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On-line analyte preconcentration with atomic spectrometric detection

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Pre-concentration of analytes, or matrix removal to overcome interferences using mini- or micro-columns of exchange media prior to atomic spectrometric detection is becoming increasingly more common. This paper is a review of some of the more recent applications of chelating, ion exchange and other resins and gels that have been used to accomplish this.

Introduction

Many atomic spectrometric methods of analysis, including electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), are prone to matrix interferences. Even inductively coupled plasma mass spectrometry (ICP-MS), which is generally regarded as being relatively free from interferences, suffers from polyatomic ion interferences, especially for the determination of first row transition metals. These interferences are summarized in table 1.

Ion exchange and chelation exchange are increasingly being used for pre-concentration and/or matrix removal prior to atomic spectrometric detection. They provide a relatively cheap, robust and repeatable method of pre-

Table 1. Polyatomic ion interferences of importance in food.

Analysis by ICP-MS/96			
Mass	Element	% Abundance	Interfering ions
47	Ti	07.32	PO ⁺
48	Ti	73.98	³² SO ⁺ , POH ⁺
51	V	99.76	³⁵ ClO ⁺ , ³⁴ SOH ⁺
52	Cr	83.76	⁴⁰ Ar ¹² C ⁺ , ³⁵ ClOH ⁺
53	Cr	09.51	³⁷ ClO ⁺
54	Fe	05.82	⁴⁰ ArN ⁺ , ³⁷ ClOH ⁺
54	Cr	02.38	ArN ⁺ , ClOH ⁺
55	Mn	100	⁴⁰ ArNH ⁺
56	Fe	91.66	⁴⁰ ArO ⁺
63	Cu	69.01	⁴⁰ ArNa ⁺
64	Zn	48.89	HPO ₂ ⁺ , ³² SO ₂ ⁺ , ³² S ₂ ⁺ , ⁶³ CuH ⁺
65	Cu	30.09	H ³² SO ₂ ⁺
69	Ga	60.16	³⁷ ClO ₂ ⁺
75	As	100	⁴⁰ Ar ³⁵ Cl ⁺
76	Se	09.02	³⁶ Ar ⁴⁰ Ar ⁺
77	Se	07.58	⁴⁰ Ar ³⁷ Cl ⁺
78	Se	23.52	⁴⁰ Ar ³⁸ Ar ⁺
79	Br	50.54	³⁸ Ar ⁴⁰ ArH ⁺
80	Se	49.82	⁴⁰ Ar ⁴⁰ Ar ⁺

treatment, both on- and off-line that is easily automated, using either flow injection (FI) or high pressure liquid chromatographic (LC) techniques. Mini-columns of exchange material with dimensions of 2.0 × 0.2 cm or less provide sufficient exchange capacity for many applications. This paper provides an overview of on-line techniques for pre-concentration and/or matrix removal with particular emphasis on atomic spectrometric detection.

Chelation

Many exchange media have been developed, including anion, cation and chelation exchange resins. Chelation exchange is one of the most common forms of sample pretreatment, which can be performed either on-line or off-line. If performed on-line it offers numerous advantages, including removal of the matrix/interferents and pre-concentration with a reduced risk of contamination. The most common chelating resin is Chelex-100, which contains iminodiacetate (IDA) functional groups. These groups readily chelate transition metal ions and other cations, for example lead (II). The IDA group is also present in a number of other chelating resins, for example Muromac-A1, Metpac CC1 and Dowex A1. The first workers to report the use of Chelex-100 are acknowledged to be Riley and Taylor [1]. Several other chelating agents exist, including 8-quinolinol and more specialized resins that chelate specific ions. A list of recent applications of chelating resins is given in table 2.

The first on-line pre-concentration with atomic spectrometric detection was reported by Olsen *et al.* [8] who used Chelex-100 to pre-concentrate metals from seawater. One problem with the use of Chelex-100 is the swelling and contracting of the resin associated with changes in its ionic form. Other resins with the same functional group, for example Metpac CC1, have been reported not to suffer this disadvantage [41]. The advantage of chelating resins is that they are fairly selective for transition metals, with alkali and alkaline earth metals being easily eluted with an ammonium acetate buffer. The analyte is then eluted with dilute nitric acid.

Chelation may also be used to decrease interferences in ICP-mass spectrometry, for example metal oxides of titanium and molybdenum interfere with copper, zinc and cadmium determinations. By complexing the titanium and molybdenum with N-methylfurohydroxamic acid they may be retained on a Hamilton PRP-1 column, thereby removing the interference [42].

Table 2. Some applications of chelating resins.

