# TRACE ELEMENT PRECONCENTRATION FROM AQUEOUS SOLUTIONS ON A SOLID PHASE

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## ABSTRACT

The practical aspects that determine the choice and suitability of a solid phase preconcentration method such as the properties of the solid

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* For further information

phase, the chemical modification of the solid phase, rapidity of preconcentration, concentration factors achieved and recovery of adsorbed elements have been critically evaluated. Experimental details for a number of preconcentration procedures involving coprecipitation, flotation, chelating groups on solid supports and electrodeposition are also presented.

The obligation to determine concentrations of analyte below direct instrumental detection limits, the non-homogeneous distribution of trace elements thus necessitating larger representative samples and interference from matrix components have made preconcentration procedures indispensable in solving present day analytical problems; this is evident from the number of reviews that have recently appeared. While some reviews have covered general aspects of many preconcentration techniques /1-3, 15, 16/, others have been concerned with specific areas like on-site preconcentration /4/ or preconcentration by coprecipitation /5-8/, use of cellular and foamed plastics /9-11/ or of cellulose containing immobilized chelating groups /12/ and by flotation /13/.

Preconcentration methods have been classified /16/ according to the initial and second phases as shown in Table 1. We have limited the present review to methods involving a solid second phase because of their simplicity and wide applicability.
These have been further classified as follows:

a. Coprecipitation (Table 2)
    i) inorganic
    ii) organic
    iii) flotation
b. Chelating groups on solid supports (Table 3)
    i) synthetic resins and foamed plastics
    ii) silica and alumina
    iii) cellulose
    iv) activated carbon
c. Electrodeposition (Table 4)

The objectives of the present review are to make readily available experimental details of an extensive (though not exhaustive) number of preconcentration methods and to evaluate critically the practical aspects that determine the choice and suitability of a particular method. These will be considered under the headings of the solid phase, chemical modification of the solid phase, the preconcentration and determination steps and conclusions.

*Purity:*

The purity of the solid phase is undoubtedly the most important criterion in preconcentration for trace analysis. This is not usually a serious problem for inorganic coprecipitants unless a large amount is used as, for example, in the collection of chromate from 2.5 l of sea water on 2g of $BaSO_4$ /41/; the barium chloride solution and all other reagents require careful purification /17/. Elaborate procedures for minimizing blanks have been described /48, 52/ which are equally effective and more economical than maintaining clean room facilities. Hydrated antimony pentoxide /231/ and titanium oxide /232/ have been used to remove matrix components such as Na, K, and P and not for preconcentration because of the inability to purify them. Trace metal contamination of organic precipitants like 1-(2-pyridylazo)-2-naphthol (PAN) often elevates detection limits /73/; purification by extraction /48, 49/ is sometimes effective. The metal content of chelating resins and polyurethane foams has been minimized by $HNO_3$ treatment HCl /109, 169-171, 153, 161/ and thiourea-HCl /136/. Careful blank corrections are needed when using natural products like soya bean protein /65/, chitosan /170, 175/ or activated carbon /208, 215/. The trace metal content and chelation efficiency of chitosan varies with different batches /176/ and although washing with distilled waterand EDTA removes some elements, Fe, Al, Cr and V concentrations remain high. Treatment of commercial activatee carbon with HF and HCl resulted in a five-fold decrease in its metal content /186/; subsequent heating in vacuum at 1000°C expels adsorbed HCl and volatilizes several elements /187/; heating of a commercial activated carbon at 350°C for 2 hours /225/ or in a stream of nitrogen at 900°C /196/ minimizes its mercury content. Activated carbon obtained by carbonizing polyvinylidene chloride is very low in metal content (except for Al) /188/ and has been used to determine Mn in natural waters /215/; this carbon, however, is not commercially available. Highly dispersed silicic acid has lower blanks /230/ but is not a better adsorbent than activated carbon.

Although solid supports like silica and cellulose are obtained in high purity, the effect of impurities in different reagents used to modify them chemically has not been studied except for Whatman No. 1 filters containing immobilized diethylenetriamine (DEN) groups /164/.

High purity aluminum foil /181/, platinum /180, 183/ and spectrographic grade graphite /178, 179, 182, 184/ have been used for electrodeposition. Even 99.99% pure platinum contains significant amounts of silver and zinc /183/ and spectrographic graphite rods must be heated to 2000°C to minimize blanks /182/.

### *Physical properties*

Resins based on polystyrene-divinylbenzene (Chelex-100) swell, shrink, or become rigid with the passage of samples /124/. Use of Chelex-100 in its $Ca^{2+}$-form /171/ or after mixing with glass powder of the same mesh size /111/ has minimized this problem. However, the swelling property has been utilized to adsorb dithizone or thenoyltrifluoroacetone (TTA) onto divinylbenzene beads which have then been used for sea water analysis /140, 141/. Foamed plastics /9-11/ are physically rigid and permit flow rates of up to 100ml/min. Swelling and shrinkage are absent with chelating groups on controlled pore glass (CPG), silica gel or cellulose; silica gel, synthetic resins and cellulose can be used for direct analysis either by neutron activation analysis (NAA) or by X-ray fluorescence (XRF) after pelletizing. Adsorbed elements from foamed plastics and CPG have to be eluted.

The solid phase should not chemically or spectrally interfere, of course, at the analytical step. Coprecipitants like lead phosphate /239/ or lead sulphide /34/ are particularly suited for NAA while the hydrous oxide of iron (III) /24, 25, 29, 30/ has been used for XRF. Organic coprecipitants, silica, cellulose and activated carbon are excellent for both NAA and XRF because the low atomic number of matrix elements limits interference.

## CHEMICAL MODIFICATION OF THE SOLID PHASE

In coprecipitation, it is always better to generate the solid phase *in situ* than to add preformed precipitates. Organic coprecipitation can involve the addition of a concentrated solution of the reagent in a water miscible solvent so that the reagent, which precipitates on contact with the aqueous solution, carries down the trace elements /72-74/ or a water soluble reagent forming insoluble chelates can be added /42 -64, 73, 76/.

### *Chelating groups on solid supports*

*Synthetic resins:* Ever since Erlenmeyer and Dahn /103/ used powdered oxine for column separation of metal ions, chelating groups (like salicylic acid /172/, 8-hydroxyquinoline /104, 160/, N-substituted hydroxylamines /173/, propylenediaminetetraacetic acid /174/) have been introduced into polystyrene-divinylbenzene or phenol-formaldehyde type resins. These have been mainly used for separation of metal ions to achieve better selectivity over conventional ion-exchange resins.

Iminodiacetate groups on a polystyrene-divinylbenzene resin (Chelex-100) appears to be the first extensively used synthetic resin for preconcentration /110, 111, 124, 125, 169-171/. Functional groups like tetraethylenepentamine on a toluene diisocyanate resin /114, 115/ and its dithiocarbamate /130/, dithiocarbamate on a polymethylene polyphenylisocyanate resin /142, 143, 168/, polyacrylamidoxime resin /148, 155/ and thiol groups on polyurethane foam /9-11/ have been prepared and used. Despite the wealth of information available for producing the polymers, the number of chelating groups anchored and used successfully appears to be meagre. This may be because of side reactions and cross linking during polymerization and it is to be expected that increased knowledge about control of polymerization reactions will result in more specificity in the future. It might also be rewarding to re-examine for preconcentration some of those previously used for metal ion separation. Chelating resins being used for industrial waste water treatment have recently been successfully applied to analytical preconcentration /136, 185/. Several commercially available ion-exchange filters (most of them based on synthetic resins) have also been used /112, 113, 152/.

