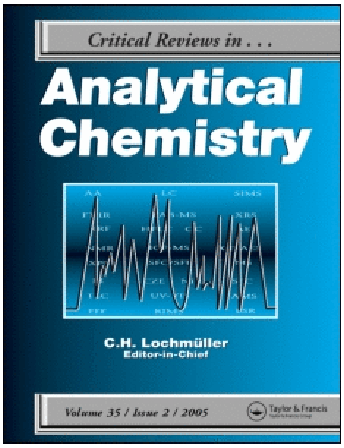

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Overview of Analytical Methodologies for Sea Water Analysis: Part I—Metals

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Overview of Analytical Methodologies for Sea Water Analysis: Part I—Metals

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A comprehensive, critical and up-to-date review of analytical methods developed during the last decade for metals present in sea water is presented. Separate sections are devoted to singular and multimetal determinations. Furthermore, a critical comparison of relative merits or demerits of a particular procedure is made in terms of sensitivity, selectivity and precision. Various aspects of analysis of sea water samples for metals are summarized, and the future trends are discussed.

Keywords sea water, singular and multimetal mixtures, analytical methodologies

INTRODUCTION

The oceans have probably been formed by reaction of primary rocks with volatile substances, which have distilled from the interior of the earth under the influence of thermal stress. The elemental species present in sea water can be classified into four main classes: dissolved atmospheric gases, micronutrient elements, major elements and minor or trace elements (1). With the development of more sensitive analytical techniques, marine analytical chemists can detect and determine inorganic metal species in sea water present at levels of g/l to ng/l level depending on the element. The more important steps prior to analysis are sampling, filtration and storage of sea water sample, which has been discussed in our recent review article (2).

PREVIOUS REVIEWS

We refer the reader to the articles (3–11) listed in Table 1 for reviews appeared during the period 1995–2004 on sea water analysis pertaining to metal ions. As a starting point to understand the complexity of sea water analysis, one can refer to a review article by Atienza et al. (12) that is specifically concerned with flow injection analysis of sea water for cationic species.

THE REVIEW: GOALS AND CONTENT

Although this review deals primarily with the developments in analytical methodologies that took place during the last decade in the determination of metals, it is not aimed solely at an analytical audience but is for all scientists with an interest in marine science. It is our belief that the information will be useful for scientists, in diverse fields such as marine chemistry, marine biology, toxicology and environmental chemistry. We earnestly hope this review caters to various researchers to the most useful techniques for a given application, and dissuade them from following less suitable techniques. A comprehensive compilation of relevant methods reported since 1995 will be presented along with a critical evaluation of these analytical methodologies based on sensitivity, selectivity and precision. The review attempts to cover the relevant work reported from the beginning of 1995 to the end of 2004.

SINGULAR METAL DETERMINATIONS

Alkali and Alkaline Earth Metals

Lithium at levels 1 μM–0.1 mM was determined by UV-visible spectrophotometry by reaction with a water soluble octabromoporphyrin [2,3,7,3,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulphonatophenyl)-21H,23H-porphyrin] in alkaline media (13). The measurement of absorbance at 490 nm results in a detection limit of the order of a few ppm. Later, Sun and Tabata (14) have developed a separation method that involves (i) the liquid-liquid extraction of ternary ion-associate lithium-octabromoporphyrin-tetrabutylammoniumchloride into chloroform and (ii) transport of lithium ion across a CHCl3 liquid membrane, based on the above described method. In both cases, lithium was selectively separated from a large excess of sodium ions, the Li/Na selectivity being >10,000. The method was applied to the separation and spectrophotometric determination of lithium in sea water and serum.