Analyte	Exchange medium	Matrix	Comments	Reference
V	Chelex-100	Biological matrices	Chemical purification	[2]
Ba, Be, Cd, Co, Cu, Mn, Ni & Pb	Chelex-100	—	Microcolumns and FI-ICP	[3]
Rare Earths	Chelex-100	Uranium	Detection by NAA	[4]
Transition metals & Pb	Chelex-100	Seawater	Detection by GFAAS	[5]
Cd, Cu, Mn, Zn & Pb	Chelex-100	Water	IC-FAAS online elution with cysteine	[6]
Cd, Cu, Pb & Zn	Chelex-100	—	FAAS detection	[7]
Cd, Cu, Pb & Zn	Chelex-100	Seawater	FI-AAS, microcolumn	[8]
Transition metals & Pb	Chelex-100	Seawater	GFAAS detection	[9]
Cd, Pb, Ni, Cu & Zn	Chelex-100	Seawater	GFAAS and FAAS	[10]
Cu	Chelex-100	—	Development of a valve	[11]
Ce, Co, Eu, Fe, Gd, Mn, Y & Zn	Chelex-100	Brines	γ spectrometry detection	[12]
Transition metals & Pb	Chelex-100	Seawater	GFAAS & ICP detection	[13]
Transition metals & Pb	Chelex-100	Seawater	GFAAS detection	[14]
Cd	Muromac-A1	Waters, CRMs	Minicolumn, FI-ICP	[15]
Cr, Ti, V, Fe & Al	Muromac-A1	—	Microcolumn, FI-ICP	[16]
Cd, Zn, Cu, Mn, Pb, Fe & Cr	Muromac-A1	Biological CRMs	FI-AAS	[17]
Fe, Zn, Cu, Ni & Cr	Muromac-A1	Water	Online-ICP or ICP-MS detection	[18]
Transition metals & Pb	Metpac CC-1	Seawater	Online ICP-MS detection	[19]
Al	8-quinolinol/EDTA	—	Comparison of chelating agents immobilised on glass	[20]
Fe	8 quinolinol	—	Minicolumn, chelator on glass. CL detection.	[21]
Cu	8 quinolinol	Waters	Chelator on glass	[22]
Transition metals	8 quinolinol	Inorganic salts	Chelator on silica gel	[23]
Cu, Co, Cd, Ni, Pb & Zn	8 quinolinol	Waters	Chelator on glass	[24]
Cu	8 quinolinol	—	Chelator on glass. FI-ISE detection	[25]
Cr	8 quinolinol	Seawater	Complexation of analyte followed by adsorption to a macroporous resin	[26]
Cu	8-quinolinol	Water	Chelator on glass. FI-AAS	[27]
Cr	Poly(hydroxamic acid) resin	Seawater	FI-AAS	[28]
Hg	Picolinic acid amide	River water	Styrene DVB beads impregnated with chelator	[29]
Ag, Au, Cu, Fe, Hg, Ni & Zn	Histidine	Water	Histidine attached to carboxyl of amberlite IRC50	[30]
Cu, Cd, Pb, Zn, Ag, Co, Fe, In, Ti, V, Bi	Carboxymethylated polyethylenimine-poly-methylene polyphenylene isocyanate	Sea water, bone	No swelling of the resin	[31]
Cu, Cd, Zn	Chelex-100 and AG-MP-I	Waters	FI-AAS	[32]
Various	EDTrA-Cellulose/HSO ₃ oxine cellulose	—	—	[33]
Hg	Thiazole & thiazoline groups	Seawater	Elution with HCl and thiourea	[34]
Pb	Various	Water	Chelating agents on silica gel	[35]
Mo and W	Kelex-100	Seawater	Catalytic current polarography detection	[36]
Transition metals	Various	—	Preparation and study of chelators on silica gel	[37]
Ca and Mg	Dowex A1	Brine	Minicolumn. Spectrophotometric detection	[38]
Various	XAD-4 with 7-dodeceny-8-quinolinol	Seawater	GFAAS and FAAS detection	[39]
Ni, Cu, Pb & Cd	Resion 122	Waters	Minicolumn, salicylic acid functional group	[40]

Table 3. Some applications of cation exchange resins.

Analyte	Exchange resin	Matrix	Comments	Reference
Rare earths	AG 50 WX 8	Geological materials	ICP detection (off-line)	[43]
Rare earths	AG 50 WX 8	Geological materials	ICP detection	[44]
Li, Na, K, Ti, Be, Mg, Ni, Ca & Al	AG 50 WX 8	Manganese	AAS detection	[45]
Rare earths	AG 50 WX 8	Geological materials	ICP detection	[46]
Pt	AG 50 WX 8	Airborne particulates	FI-ICP-MS detection	[47]
Mo	AG 50 WX 8	Plants	Interferents adsorbed by resin—Mo not	[48]
Te	AG 50 WX 8	—	HCl-acetone mobile phase elutes interferents	[49]
Rare earths	AG 50 WX 8	Rocks	ICP detection	[50]
Rare earths	AG 50 WX 8/ AG 50 WX 12	Geological	ICP detection	[51]
Rare earths	AG 50 WX 8/ AG 50 WX 12	Geological	ICP detection	[52]
Mn, Co & Ni	AG MP 50	Te	HCl-acetone mobile phase	[53]
Mn	Amberlite CG-120	Ti, Si, HF, HCl, & HNO ₃	Spectrophotometric detection	[54]
Rare earths	Amberlite XAD-7 with PC-88A	Tb	Reduction of interferences	[55]
Eu, Th, U & Pu	Amberlyst A-15	—	Extraction of metals from non-aqueous solutions	[56]

Table 4. Applications of anion exchange resins.

