 0.18 (Nb) $\mu g\,L^{-1}$	10	Fe(III)	Geological samples, water samples	Hang et al. 2007
Dimercaptosuccinic acid modified mesoporous titanium dioxide	ICP-OES	As, Sb	0.53(As(III)), 0.49(As(V)), 0.77 (Sb(III)), 0.71(Sb(V)) $\mu g\,L^{-1}$	10	Fe(III)	Water samples	Huang, Hu, and Jiang 2007
α- amino pyridine immobilized to a cross-linked polyphenylethene support	FAAS	Pd, Pt, Ir	0.017 (Pt) 0.009 (Pd) 0.11 (Ir) $\mu g\,mL^{-1}$	—	Fe	Ore	Di and Davey 1995
8-hydroxyquinoline, immobilized onto vinyl polymer gel	Spectrophotometric	Fe	0.025 nM	—	—	Seawater	Measures, Yuan, and. Resing 1995
Chromosorb 105	FAAS	Co	2.5 $\mu g\,L^{-1}$	50	—	Table salt, natural water	Karatepe, Soylak, and Elçi 2002

applications. Chemically modified Alumina with 3-(8-quinolinylazo)-4-hydroxyben-
zoic acid has been used for the multi element determination of Ag, Pd, Au, Ga, In,
and Nb in geological samples and water samples using ICP-OES detection (Hang
et al. 2007). Dimercaptosuccinic acid modified mesoporous titanium dioxide has been
used for the determination of As and Sb in water samples using ICP-OES detection
(Huang, Hu, and Jiang 2007). α-amino pyridine bound to a cross-linked polypheny-
lethene support has been used for Pd, Pt, and Ir determination in ore samples using
FAAS detection (Di and Davey 1995). Measures and co-workers have developed a
flow injection spectrophotometric method for the determination of Fe in Seawater
using 8-hydroxyquinoline immobilized onto vinyl polymer gel. Spectrophotometric
detection of the iron eluted from the column was achieved through its catalytic effect
on the oxidation of N,N-dimethylphenylenediamine dihydrochloride (DPD) by
hydrogen peroxide (Measures, Yuan, and Resing 1995).

CONCLUSIONS

On-line flow injection methods are fast, selective, inexpensive, virtually solvent
free methods, which provide a high degree of enrichment and matrix removal. There-
fore, these resins are increasingly being used primarily as a means to separate the
ions of interest from the bulk matrix. Some of the different chelating solid phase
materials used in on-line flow injection systems have been evaluated in this review
and specific information in reference to limits of detection, preconcentration factors,
and interferences, etc., have been described. From the methods given in the Tables, it
can be seen that very low limits of detection are obtainable especially when ICP-MS
and ICP-OES detection systems are used, but the LOD for other detection methods
can be impressive, depending on the preconcentration factor.

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