A disposable single-use optical sensor to determine potassium in sea water in the range 0.0125–76.8 mM was developed based on an ion exchange mechanism (15). The test strip is

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TABLE 1
Some recent reviews dealing with sea water analysis pertaining to metals and complimentary to this review

S. No.	Title	Comments	Ref.
1	Sample filtration as a source of error in the determination of trace elements in marine waters	Current practices of filtration need to be reviewed if contamination errors are to be controlled	(3)
2	Automated in-line sampling and analysis of trace elements in surface waters with voltammetric detection	Instrumentation and methods for collecting surface sea water using pumping and subsequent inline analysis by stripping potentiometry or chronopotentiometry has been reviewed	(4)
3	Recent progress in trace in trace element analysis of sea water (Japanese)	Concerns with publications related to the determination of trace elements in sea water with coverage of publications since 1998–2000	(5)
4	Analytical methods for trace elements in sea water (Japanese)	Presents advances in the determination of trace elements in sea water using anodic stripping voltammetry fluorimetry and chemiluminescence	(6)
5	Analysis for environmental monitoring: on-site analysis of sea water	Overview is given on the analysis of the water samples on board ships and submarines with some discussion on sampling techniques	(7)
6	Automated flow-through analysis of trace elements in marine chemistry	Presents automated flow through analysis of sea water with electrolytic and chelating resin. Preconcentration as well detection methods suitable for in situ ship board analysis	(8)
7	Determination Co in sea water by FI analysis	Brief review with 5 references on in-situ flow injection analysis of sea water from various depths from on board of researchship.	(9)
8	Hypenated techniques combined with atomic spectrometry for environmental studies	Development and application of hyphenated techniques combined with atomic spectrometries for environmental analysis at Xiamen University, China are described	(10)
9	Determination of Fe in sea water	Concerns with analytical methods for the determination of Fe in sea water	(11)

formed by a circular film zone 6 mm in diameter and 4.7 μm in thickness that contains all the reagents necessary to produce a selective response to K^+ on a polyester sheet. The sensing zone is formed by plasticized PVC that incorporates the cation-selective neutral ionophore-dibenzo-18-crown-6, lipophilised Nile blue and a lipophylic salt. At pH 9, the absorbance response of the test strip at 660 nm shows a good correlation with K^+ concentration in sea water, human plasma samples and pharmaceutical compounds. Ljung and Axner (16) developed a sensitive procedure employing wavelength modulation diode laser absorption spectrometry for the determination of as low as 10 fg of rubidium in several reference materials of tap water and sea water. The results agreed with certified values. Suppressed ion chromatography was employed for the determination of lithium, sodium, ammonium and potassium in brine, sea water and ground water after dilution (17). Calibration graphs were linear upto 35 μg/l of Li^+, 54 mg/l of Na^+, 0.7 mg/l of NH_4^+ and 2.5 mg/l of K^+. Intra–ssay RSDs were 0.7% for Na^+ and 2.4% for K^+ in sea water, which are quite good.

Beryllium in sea water was determined by graphite furnace atomic absorption spectrometry (GFAAS) after coprecipitation with magnesium hydroxide (68). The calibration graph was linear up to 2 ng/ml of Be and the detection limit was 0.5 μg/l, which are quite good. Nukatruka et al. (19) have preconcentrated trace amounts of beryllium present in sea and lake water onto the surface of silica fibres prior to the determination by electrothermal (ET) AAS. Impressive detection limit of 0.3 ng/l of Be^{2+} was reported by these authors. In 2001, Goto et al. (20) have preconcentrated trace amounts of beryllium present in sea water using xylenol orange and capriquat loaded silica gel prior to determination by GF AAS. The calibration graph was linear from 0–0.02 μg/ml with a good precision of 1.9–3.8% (RSD).

Capillary electrophoretic separation using quaternary amine coated capillary of alkali and alkaline earths was possible to such an extent that a large excess of Na^+ did not interfere with the determination of Mg^{2+} as illustrated by the analysis of diluted sea water (21). A non-suppressed ion chromatographic method was developed for monitoring strontium in the presence of a large excess of alkali and alkaline earth metals (22). The developed method was successfully applied to monitor strontium in coastal Arabian sea water with a RSD of 2%. The results obtained agreed with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Simultaneous determination of calcium and magnesium in sea water upto 20 and 10 mg/l was possible by using capillary electrophoresis with detection limits 0.13 and 0.26 mg/l, respectively (23). The precision of the procedure is quite good as the RSD values are 0.8 and 1.2% for samples containing 5 mg/l of Mg and 8 mg/l of Ca. Paull et al. (24) have determined Ca and Mg in sea water by passing through a Hypercarb graphitic C column with a guard column coated with *o*-cresolpthalein complexone. The RSD values were 5.8% and 7.8% for Mg and Ca, respectively. Mixtures of Na^+, K^+, Mg^{2+} and Ca^{2+} ions in sea water and formation of water from oil wells were analysed by capillary zone electrophoresis (CZE) on a fused silica capillary with indirect UV detection at 185 and 254 nm (25). Reasonably good detection limits of 0.14, 0.15, 0.08, 0.08, 0.18 and 0.15 mg/ml of Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} were reported by using this method. Vogt et al. (26) for the first time have employed infrared attenuated total reflection spectroscopy for the detection of as low as 0.1 M of Na^+ plus K^+, Cl^-, Br^-, Ca^{2+} and Mg^{2+} and 0.3 mM of SO_4^{2-}. The method was used to determine Na^+ plus K^+, Cl^- and SO_4^{2-} in artificial sea water.