Analyte	Exchange medium	Matrix	Comments	Reference
Mn, Cu, Co, Zn, Cd, Pb & U	Dowex 1 × 8	Mn nodules	Elution with either 6M HCl 1M HCl or 2M HNO ₃ AAS detection	[57]
Ni	Dowex 1 × 8	Mn nodules	Ni elutes with ethanol/HCl mobile phase. AAS detection	[58]
Ga	Dowex 1 × 8	Mn nodules	AAS detection	[59]
Co	Dowex 1 × 8	Water	GFAAS detection	[60]
Tl, Mo & V	Dowex 1 × 8	Mn nodules	Chloro-complexes sorbed from sample	[61]
Th and U	Dowex 1 × 8	Mn nodules	Fluorimetric detection	[62]
Zn	Dowex 1 × 8	Plants	Zinc chloro complexes retained. Spectrophotometric detection	[63]
Pt & Pd	Dowex 1 × 8	Geological samples	GFAAS detection	[64]
Mn, Mg, Ti, Cr, W, Mo, Ta & Fe	Dowex AG 1 × 8	Niobium	IC-ICP	[65]
Pt & Ir	AG 1 × 2	Marine waters, sedi- ments & organisms	GFAAS detection IC-ICP	[66]
Cd, Cr, Cu, Fe, Mn, Ni, Pb & Zn	AG MP 1	River and seawater	ISOX complex adsorbed	[67]
B	IRA 743	Water	Spectrophotometric detection	[68]
Zn & Cd	IRA 400	—	CL detection	[69]
Al	IRA 400	Biological samples	Microcolumn ICP or AAS detection	[70]
Ca	IRA 400 and De-acidite FF	—	Removal of phosphate and Sulphate interferences	[71]

Cation exchange

Cation exchangers have also been used for pre-concentration and matrix removal prior to atomic spectrometric detection. The most common cation exchange resins are AG 50W and Amberlite 120, both of which contain sulphononic acid functional groups. Recent applications of cation exchange resins are detailed in table 3. The eluent for cation exchange chromatography ranges from dilute

acids to 8M nitric and 6M hydrochloric acids, depending upon the analyte. Further dilution may therefore be required before analysis by atomic spectrometry.

Anion exchange

Anion exchange has also been used to facilitate analyses with atomic spectrometric detection. Anion exchange resins, such as Dowex 1 and Amberlite IRA 400, contain

Table 5. Other exchange media used.

Analyte	Exchange medium	Matrix	Comments	Reference
Pb	Activated alumina	Water	FI-AAS microcolumn	[72]
Cr	Activated alumina	Urine	FI-ICP, minicolumn	[73]
S	Activated alumina	Water	FI-ICP, micro-column	[74]
Lanthanides	Na β aluminogallate crystals	—	Na exchange with lanthanides	[75]
Cr	C-18 Rainin column	—	Ion pairing of Cr VI with tetrabutylammonium phosphate	[76]
Various	Retardion II A 8	—	Amphoteric resin	[77]
Se	Sephadex G-25M	Serum	Column used to de-salt serum ICP-MS detection	[78]
Cu, Pb	C-18	—	Chelate formed with DDC, 8HQ PAR or PAN	[79]

quaternary ammonium functional groups. Anion exchange can be used to quantitatively retain complexes of analytes with negatively charged ligands, whilst allowing other interfering cations to elute. Table 4 details some applications of anion exchange chromatography. In addition to retaining complexes of the analytes, there have been other applications. Kamson and Townshend [71] used an Amberlite IRA 400 and a De-acidite FF column to remove the interference effects exerted by phosphate and sulphate on calcium determinations by flame AAS.

Others

Table 5 shows some novel methods of ion exchange. Activated alumina has the advantage of being amphoteric, i.e. in its basic form it may be used to adsorb cations, such as lead [72] and chromium [73]; and in its acidic form it may be used to adsorb anions, such as sulphate [74]. Similarly, Retardion 11A8 is an amphoteric resin with both benzyltrimethylammonium and carboxylic acid exchange groups. Non-polar C-18 (octadecylsilane) columns have also been used for some applications, such as the adsorption of the diethyldithiocarbamate complexes of copper and iron [79].

In addition to the papers detailing specific applications of FI and LC, there have been a number of authoritative reviews, for example on FI-ICP [80–83] and FI-atomic spectrometry [84–86]. A very comprehensive review of the literature is the second edition of Ruzicka and Hansen's book [87].

Several other papers concerned with FI-ICP or FI-ICP-MS also exist [88–95], however many were performed off-line [93–94].

Conclusions

There is a growing trend towards the use of on-line mini- or micro-columns of exchange resins to pre-concentrate the analyte, or remove interfering species from the matrix, prior to atomic spectrometric detection. This may, in part, be due to the simplicity of the apparatus, and to the ease of automation of such systems. The use of

on-line columns also leads to a decrease in the chances of contamination associated with the sample handling of off-line batch methods.

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