*Silica:* The silylation reaction typically involving stirring of a silica containing material with N-$\beta$-aminoethyl-$\gamma$-aminopropyltrimethoxysilane /120/ for 15 min is simple, rapid and has played a very important role in anchoring many chelating groups. For example, an arylamine has been coupled to CPG to which 8-hydroxyquinoline was attached after diazotization /105/. Similar reactions were used to anchor EDTA /126-128/, $\beta$-diketones /158/, N-substituted ethylenediamines /115-121, 159/ which were converted to dithiocarbamates /115, 129, 131/ and several others recently /162, 163/ which have yet to be evaluated analytically.

*Cellulose:* Various reaction sequences used to introduce different functional groups onto cellulose have been recently reviewed /12/. An ion-exchange cellulose with up to 10mM/g capacity can be obtained, but chelating groups offer better selectivity. Mild and well optimized reaction conditions are required to minimize side reactions and breakdown of the fibrous structure of cellulose and the maximum capacity so far obtained is ~1mM/g. The most successfully used chelating groups on cellulose are 1-(2-hydroxyphenylazo)-2-naphthol (HYPHAN) /147/, bis-salicylaldehydeethylenediamine (SALEN) /166/, DEN /122, 123, 154/ and dithiocarbamate /88/.

*Adsorption of reagents on solid supports:* Simple approaches such as the spreading of different sulphide precipitates onto filter paper /38/ and blotting paper /99/ have been quite effective. Immobilization of several chelating groups by adsorption and/or ionic interaction with a cellulose substrate has also been reported /12/. Convenient and easily available supports include p-dimethylaminobenzylidenerhodanine on silica gel /148/, dithizone and TTA on divinylbenzene beads /140, 141/, aniline-sulphur on alumina /137-139/, reagents on polyurethane foam /9-11/, 8-hydroxyquinoline-5-sulphonic acid /156/ and zincon /151/ adsorbed on conventional anion-exchange resins and ferroin-type chromogens on Amberlite XAD-2 /150/.

*Activated carbon:* The use of the classical adsorbent, activated carbon, for analytical preconcentration of inorganic species is quite recent. The large surface area adsorbs metal ions and neutral atoms; however, use of a chelate forming reagent in solution enhances the efficiency and number of elements adsorbed. Activated carbon with adsorbed reagent has also been effective.

### *Chemical stability*

The functional group usually determines the chemical stability. Silylated surfaces are quite stable except at high acid or base concentrations. Dithiocarbamate groups are susceptible to oxidation or decomposition in acid. On silica-coated filter paper, the dithiocarbamate was stable for only three days in a refrigerator /131/ while on cellulose they were stable for at least 15 days if stored in a stoppered bottle containing ammonium carbonate /88/. Functional groups on synthetic resins are particularly stable to acid and base and hence can be easily regenerated.

### *Capacity*

Caution should be exercised when comparing reported capacity values because some are reported as breakthrough capacity (by column technique) and others as saturation capacity (by batch technique). It is preferable to compare capacities for the same technique (batch or column) being used for preconcentration. In general, the capacity of silylated surfaces is low, ranging from 0.05mM/g for EDTA on CPG /126-128/ to 1.05mM for N-substituted ethylenediamines on silica gel /119/. The capacity of polyurethane foams containing adsorbed reagents (0.023mM/g) /177/ and chelating groups on filters (0.015mM/filter) /152/ is also low. Synthetic resins and cellulose have higher capacities with values ranging from 1.35mM/g for a polydithiocarbamate resin /142/ to 1.52mM/g on cellulose /88/. The capacity of activated carbon is determined by its surface area and is generally about 0.5mM/g /207/; the capacity of activated carbon with adsorbed 8-hydroxyquinoline is 0.4–0.9mM/g /219/. High capacity is desirable when analysing unknown samples which may contain high concentrations of elements with strong affinity for the functional groups.

### *Selectivity*

The achievement of better selectivity for heavy metals relative to the alkalis and alkaline earths (more abundant in natural waters) has been an important aim. Chelex-100, although used extensively, has a high affinity for Ca and Mg. The negative charge of the iminodiacetate group will be neutralized with $Na^+$ ions which particularly interfere with NAA. Hence, Ca and Mg are eluted with ammonium acetate /124/ or acid /111, 126/. Polyamines such as ethylenediamine or DEN have no affinity for alkali and alkaline earths; the positive charge on the nitrogen helps collect metal-humic acid complexes /122/ and other oxyanions /123/ although high concentrations of simple anions like chloride suppress their adsorption. The conversion of amine groups to dithiocarbamates improves selectivity to Hg, Cd, Pb and Cu /88/. With a multi-element technique, it is desirable to collect 'all' heavy metals, but further selectivity is sometimes needed. Arsonic acid on a macroporous resin is selective to actinide elements /144/ although it collects a high concentration of Ca which can be eluted with pH 4 buffer. β-diketone groups on silica /158/ have no significant affinity for Co, Ni, Zn, Mg, Ca, La and Th, but collect only Cu, Fe (III) and U (VI). Various 6-substituted-1, 3, 5-triazine dithiols precipitate Cu, Cd, Pb, and Hg /79/ even in the presence of several mg of Al, Fe (III), V (V), Zn, As (III & V), Ni, Co, Mn and citrate. With improved techniques, it should be possible to introduce more than one functional group onto the same support thus increasing the range of elements that can be adsorbed just as the sequential use of two chelating reagents under different conditions can improve the adsorption of many metal ions on activated carbon /210, 220/. Adsorption on activated carbon does not involve competitive equilibrium for coordination. Hence it has not only been used to preconcentrate trace elements from natural waters /191, 192, 196-199, 202, 204, 207-216, 219, 220, 222-228/, but also from high purity salts and alloys containing Cd, Mg, Al /193/, W /194/, Ag, Tl /195/, Mn /205/, Zn /206/, Cr /217/, Pb, In, Co, Ni, Zn /218/ and Co, Ni /221/. None of the other chemically modified supports can be used for this purpose. However, matrix precipitation /33, 39, 40/ or partial dissolution of matrix /100-102/ results in a trace concentrate or residue, respectively.

The necessity to differentiate and quantitate various chemical forms of trace elements (rather than their total concentration) in the natural environment is now well recognized /18/. Although electroanalytical techniques are best suited and extensively used to quantitate ionic species with different oxidation states or labile and inert complexes with different ligands, other analytical techniques, particularly in conjunction with a preconcentration step, are also being used. Differentiation between oxidation states is the most easily achieved speciation; for example, Cr (VI) and (III) can be differentiated by coprecipitation with the hydrous oxide of iron /29/ or $BaSO_4$ /41/ or adsorption on activated carbon /211/; Se (IV) and (VI) in sea, tap, and surface waters can be differentiated by adsorption on activated carbon /209, 229/. The differentiation of inorganic and more toxic organic mercury has been accomplished after their preconcentration on an aniline-sulphur resin on alumina /137-139/, on a dithiocarbamate-loaded polyurethane foam /234/ and by using different reduction conditions in the estimation step after preconcentration on a dithiocarbamate resin /136/. The concentrations of labile and total Pb, Co, Ni in sea waters were obtained, after electrodeposition under two different conditions, in a flow-through graphite tube prior to analysis by atomic absorption spectrometry or anodic stripping voltammetry /178/. Similarly, labile fractions of Cd, Cu, Pb, and Zn in the presence of model ligands were obtained after preconcentration on Chelex-100 in $Ca^{2+}$-form /235/. The adsorption of metal-humic acid complexes on activated carbon /216, 224/ should be useful in differentiating the ionic and humic acid bound fractions.