3d-Transition Elements

Titanium. Adsorptive cathodic-stripping square-wave voltammetric procedure was developed for the determination of titanium(IV) in artificial sea water in the presence of mixed ligand system acetyl acetone-lumazine (2,4-dihydroxypteridine) maintaining the pH at about 6 (27). Interferences of other trace metal ions and surface-active substances were also investigated.

Vanadium. Traces of vanadium present in sea or natural water samples were determined by catalytic spectrophotometric procedure based on the bromate oxidative coupling reaction of metal and 2,3,4-trihydroxybenzoic acid (28). The limits of detection reported by these authors were 0.008 and 0.018 ng/ml at 380 and 570 nm, respectively. Simultaneous preconcentration of vanadium(V) from artificial and real sea water with a palmitoyl oxine bonded Amberlite XAD-2 copolymer resin column prior to determination by spectrophotometry using 4(2-pyridylazo) resorcinol (PAR) (29). The speciation of the above mentioned species was possible by determining total vanadium and vanadium(V) by masking with cyclohexyldiaminetetraacetic acid using PAR as colorimetric reagent. The limit of detection with spectrophotometry was 1.6 μg/l, which is quite good. Vanadium(V) in sea water was determined by spectrofluorimetry on reaction with sodium 1,2-dihydroxy anthraquinone-3-sulphonate in cationic micellar (hexadecyl trimethyl ammonium bromide) medium (30). The calibration graphs were rectilinear from 10–100 and 41–1000 ng/ml of V(V) respectively, for excitation and emission slits at 12 and 7 nm and the corresponding detection limits were 3 and 10 ng/ml.

The precision of the developed procedure determined at 60 and 400 ng/ml were 2.1 and 1.5%, which are quite good. An on-line flow injection analysis method was developed based on the adsorption of V-cupferron complex onto a Hg film electrode followed by cathodic stripping (31). The calibration was linear upto 3.5 μg/l of V with an impressive detection limit of 8 ng/l. The RSD for determination of 1.3 μg/l of V in sea water was $\sim$7%, which is rather high. Sander and Henze (32) in 1996 have developed adsorption stripping voltammetric procedure for the determination of as low as 21 ng/l vanadium based on adsorption of its chloroanilic acid complex onto hanging mercury drop electrode. Speciative solid phase extraction of species of V viz. V(IV) and V(V) present in sea water with chromazurol B and *N*-cinnamoyl-*N*-2,3-xylyl hydroxylamine respectively and determined separately by ETAAS (33). Reasonably good detection limit of 0.02 ng/ml was reported by these authors. ETAAS was also used for the determination of vanadium in the range 0.05–2.5 μg/l after a preconcentrative separation using trioctyl-methyl ammonium chloride loaded silica gel column (34).

Preconcentrative separation of traces of vanadium present in sea water by adsorption of V-organic complexes using synthetic complexing agents such as dithizone, luminol or 8-hydroxyquinoline onto C18 columns (35). ICP-AES is used for quantification of HNO_3 eluents. Vanadium species in sea water were determined by liquid chromatography (LC)-ICPMS (36). Calibration graphs for V(IV) and V(V) were linear for 0.1–20 ng/ml with detection limits of 25 and 4 ng/l. The precision of the developed procedure at 5 ng/ml of V(IV) were 2.3 and 5.6%, respectively. Picogram amounts of V in calcite and sea water was determined by using isotope dilution ICPMS with electrothermal vaporization (37). A very good detection limit of 6 pg of V was reported by these authors.