## *Mechanism*

Understanding the operating mechanisms in these preconcentration steps is as important as applying them to real sample analysis. The mechanisms for even classical coprecipitation are still not completely understood. The inadequacy of many recently developed theories /19-23/ is evident from the limited cases for which they have been proved to be experimentally valid. Mechanisms operating at a chemically modified solid support are more complicated although surface analytical techniques are now being used to unravel them. Electron spectroscopy for chemical analysis (ESCA) studies show that dichromate and permanganate ions oxidize the diamine groups on CPG and then complex with the oxidized or other amine groups /118/. Infrared and photoacoustic spectroscopy show that the white precipitate formed with molybdate and ethylenediamine (en) at pH 3 contains polymeric molybdate, while monomeric species are involved when it reacts with immobilized en /119/. Steric factors restrict the formation of more stable 1:2 complexes with immobilized dithiocarbamate /130/ or iminodiacetate /167/ groups. Although one may wish, therefore, to extend the wealth of information available from solvent extraction studies to chelating resins, the behaviour is not always comparable, both in stoichiometry and kinetics. The distribution coefficients were higher by $10^2$-$10^3$ for HYPHAN on cellulose compared to its use as an extractant into MIBK /146/ demonstrating an advantage of immobilized chelating agents over solvent extraction.

ESCA studies of silylated silica gel showed /132/ that amine groups were partially (25%) converted to dithiocarbamate groups and many of these had been oxidized to thiuram disulphide. Formation of bisdithiocarbamate was not observed probably because only 5 min was used for the dithiocarbamate conversion reaction; one day /88, 168/ or as long as three weeks /142/ has been used. The silica gel (similarly the polyamine-polyurea resin /130/) therefore contained appreciable concentrations of unreacted amine which scavenged Ba and Ca /133/.

In spite of extensive work on the adsorption of organic molecules onto activated carbon /189/, and more recently of trace metal complexes, little is understood about the adsorption forces. The studies of Piperacki *et al.* /190/ on the adsorption of Ni and its amino acid complexes suggested that aromatic rings or hetero atoms and hydrophobic groups are desirable for good adsorption. This still does not explain those cases where even water-soluble, charged complexes are adsorbed.

Interpretation of results obtained by measuring the equilibrium concentration of adsorbate in solution is complicated by many mechanisms operating simultaneously. For example, in addition to pi-electron interaction between the graphitic planes and the ligand molecule /207/, nonspecific adsorption in the electrical double layer (whose nature is dependent on the surface oxygen groups on activated carbon and the nature of the electrolyte in solution) is at least partially responsible for the adsorption of charged complexes /187/.

## THE PRECONCENTRATION STEP

The entire preconcentration step should be simple and involve minimum addition of reagents. Some procedures therefore avoid even pH adjustment of natural waters /108, 111, 114, 136, 147, 199, 207, 212/. Addition of buffer and reagents for precipitation or complex formation is, however, inevitable and the possibility of contamination must always be checked. Although high and constant recovery is desirable and often obtainable, radioactive tracers can be used to calculate the chemical yield. It should be emphasized here that quantitative recovery of an ionic spike from natural waters does not of course guarantee quantitative recovery of all the species of the element /18, 169, 170/

The rapidity of preconcentration is determined by the functional group and the solid support. Diffusion through a surface gradient film has been shown to be the rate determining step in the kinetics of exchange of metal ions with 8-hydroxyquinoline immobilized on CPG /106/; air trapped in the porous glass surface interferes with exchange and CPG has to be vacuum degassed. Easy accessibility of functional groups on chemically modified microcrystalline cellulose gave increased capacity and more rapid kinetics than cross-linked amorphous cellulose /165/. $\beta$-diketone groups on silica exchanged metal ions rapidly ($<10$ min) /158/ compared to the several hours required for a diketone on polystyrene-divinylbenzene resin /233/. The slow kinetics with a polyacrylamidoxime resin necessitated a 24 hour batch extraction mode /145/; a column mode is preferable for most solid supports to facilitate passage of large volumes of sample.

The simple procedure of passing solution through a filter paper containing either adsorbed reagents /38, 99/ or anchored chelating groups /122, 123, 131, 152, 154, 158/ to provide ideally thin targets for XRF is sometimes complicated by the need to pass the solution several times to achieve quantitative recovery /131, 152/ or to limit the volume treated without elution /123/; decreased flow rates due to swelling /131/ and limited capacity /152/ are other difficulties.

Although collection by coprecipitation may be rapid, the need to collect the precipitate in an easily filterable form often requires lengthy digestion and cooling. Use of poly-5-vinyl-8-hydroxyquinoline /60/ which precipitates at room temperature in less than 2 min (compared to digestion with 8-HQ at 80°C for 1 hour /61/), flocculants like zephiramine /50/, dibenzylidene-d-sorbitol /44/, β-naphthol /54/, polyvinylpyrrolidone /76/ and thionalide /53/ have resulted in rapid settling of the precipitate. To obtain higher concentration factors (defined as the ratio of the initial matrix weight to the final matrix weight when the recovery of the trace elements is quantitative; with 1000 ml of sample and 0.1g of the solid phase, the concentration factor will be $10^4$) large volumes of sample can be processed. This is an advantage over solvent extraction (which has been the most used preconcentration step according to an IUPAC study /14/) where a decrease in the distribution ratio with an increase in aqueous-to-organic volume ratio, solubility of organic solvent and difficulty in recovering small volumes of organic solvent restricts the concentration factor obtainable to $10^2$. Up to 5 1 volumes have been used with coprecipitation; flotation from 1 1 of sample is claimed to be rapid, simple and convenient /93-97/. Although only 50% of added PAN is recovered from 2 1 of water sample, it is enough to collect several metal ions quantitatively giving a concentration factor of $2 \times 10^5$ /67/. Column techniques are still the best for processing large volumes of sample, but as seen above, the kinetics of exchange and physical properties of the solid phase determine the attainable flow rates (ranging from 0.2ml/min for Chelex-100 /124/ to 50ml/min for chelating groups on CPG /118, 121/). Flow rates of up to 100ml/min are possible with polyurethane foams /153, 161/. Although quantitative recovery of added spikes has been demonstrated for many metals on polyurethane foams /9-11/, very few preconcentrations at natural levels have been performed but continues to be used for separation of metal ions /157/. Even with intermediate flow rates, use of 10 1 /150/ or 20 1 /136/ volumes is not uncommon. A combination of column and batch techniques has been used to obtain a concentration factor of $2 \times 10^4$ using cellulose containing immobilized HYPHAN /147/.

Electrodeposition often has to be performed for 15-30 hours /182, 184/ and a limit of concentration may be reached or matrix components may also be deposited.

The importance of on-site preconcentration has been recently emphasised /4/. This eliminates handling and storage of large volumes of sample leading to loss or change in analyte concentration. Digestion has precluded the use of coprecipitation except for ammoniumpyrrolidinedithiocarbamate /47/ but slow filtration is still a problem /46/. Flotation with hydrous oxides of iron /86/ and aluminium /85/ have been used; however, flotation requires careful pH control because it determines the charge on the precipitate and hence quantitative collection. Complete collection of the foam is reported /98/ to be sometimes difficult and the foam physically carries the matrix components /85, 97/. Flotation is still attractive, however, because it is simple and rapid; more studies, particularly for multielement analysis, must be done. Adsorption on activated carbon has been used for on-site preconcentration /196, 209, 211/. Ship-board /115, 124/ and on-site preconcentration /121/ using column techniques has also been done. Other procedures should also be applicable to on-site preconcentration and these need to be evaluated.