Chromium (Cr). The salient features of various analytical procedures developed for the direct or speciative determination of chromium in sea water either with or without preconcentration are summarized in Table 2.

Manganese (Mn). Traces of Mn in sea water was determined spectrophotometrically by reaction with 3,3,5,5,-tetramethyl benzidine (61). The calibration graph was linear for 0.02–0.8 mg/l of Mn with detection limits and RSD of 3 ng/ml and 0.9% respectively which are rather good. Nakano et al. (62) have described a FI-spectrophotometric method for the determination of as low as 0.02 ng/ml of Mn in sea water based on its catalysis of the periodate oxidation of 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid). The calibration graph was linear from 0.05–1 ng/ml of Mn(II) with a precision of 1.6% for 0.5 ng/ml of Mn(II) and throughput was 30 samples/hour. A palmitoyl oxine functionalized Amberlite XAD-2 copolymer resin was used in the column mode to preconcentrate traces of Mn(II) from artificial and real sea water and Mn in the eluate was determined by formaldoxime spectrophotometric method (63). The most serious interferent is iron(III), which was eliminated using the resin retention and elution procedure. Klinkhammer (64) have described zero angle photon spectrometer (ZAPS)—a

TABLE 2
Salient features of analytical methodologies developed for chromium in sea water during 1995–2004

S. No.	Preconcentration method/Highlights	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Polymer inclusion sorbent	Spectrophotometry/NAA	—	—	—	(38)
2	Polymer inclusion sorbent	Spectrophotometry	—	—	—	(39)
3	Chemical amplification	Spectrophotometry	Upto 400 ng	—	3.2 (300ng)	(40)
4	Sequential injection wetting film extraction	Spectrophotometry	5–100	2	2–2.8	(41)
5	Solvent extraction	FAAS	0–2	0.024	—	(42)
6	Online SPE, chromatrope 2R-coated Amberlite XAD-1180	FAAS	—	2.59	<5	(43)
7	Multi-injection	ETAAS	—	0.05	2.7–7.2	(44)
8	Ion pair liquid-liquid extraction	ETAAS	—	0.1 nM	—	(45)
9	Coprecipitation (Cr(III))	ETAAS	Upto 80	2 μg	—	(46)
10	Coprecipitation (Cr(III))	WD XRF/EDXRF	Upto 80	0.10–0.88	5–10	(47)
11	Online, cloud point extraction	Chemiluminescence	0.002–0.2	—	0.9–1.6	(48)
12	Online, speciation	Chemiluminescence	—	—	—	(49)
13	Online, speciation	ICPAES/ICP-MS	—	0.2/0.12	3.8	(50)
14	Solid phase microextraction	GC/ICP-MS	—	0.011–0.015	—	(51)
15	SPME	Sector field ICP-MS	—	0.004	—	(52)
16	5-Palmtoyl oxine functionalized Amberlite XAD-2, speciation	Spectrophotometry	—	9.3nM	—	(53)
17	LLE, cryptand 2.2.1, speciation	Fluorimetry	1–150	—	1.6	(54)
18	Cloud point extraction, speciation	FAAS	—	0.6	2.0	(55)
19	Cation exchange resin, speciation	Derivative FAAS	0–90	0.65	3.63	(56)
20	Cloud point extraction	FAAS	Upto 130 (Cr(III)) & 80 (Cr(IV))	1.4 and 0.65	2.2	(57)
21	Speciation	FAAS	—	—	—	(58)
22	Chitosan, Speciation	ETAAS	—	0.047	7.8	(59)
23	Maleic acid functionalized XAD resin	AAS/spectrophotometry	—	—	—	(60)

fibre optic instrument which combines a Xe flash source and photomultiplier detector.