Automation of preconcentration is still an unexplored area but, the column technique using EDTA on CPG has been automated /126-128/ to minimize human error. A dust-proof teflon apparatus for unattended preconcentration of a number of samples has also been described /124/.

## THE DETERMINATION STEP

The most obvious analytical technique to use with a solid phase is NAA or XRF. A suitable binder is used to form pellets for XRF. Chelating filters and precipitate spread onto filters are very attractive to XRF as it offers ideally thin targets. The precipitate or the metal ions on chelating filters become spread over a wide area while the X-ray beam is narrow. Special apparatus has been designed to confine the filtered dot to 1.27mm diameter thus achieving lower detection limits /55/; but this restricted the volume of sample to 3ml. With both NAA and XRF the quantitative recovery of the precipitate is mandatory (and sometimes difficult) to obtain good precision. In solid state reflectance or luminescence /68-74/ procedures, the solid phase need not be recovered quantitatively, because the preconcentrated element is evenly distributed throughout the matrix. Electrodeposited elements have been estimated by XRF /179, 181/ or NAA /184/. The combination of flame /183/ and graphite furnace /178, 182, 184/ AAS with electrodeposition did not fully utilize the latter's multielement capability but this was overcome by grinding the graphite electrode and then using portions of the powder directly in a graphite furnace /182/; contamination, achieving homogeneity and low precision in solid sampling for AAS are some problems. Other techniques that can also be used directly on solid-state concentrates include emission spectrography /191/ and spark source mass spectrometry /224/.

Preconcentration on solid supports may not seem attractive for techniques requiring a solution for analysis but it does offer higher concentration factors. Elutions with a minimum volume should be checked for recovery. Complete destruction of a resin can give better recovery and precision /143/ than simple elution /142/. Dry ashing of a solid phase should be checked for volatility losses; cellulose is an attractive solid phase as it can be ashed by low temperature plasma. Adsorbed elements can also be recovered by soxhlet extraction /150/ or elution with organic solvents /153, 161/.

## CONCLUSIONS

The foregoing discussion has shown that binding of trace element species present in aqueous solution onto a solid support either by physical or chemical forces is an elegant and widely applicable preconcentration step. Improvement in the synthesis of chelating groups onto solid supports, re-examination of others previously tried for separation of metal ions, further application of flotation and polyurethane foams to real sample analysis, on-site studies and automation of preconcentration appear to be some areas for future development. The ideal preconcentration step, needed because the ideal analytical step still eludes us, has yet to be achieved.

TABLE 1: Classification of concentration methods for trace elements according to initial and second phase.

| Initial phase | Second phase | Method of concentration |
|---|---|---|
| solid | gas | evaporation of trace elements or matrix; volatilization by reaction with a reactive gas. |
| solid; liquid | gas | gas chromatography |
| liquid | liquid | solvent extraction of trace elements or matrix |
| liquid | liquid | extraction chromatography |
| liquid | solid | sorption of trace elements or matrix |
| liquid | solid | precipitation and coprecipitation of trace elements or matrix |
| liquid | solid | electrolytic deposition of trace elements or matrix |
| liquid/ solid | liquid/ solid | selective dissolution of trace elements or matrix |

TABLE 2: Preconcentration by coprecipitation

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| INORGANIC COPRECIPITANTS: | | |
| | *Hydrous oxides of:* | |
| 24, 30 | Fe(III) | River water (400ml); Fe, Zn, Pb collected on 1mg Fe for XRF |
| 25 | Fe(III) | Sea water (2-5 l); Vanadium collected on 50mg of Fe at pH 6-7 for spectrophotometry with N-benzoyl-N-phenylhydroxylamine |
| 29 | Fe | Waste water; Cd, Cu, Zn, Cr(III) collected at pH 10 for XRF |
| 27 | Al | Sea water (1 l); phosphate collected and precipitate dissolved in 0.5M sulphuric acid for spectrophotometry as molybdenum blue. |
| 32 | Th | Crude oil (10g) decomposed; Pb collected with 10mg Th at pH 10 for GFAAS |
| 26 | Zr | Sea water; As(III), Cr(VI), Pb collected at pH 8.3-11; dissolved in hot 2M HCl for GFAAS |
| 28 | Zr | Sea water (1 l); Be and Bi collected; precipitate dissolved in 2N HCl for GFAAS |

TABLE 2 (cont)

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| 31 | Mg | Ground water; Fe, Mn collected on 65mg of $Mg(OH)_2$ at pH $>$ 7; dissolved in 6M HCl for AAS |
|  | *Sulphide of:* |  |
| 38 | Zn, Mn, Cu, or Pb | Surface water (up to 6 1) passed through sulphide precipitate spread on filter to collect Hg, Ag, Cu, Bi, Pb, Cd for XRF or GFAAS after dissolution in nitric acid |
| 99 | Zn | Waste water; Hg, Ag, Cu collected on ZnS precipitate spread on filter paper for XRF |
| 36 | Cu | Ores dissolved in $HCl:HNO_3$; Au, Pt, Pd collected on 20 mg CuS for NAA |
| 35 | Cu | Sea water; flameless AAS for Hg and flame AAS for Pb and Cd |
| 37 | Ni | Ores, plant materials; Platinum group elements collected for ICP-AES |
| 34 | Pb | Sea water; Hg and Au collected by passing through 3-cm column of PbS for NAA |
| 41 | $BaSO_4$ | River water (2.5 1); Cr(VI) collected at pH 3-5 on 2g $BaSO_4$ by standing overnight; solid fused with $K_2CO_3$ and Cr estimated by spectrophotometry with diphenylcarbazide; Cr(VI) and Cr(III) differentiated. |
|  | *Precipitation of matrix as:* |  |
| 39 | $PbSO_4$ | High purity Pb salts; Zn, Cd, Co, Sb, In, Tl quantitatively recovered from the mother liquor for ASV. |
| 40 | $Pb(NO_3)_2$ | High purity Pb salts; Ag, Al, Bi, Cd, Co, Cu, In, Mn, Ni, Pd quantitatively recovered from the mother liquor after separating the matrix as $Pb(NO_3)_2$ for AAS; precipitation as $PbCl_2$ or $PbSO_4$ gave erratic recovery. |
| 33 | CuS | High purity Cu salts; Cd, Co, Fe, In, Mn, Ni, Pb, Tl, Zn quantitatively recovered from filtrate after separating the matrix as CuS for flame AAS |
|  | *Partial dissolution of matrix:* |  |
| 100 |  | High purity Cd metal (20g) amalgamated with mercury & dissolved in 100ml 40% HBr; residue containing electrochemically more noble metals like Ag, Au, Bi, Co, Cu, Fe, In, Pb, Pd in $>$ 95% recovery dissolved in 5ml 65% nitric acid for flame AAS |

TABLE 2 (cont)

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| 101,<br>102 | | High purity Mn(10g) /101/ or Ga (5g) /102/ dissolved by boiling with 50ml 3M HCl or 300ml (3M HCl: 0.15M HNO$_3$) and residue analysed for Ag, Au, Bi, Co, Cu, Fe, Hg, Ni, Pb, Pd by flame AAS |
| ORGANIC COPRECIPITANTS | | |
| | *Sodium or diethylammonium diethyldithiocarbamate:* | |
| 43 | | Titanium metal; Mn, Fe collected at pH 7-9 for XRF |
| 44 | | River, industrial waste water; Pb, Fe, Cu, Zn, Mn, Cd, Cr, Sb, As collected at pH 5-5.5; dibenzylidene-d-sorbitol in dimethyl-sulphoxide added as a flocculant; XRF |
| 45 | | Saline water (250ml); Cu, Zn, Hg, Fe collected at pH 4 for XRF |
| 52,<br>55 | | Standard reference materials; Fe, Cr, Co, Cu, Ni collected using Ti as carrier at pH 8-8.2; precipitate filtered in special apparatus to confine to 1.27mm diameter dot for XRF; this limits the sample volume to 3ml; elaborate procedures described for minimizing blanks. |
| 53 | | Aqueous sediments and airborne dust; Fe, Zn, Pb collected for XRF |
| 54 | | Coastal water; Ni, Co, Cu, Pb, Mn, Zn, Cd collected using β-naphthol as flocculant for AAS |
| 57,<br>58 | | Drinking and waste water, biological solutions; Cr, Ni, Fe, Cu, Zn, Cd, Pb, As, Se collected prior to XRF |
| 59 | | Suitability of DDTC coprecipitation for XRF analysis for heavy metals from biological fluids and waters with regard to yield and homogeinity were investigated using tracers |
| | *Ammonium pyrrolidinedithiocarbamate:* | |
| 42 | | Mg and Al metal; Cu, Zn, Fe, Ni collected at pH 3 for XRF |
| 46 | | Fresh water (500ml); V, Cr, Mn, Ni, Cu, Zn, Se, Hg, Pb collected at pH 4 using Fe(III) as carrier for XRF |
| 47 | | Water; ppb levels of U, Th, Mo collected at the sampling site for XRF |
| 48 | | Sea water (100ml); Cu, Ni, Cd collected at pH 2 using Co(II) as carrier; elaborate procedures for minimizing blanks are described for AAS |

TABLE 2 (cont)

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| 49 | | Potable water, sediment digestate; Pb, Ni, Cr(VI) collected using Co(II) as carrier for flame AAS |
| 50 | | Biological samples (1g) decomposed in $HNO_3/HClO_4$; Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb collected at pH 6-8 using zephiramine for coagulation; proton activation and AAS |
| 51 | | Mineral water (200 ml); Cd, Co, Cr, Cu, Ni, Pb, collected in easily filtrable form at pH 2-3 using Fe(III) carrier for GFAAS |
| 56 | | River, estuarine water (100ml); Fe, Co, Ni, Cu, Zn, Cd, Pb, collected at pH 4.4 using Mo(VI) (a 4d element) carrier which does not have interfering lines when analysing for 3d elements by XRF |
| | *8-hydroxyquinoline:* | |
| 61 | | Sea water (250ml); Mn, Cu collected at pH 7-8 after digestion at 80°C for 1 h and cooling for 1-2 h; precipitate irradiated and radiochemically separated prior to x-ray spectroscopy |
| 62 | | Soil and sewage sludge; Ag, Au, Cu collected using tannic acid and thionalide for collection prior to spark source mass spectrometry. |
| | *Poly-5-vinyl-8-hydroxyquinoline:* | |
| 60 | | Saline water; Al, Co, Cu, Fe, Pb, Ni, V, Zn collected in less than 2 min in cold |
| | *Thiooxine with 8,8'-diquinolyldisulphide:* | |
| 63,<br>64 | | Sea water; Fe, Co, Ni, Zn, Ag, Hg, Au, Sc collected for NAA |
| | *Thionalide with polyvinylpyrrolidone:* | |
| 76 | | Drinking, river water and effluent (up to 1 l); Cu, Fe, Zn, Se, Cd, Sn, Te, Hg, Pb collected at pH 4 in less than 15 min prior to XRF |
| | *Soya bean protein:* | |
| 65 | | Artificial sea water (1 l); Au, Ag, Cd, Ce, Ga, In, Hg, La, Sb, Th collected at pH 4.5-5 by boiling for 2-3 min; precipitate centrifuged, washed, ashed in a low temperature plasma asher for estimation by emission spectrography |

TABLE 2 (cont)

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| | *1-(2-pyridylazo)-2-naphthol (PAN):* | |
| 66, 67 | | River, drinking water (up to 4 1); Cr(III), Mn, Ni, Cu, Zn, Hg, Eu collected at neutral pH using 20 mg PAN and heating at 70°; recovery of PAN from 4 1of water is 50% but enough to recover trace metals quantitatively for XRF; results compared with that obtained after adsorption on activated carbon |
| | *α-benzoin and β-naphthoin oxime:* | |
| 82, 83 | | Sea water (up to 1 l); Mo collected at pH 2 after settling for 2 days prior to NAA |
| | *Calcium oxalate:* | |
| 68, 71 | | Leaves and synthetic blood; Bi, Pb collected; precipitate ignited at 850°C and solid state luminescence measured |
| | *Dinaphthoylmethane:* | |
| 72 | | Aqueous solution (100 ml); Be collected at pH 7.2; precipitate dried at 100° and solid state luminescence measured |
| | *α-benzildioxime:* | |
| 73, 74 | | Sea water (500ml); Ni collected at pH 9.5; solid state reflectance measured |
| | *Polyhydroxyflavones:* | |
| 75 | | Natural water; Al, Sc, Zr, Hf collected and solid state luminescence measured |
| | *Bulky organic molecules:* | |
| 77, 78 | | Sea, estuarine water; soluble complexes of Cd (Cadion IREA), Cu (2,2'-bicinchoninic acid), Mo (Tichronin), Zn, Cd, Pb, ($SCN^-$) were precipitated with β-naphthol, stilbene, diphenylguanidine, methyl violet and crystal violet prior to polarography. |
| 80 | | Aqueous solution, organic compounds, waste water; rare earths precipitated as $SCN^-$ complexes with diantypyrinyl methane prior to emission spectrography; Ni, Cr(III), Mn(II), Fe(II & III), Mg, Ca, Na, K at mg/ml level did not interfere. |

TABLE 2 (cont)

| Ref. | Coprecipitant | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| | *6-substituted-1,3,5-triazine-2,4-dithiols:* | |
| 79 | | Standard reference material and water (up to 500 ml); Cu, Cd, Pb, Hg collected at pH 7 in presence of a quaternary ammonium salt; mg levels of Al, Fe(III), Zn, As(III & V), Ni, Co, Mn did not interfere in the presence of citrate prior to XRF. |
| | *1,10-phenanthroline and tetraphenyl boron:* | |
| 81 | | Water; Mn, Fe, Ni, Cu, Co, Zn, Sn, Hg, Pb collected prior to XRF; large concentrations of Ca and Mg do not interfere. |
| FLOTATION PROCEDURES: | | |
| 84 | Arsenazo III, zephiramine | Sea water (500 ml); U(VI) floated at pH 3.5 for spectrophotometry |
| 86 | Hydrous ferric oxide-surfactant | Sea water (500 ml); V(V) floated at pH 5.00±0.02 for AAS after dissolution and extraction into MIBK as cupferron complex; on-site preconcentration performed |
| 91 | as above | Sea water (500 ml); As(III or V) floated at pH 8-9 for AAS by arsine generation |
| 92 | as above | Tap water (500 ml); Se(IV) floated at pH 3.5-5.3; tedious separation needed to apply catalytic method of estimation |
| 93 | as above | Sea water (1 l); Se(IV) floated at pH 4.0±0.2 prior to AAS by hydride generation |
| 94 | as above | Sea water ( 1 l); Sn(II & IV) floated at pH 4.0±0.2 for AAS |
| 96 | as above | Sea water (1 l); Bi floated at pH 4.0±0.2 prior to AAS by hydride generation |
| 85, 89 | Hydrous aluminium oxide-sodium oleate | Sea water (1 l); Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb floated at pH 9.5 for AAS; 20-30 mg Mg gets collected; on-site preconcentration performed |
| 95, 97 | Hydrous indium oxide-surfactant | Water (1 l); Cr, Mn, Ni, Co, Cd, Pb floated at pH 9.5 for ICP-AES; collects 2-3 mg Mg |
| 90 | Hydrous bismuth oxide-surfactant | Water, high purity zinc metal; Pb, Fe floated for AAS |

TABLE 3: Chelating groups on solid supports

| Ref. | Chelating gp./ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| SYNTHETIC RESINS AND FOAMED PLASTICS | | |
| 110 | Iminodiacetate gps-synthetic resin (Chelex-100) | Ground water (1 l) at pH 4 stirred for 3h; $UO_2^{2+}$; pelletized for XRF |
| 124 | As above | Sea water (1 l) at pH 5-5.5 passed (0.2-0.8 ml/min); alkaline earths eluted (70 ml 1M ammonium acetate) Cd, Co, Cu, Fe, Mn, Zn eluted (10 ml 2.5M nitric acid) for GFAAS; dust-proof teflon apparatus devised for overnight, shipboard or on-site operation |
| 111 | Chelex-100 mixed with glass powder | Sea water (1 l) at pH 8 passed (3.5 ml/min); alkaline earths eluted (100 ml 0.01M nitric acid); Cu, Cd, Mn, Zn, Co, U, V, Fe eluted (50 ml 4M nitric acid) for NAA; glass powder facilitated faster flow rates |
| 125 | Chelex-100 in $Ca^{2+}$ form | Sea water; alkaline earths eluted (dil. acetic acid); Cu, Pb, Ni, Zn, Cd, Co eluted (dil. Nitric acid) for AAS; Ca-form does not shrink and helps maximum retention of heavy metals |
| 113 | Chelex-100 filters | Drinking water (8 ml diluted to 200 ml) passed through 2 filters (10ml/min); affinity for ions: $Sr > Ni > Mn \geqslant Pb \geqslant Co \geqslant Ca \geqslant Zn \geqslant Cu$; XRF |
| 114, 115 | Tetraethylene pentamine-toluene diisocyanate resin | Sea water (4 l) at pH 8.2 passed (3 ml/min); for XRF or eluted (4 ml 4M nitric acid) for AAS (Cu, Ni, Zn) |
| 130 | Dithiocarbamate gps/polyamine-poly urea resin | Capacity order: $Ag > Hg > Cu > Sb(III) > Pb > Cd > Ni > Zn > Co$: (AAS) |
| 136 | Dithiocarbamate (DTC) on vinyl polymer | River, lake, rain water (20 l) passed (30 ml/min), 0.5-5000 ppt Hg eluted (3 ml acidic thiourea) for cold vapour AAS; Total & inorganic Hg (organic Hg by difference) obtained; 35-60% of total Hg in river & lake water & 6% in rain water is in organic form; resin is stable to acid |
| 185 | as above | Sea and river water (10 & 20 l) passed (50 ml/min) at pH 2-3; resin washed and decomposed under reflux with nitric acid for cold vapour AAS; on-site preconcentration possible and the resin with adsorbed mercury stable for 9 weeks |

TABLE 3 (cont)

| Ref. | Chelating gp/ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| 142 | Polydithiocarbamate on polyethyleneimine resin | Pb in melted snow, Cu in whole milk, Cu, Cd, Pb in sea, tap & fresh waters analysed (AAS) after elution with hot nitric acid |
| 143 | As above | Urine and lab water analysed for Al, Au, Bi, In, Ir, Pd, Pt, Re, Rh, Ru, Se, Sn, Te, Tl by ICP-AES; total destruction of resin improves recovery |
| 144 | Arsonic acid on macroporous resin | Tap, sea water (1 l) at pH 5 passed (7 ml/min): eluted (25 ml 4M perchloric acid) for plasma emission (Cd, Co, Cu, Ni, Pb, Zn, Th) and spectrophotometry (U); 80% Ca adsorbs, but can be removed by washing with pH 4 buffer; Th & U separated from each other. and from other elements; resin stable to acid and base |
| 145, 155 | Polyacrylamidoxime resin | Sea water (1 l) at pH 6 shaken with 0.5g resin for 24h; stripped with 5ml 1:1 HCl (3h) for AAS (Fe, Cu, Pd, Zn); slow kinetics prevents use of column technique |
| 140, 141 | Dithizone, thiothenoyltrifluoroacetone on divinylbenzene beads | Sea water (1 l) at pH 1-2 passed (4ml/min); eluted (30ml 8M HCl) for spectrophotometry (Hg) and AAS (Cu, Zn); sample has to be pre-equilibrated with chlorobenzene used to swell the beads |
| 149 | 2-(3′-sulphobenzoyl) pyridine-2-pyridylhydrazone (I) on anion exchange resin (Bio Rad AG1-X2) | Artificial sea water (3 l) containing 10ml of 2mM I/100ml at pH 10 passed (10ml/min); eluted (10ml 2M nitric acid) for AAS (Co, Cd, Zn); 10% reagent loaded resin can also be used; on-site preconcentration possible; resin containing adsorbed metals stable for 96h |
| 156 | 8-hydroxyquinoline-5-sulphonic acid on Bio Rad AG1-X2 | Solution (1 l) containing 5ml 2mM reagent at pH 8 passed (10ml/min); eluted (2M nitric acid) for AAS or $\gamma$-spectrometry (Zn, Cd, Pb, Co); ligand loaded resin is also effective |
| 150 | Ferroin-type chromogens on Amberlite XAD-2 resin | Synthetic sea water (10 l) passed (5ml/min); soxhlet extracted with methanol (5h) for AAS (Co, Ni, Cu, Fe); out of four compounds, 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) most effectively adsorbed; $I^-$, $ClO_4^-$ enhance adsorption of cationic complexes |

TABLE 3 (cont)

| Ref. | Chelating gp/ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| 151 | Zincon on anion exchange resin | River water (1-2 l) passed; resin irradiated and analysed by γ-ray spectrometry for Cu, Zn, Hg |
| 153 | 1-(2-pyridylazo)-2-naphthol (PAN) on polyurethane foam | Water (10 l) containing 192g KSCN at pH 5 passed (100ml/min); eluted (50ml acetone); interfering ions separated on Dowex 1-X8 before spectrophotometry for Co with 4-(2-pyridylazo) resorcinol (PAR); described procedure has not been applied to the analysis of natural water samples |
| 177 | TBP-Zn-DDTC on polyurethane foam | Aqueous solution spiked with 0.72ppb Hg passed (40ml/min) and quantitatively recovered |
| 237 | -SH groups on polyurethane foam produced by electrical discharge | Aqueous solution spiked with 4-0.0004ppm Hg and 2-0.0004ppm MeHg recovered quantitatively |
| 238 | Dithizone on polyurethane foam | Double distilled, tap, river water and sewage sludge spiked with radioactive Hg to check recovery which was lower from natural samples than from DDW |
| 234 | Diethylammonium DTC-polyurethane foam | Tap, saline water spiked with 1ppb of inorganic, & organic Hg passed (120ml/min) and recovered quantitatively |
| 236 | Ethanedithiol on polyurethane foam | River, sea water spiked with 6ppb Sb(III) at pH 1-2.5 passed (5ml/min) and quantitatively recovered; As, Hg also get adsorbed |
| SILICA AND ALUMINA | | |
| 105 | 8-hydroxyquinoline on controlled pore glass (CPG) | Distilled, deionised water (1 l) at pH 5 passed (5ml per minute); eluted (50ml 1M HCl) for spectrophotometry for Fe, Cu |
| 108 | as above | Natural water (2 l) at pH 6 passed (10ml/min); washed (10ml water) and eluted (25ml 1M HCl) for AAS (Cu); rapid flow rate and kinetics; capacity is low (0.57mM/g); 8-HQ-CPG has to be degassed at 1-2cm Hg |
| 107 | Poly-5-vinyl-8-HQ on CPG | Spiked sea water (1ml) irradiated; adsorbed on 10ml column; washed (30ml pH 9 buffer); Cu, V, Mn, Al on CPG estimated by γ-spectrometry; no advantage over 8-HQ on CPG; achieves only separation from matrix components |

TABLE 3 (cont)

| Ref. | Chelating gp/ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| 126-128 | EDTA on CPG | Sea water (2-5 l) at pH 5.6 passed (5 ml/min); eluted (10ml 1M HCl) for AAS (Cu, Pb, Zn) and polarography (Cd); automation of preconcentration eliminates human error |
| 116 | N-substituted ethylenediamine on silica gel | Quantitative adsorption at pH 3-5.5 (Hg), > 5 (Cu), > 7 (Zn), > 8 (Co), > 10 (Mn); pelletized for XRF; capacity 0.5mM for Cu |
| 117 | As above | Phosphate at ppb levels extracted (ethyl acetate) as heteropoly acid and adsorbed; pelletized for XRF; 1000-fold silicate and 10-fold arsenate do not interfere. |
| 118 | As above | Aqueous solution spiked with ng/ml of arsenate, molybdate, dichromate, selenate, tungstate, vanadate passed (50ml/min) for XRF; capacity 0.54 mM dichromate, 0.67mM molybdate/g. |
| 119 | As above | Saline water (1 l) passed (25ml/min) and pelletized for XRF (W, Mo) |
| 159 | N-substituted ethylenediamine on silica coated filter paper | Extractive process solution (25ml) containing U adsorbed as $[UO_2(CO_3)_3]^{4-}$ by passing several times through the filter prior to XRF; filters stable in cool, dark, dry place for several months |
| 115 | N-substituted ethylenediamines & their dithiocarbamates on silica gel | Hg, Cu, Fe, Zn, Ag, Ni, Pb, Cd, Cr, Eu, Co, Mn, collected quantitatively for XRF |
| 120, 121 | As above | Lake water, industrial water (1 l) containing ng/ml Cu, Ni, Co passed (50ml/min); pelletized for XRF; on-site preconcentration performed |
| 131 | Dithiocarbamate gps. on silica coated filter paper | High purity water (50ml) passed (10ml/min/cm$^2$) ten times to adsorb Cu, Fe(II & III), Zn, Cd, Ni, As(III), Sb(III), Hg, V, U, for XRF; filters stable for 3 days in refrigerator; swelling reduces flow rates; DTC content is 10.3 $\mu$M/filter |
| 129 | DTC gps. on glass fibres | 100ml solution passed (5ml/min); ppb detection limits for Pb, Tl, Hg, Cu by ESCA |

TABLE 3 (cont)

| Ref. | Chelating gp/ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| 158 | $\beta$-diketone gps. on silica, CPG, filter paper containing silica | Dependence of pH, equilibration time on capacity & affinity studied for Cu, Fe, V, Ni, Co, Th by spectroph.; high affinity for Cu, U & Fe and no affinity for Co, Ni, Zn, Mg, Ca; stable & inexpensive to prepare |
| 148 | p-dimethylbenzylidinerhodanine on silica gel | Sea water (1-5 l) passed (20ml/min); Ag, Au, Pd eluted (20ml 0.1% thiourea in 0.1M HCl) for $\gamma$-spectrometry using tracers |
| 137-139 | Aniline-sulphur resin on alumina | River water (5 l) passed (2ml/min) for NAA; inorganic (at 0.5M acid) & organic (at pH 6-7) Hg collected; capacity: 0.6 mM Hg/g; Au, Se, U also adsorbed. |
| CELLULOSE | | |
| 147 | 1-(2-hydroxyphenylazo)-2-naphthol (HYPHAN) on cellulose | Mineral water (2 l) at pH 6-8 passed (2 g resin at 30ml/min); Mn, Co, Fe, Ni, Cu, Zn, Ta, Pb, U eluted (50ml 1M HCl) & readsorbed on 0.1g resin by stirring for 30 min at pH 7.5; pelletized for XRF |
| 122, 154 | Diethylenetriamine (DEN) on cellulose filters (Whatman 1) | Selectivity order: Hg > U > Cu > Pb > Cr > Zn > Co > Ni > Cd > Mn collected from near neutral pH at 1-2ml/cm$^2$/min for XRF; 10,000ppm Ca does not affect collection; positive charge on DEN collects metal-humic acid complexes and anions |
| 123 | As above | Water (200 ml) at pH 4.5 passed (0.5 ml/cm$^2$/min) to collect anions with affinity order: tungstate vanadate molybdate chromate selenate arsenate Br for XRF; NaCl (> 0.01M) affects collection |
| 134, 135 | DTC of different amines on cellulose | Capacity order: Hg > Cr(VI) > Ag > Se(IV) > Cu > Pb and effect of pH studied |
| 88 | DTC of triethylenetetramine on cellulose | Sea, tap water (5 l) shaken (1 l at a time for 30 min) to collect Cu, Cd, Hg, Pb for NAA and GFAAS (Pb); effect of pH and capacity studied for ethylenediamine, DEN & trien and their DTC |
| 152 | Chelating ion-exchange filters (Whatman SA 2) | Sea water (1 l) processed through Chelex-100 resin /124/ to remove Na, K, Mg, Ca; Ni, Mn, Zn, Cu, Pb eluted (10ml 2.5M nitric acid) and passed through filter at pH 2-3 at least seven times for XRF; NBS standard reference materials analysed. |

TABLE 3 (cont)

| Ref. | Chelating gp./ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| ACTIVATED CARBON | | |
| 197, 198, 214 | Activated carbon (AC) | Water, rocks, plants; U(VI) adsorbed and estimated by spectrophotometry with arsenazo III |
| 196 | AC | Natural waters (1 l) acidified to pH 1 (for total Hg) and unacidified sample (for organic and particulate Hg) passed through 1.5g AC at the sampling site; AC transported for NAA |
| 201 | AC | Saline solution; Mg collected as $Mg(OH)_2$ at pH $> 12$ for spectrophotometry with Eriochrome Black T |
| 229 | AC | Sodium perchlorate (100g in 200ml); Ag, Bi, Co, Cd, Cu, Fe, In, Mn, Ni, Pb, Hg collected at pH 6 by passing solution through filter covered with AC for AAS |
| 209 | AC and ascorbic acid | Sea, surface, tap water (500 ml); Se(VI) reduced to Se(IV) by refluxing with HCl; Se(IV) reduced with ascorbic acid and adsorbed on AC at sampling site for NAA |
| 98, 226 | AC and ascorbic acid | Natural waters (1 l); Se(VI) reduced to Se(IV) by refluxing with thiourea-sulphuric acid (reduction with HCl was not possible due to high bromide content of HCl which interfered spectrally); Se(IV) reduced with ascorbic acid and adsorbed on AC for XRF; recovery not affected by salt or humic material content of water. |
| 199, 202 | AC with ascorbic acid | Sea, surface, tap water (500 ml) at pH 6-8 stirred with 50mg AC for 15 min with ascorbic acid to collect U (VI) for NAA |
| 211 | AC with sulphite | Sea, fresh water; Cr(VI) reduced with sulphite at pH 1.5 and adsorbed on AC from neutral medium at sampling site for NAA; Cr(III) and Cr(VI) differentiated; Cr content of AC determines the detection limit |
| 204 | Ammonium-pyrrolidine dithiocarbamate/ AC | Sea, surface waters (500 ml) at pH 1.3 stirred with 60 mg AC and 75mg APDC for 40-60 min to collect Mo and W for NAA; W has to be separated by ion-exchange |
| 208 | As above | Sea, surface waters (200 ml) at pH 3.6 stirred with • 30 mg AC and 75mg APDC for 10 min to collect V |

TABLE 3 (cont)

| Ref. | Chelating gp./ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| | | for NAA: V content of AC and reagents determine detection limits |
| 213 | As above | Fresh waters stirred with AC for 30min at pH 6-8 to collect Hg and Cu as APDC complexes on spectrographic carbon powder for NAA |
| 215 | As above | Sea, rain waters (200ml) stirred with 40mg AC at pH 5-9, 50mg APDC to collect Mn (also Cu, Cd, Zn, Co) for NAA; AC obtained from carbonizing polyvinylidene chloride used as commercial AC contains high concentration of Mn |
| 221 | As above | Cobalt & nickel salts (50g) at pH 3.5-4.3 containing APDC passed through 50mg AC on filter to collect Ag and Bi for AAS by injection method |
| 194 | Sodium diethyldithiocarbamate/ AC | Powdered tungsten (5g) dissolved in hydrogen peroxide; NaDDTC added, at pH 7.5 passed through 50mg AC on filter to collect Ag, Cd, Co, Cu, In, Pb, Tl, Zn for AAS or XRF |
| 200 | As above | Alkali and ammonium salts (10g) solution containing NaDDTC passed through 50mg AC on filter for flame AAS analysis of Ag, Bi, Cd, Co, Cu, In, Ni, Pb, Tl, Zn |
| 218 | As above | High purity lead, indium, nickel, zinc salts (5-10g) dissolved; matrix elements masked with EDTA; NaDDTC complexes of Ag, Bi, Cu, Tl adsorbed on AC for AAS |
| 217 | Hexamethyleneammonium hexamethylenedithiocarbamate/AC | Chromium salts (20g) dissolved; Ag, Bi, Cd, Co, Cu, In, Ni, Pb, Tl, Zn complexed with the reagent at pH 4 and adsorbed on AC spread on filter for AAS |
| 205 | Ethyl xanthogenate/AC | Pure manganese salts (10-50g) dissolved and Bi, Cd, Co, Cu, Fe, In, Ni, Pb, Tl, Zn complexed and adsorbed at pH 6.5-7 on AC spread on filter for AAS |
| 206 | As above | High purity zinc salts (10-50g) dissolved and Ag, Bi, Cu, Co, Cd, Pb, In, Tl, Ni, Fe collected at pH 4.8 - 5.5 on AC spread on filter for AAS |
| 210, 220, | Sodium diethyldithiocarbamate, | Sea water (1 l) shaken with 30 mg AC and NaDDTC at pH 5.5 and later again with 30mg AC and dithizone at |

TABLE 3 (cont)

| Ref. | Chelating gp/ solid support | Matrix; experimental conditions; elements adsorbed; analytical finish; remarks |
|---|---|---|
| 228 | dithizone/AC | pH 8.5; AC combined and analysed for Ag, Au, Cd, Co, Ce, Hg, Eu, La by NAA; use of two reagents improves recovery; on-site preconcentration performed |
| 207, 212 | 8-hydroxyquinoline/AC | Natural waters (1 l) at pH 7-8.5 shaken with oxine and AC to collect Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hf, Re, Hg, Pb, Sm, Eu, Tb, Dy, Yb, Lu for NAA /207/ or XRF /212/. |
| 216, 224 | As above | Natural waters containing humic materials; significant fraction of total metal present as humic acid complexes or in colloidal form collected on AC for analysis by XRF /216/ or spark source mass spectrometry /224/ |
| 223 | As above | Natural water and urine; U collected with oxine on AC for thermal and epithermal NAA |
| 203 | As above | Silicate rocks irradiated, fused with sodium peroxide and pH adjusted to 1.3 to adsorb W as oxine complex on AC |
| 193 | Zincon, dithizone/AC | Cd, Mg, Al salts (5-50g) dissolved and Ag, Cd, Co, Cu, In, Ni, Pb, Zn complexes of zincon or dithizone adsorbed on AC spread on filter at pH 8 for AAS |
| 195 | Xylenol orange/ AC | Silver and thallium salts (5g) dissolved and xylenol orange complexes of Bi, Co, Cu, Fe, In, Pb collected on AC spread on filter for AAS |
| 191 | Dithizone, 8-hydroxyquinoline, NaDDTC or thioacetamide adsorbed on AC | Sea water (1 l) at pH 5-8 passed through column packed with reagent adsorbed AC; Cu, Zn, Pb, Cd, Bi, Sb, Au, Mo, Sn at ng/ml estimated by spectrography |
| 219 | 8-hydroxyquinoline adsorbed on AC | Adsorption of 0.05ppm Cu, Zn, Cd, Mn(II) not affected by 0.5M NaCl; capacity was 0.4-0.9 mEq/g AC |

TABLE 4: Preconcentration by electrodeposition

| Ref. | Solid support | Matrix; experimental conditions; elements collected; analytical finish; remarks |
|---|---|---|
| 178 | Pyrolytic graphite tube | Sea water (50ml) at pH 4.6 (for labile metal) and after boiling with nitric acid (for total metal) passed through tube at 120ml/min for 5min at -0.8 (for Pb), -1.8 (for Co), -1.6 (for Ni)V versus Ag/AgCl; tube used for AAS |
| 179 | Spectrographic graphite rods | Aqueous solution (100ml) at pH 6 electrolysed at -1.7V vs. saturated calomel electrode for 18h to deposit Cu for XRF |
| 180 | Platinum electrode | ng of Cu and Au from one drop of solution deposited for microprobe analysis; quantitative collection is not possible hence constant conditions have to be maintained |
| 181 | Aluminium foil | Synthetic river water (250ml; spiked) passed through Dowex 50W-X8 resin to adsorb cations; eluted with KCN solution at pH 10.5 and cyano complexes of Fe, Co, Ni, Cu, Cd, Zn deposited on aluminium foil at 300-1500V for 15-30 min for XRF |
| 182 | Graphite rods | Alkali, alkaline earth salt solution (50ml) electrolysed for 50h at -1.0V vs. Ag/AgCl to deposit In, Tl, Bi, Sb, Mn, Ag, Hg, Cu, Pb, Cd; exposed part of electrode is ground in agate mortar and solid introduced for GFAAS |
| 183 | Platinum wire loop | Sea water (25ml; spiked) at pH 5 electrolysed for 2 min at -1.0V vs. Ag/AgCl; wire introduced into flame for AAS of Ag, Bi, Cd, Hg, Pb, Se, Te, Tl, Zn |
| 184 | Graphite tube | Aqueous solution containing ammonium fluoride (40 ml) at pH 4-6 passed through tube at 30ml/min for up to 22h to collect Fe, Co, Zn, Bi for AAS, ICP-AES or NAA |

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