The ZAPS was deployed as a UV-fluorimeter and chemical sensor for the determination of Mn in sea water. Mn present in sea water was preconcentrated by pumping through two cartridges containing periodate embedded acrylic beads and N,N′-diethylaniline adsorbed into a rod of fibrous fluorocarbon arranged in tandem in a flow cell. Mn catalysed formation of N,N′,N′-tetraethyl benzidine was measured fluorimetrically using ZAPS. The calibration graph was linear upto 23 nM – Mn and the detection limit was <0.1 nM. Mn(II) in sea water as its 4(2-pyridylazo)resorcinol chelate was preconcentrated onto activated carbon sorbent prior to determination by FAAS (65). Multivariate optimization of various parameters was carried out during preconcentration. This method allows the determination of as low as 16 ng/l of Mn present in shore water of Salvador City, Brazil. Rangel et al. (66) have compared the efficacy of several procedures for the determination of Mn in coastal waters by GFAAS. An on-line FI-ETAAS procedure was developed for the determination of Mn in sea water after the preconcentration of its Eriochrome Black T complex onto an anion exchanger resin and elution with HCl (67).

Grotti et al. (68) have employed multiple linear regression technique to develop a mathematical model for correcting the interfering effect of Na, K, Mg and Ca on the determination of Mn by ETAAS. The corrected results for Mn were in good agreement with the certificate value of CASS-3, a certified reference material of sea water after preconcentration on chelex-100 resin and elution with 1 M – HNO_3. Okamura et al. (69) in 1998 have determined traces of Mn in sea water by flow through technique using luminol – H_2O_2 chemiluminescence detection. The calibration graph was linear up to 2000 nM – Mn with a detection limit of 0.029 nM. A similar chemiluminescence detection was employed for shipboard analysis of picomolar levels of Mn in sea water (70). In this method, Mn in sample solution was selectively collected on newly developed iminodiacetate-immobilized chelating resin and then eluted with acidic H_2O_2. The resulting eluent is mixed with luminol solution and removed iron with NH_3 before introducing into chemiluminescence cell. The detection limit of manganese is lower than above mentioned procedure by Okamura et al. i.e., 5 pmol/l. Mn in waste and sea waters was determined by stripping potentiometry (71).

The calibration graph was linear for 0.025 to 5 μg/l of Mn and the RSD was 5.4% at 5 μg/l of Mn. Interference from iron was masked by standing overnight in the pH 9 buffer to precipitate Fe, which is rather tedious. DPCSV procedures were developed for the determination of Mn(II) and Mn(II) and Mn(VII) by using a pretreated rotating glassy carbon electrode (72) and 1(2-pyridylazonaphthol) modified carbon paste electrode (77). The respective detection limits were 6 and 6.9 nM of Mn(II). In the latter procedure the Mn(VII) content was found from the difference from Mn(II) content and total Mn determined as Mn(II) after sample oxidation with H_2O_2.

Iron (Fe). The distinct features of various analytical methods for the offline or FI determination of traces of iron in sea water samples are summarized in Table 3.

Cobalt (Co). A rapid, sensitive and reproducible flow injection analysis—spectrophotometric method is described for the determination of Co(II) in sea water using 4-benzyl piperidine dithiocarbamate as a chromogenic reagent (104). The linear calibration range for the proposed method was 0.6–100 μg/l and a limit of detection was 0.1 μg/l at a sampling rate of 60 h-1. The relative standard deviation is $<1\%$ which is quite good. Shipboard analysis of dissolved Co in sea water was carried out by using flow injection with catalytic spectrophotometric detection (105). The calibration graph is linear in the range 0–300 ng/l of Co; the detection limit was 1 ng/l which is better than the procedure developed by Andae et al. (104). The RSD and throughput of samples were 1.6–10.6% (which is reasonable at the levels of Co involved) and 50 samples/h. Cobalt in sea water is coprecipitated with disulphide and determined subsequently using ETAAS (106). The calibration graph was linear upto 20 ng/ml of cobalt with a detection limit of 3 ng/l. The RSD was 2.7% and 1.8% for 5 and 10 ng/ml, respectively, which is quite good.

Traces of cobalt present in sea water were preconcentrated by (i) synergistic liquid-liquid extraction using thenoyltrifluoroacetone and dibenzo-24-crown-8 (107) and (ii) coprecipitation with Ni-8-quinolinol-1-nitroso-2-naphthol-1-nitroso-2-naphthol complex (108) and determined subsequently by GFAAS. The detection limits for the above two procedures are 1.5 and 1.0 ng/l respectively and are quite impressive. A flow injection, semi-online microcolumn preconcentration system consisting of C18 functional groups integrated with laser excited atomic fluorescence spectrometry method was described for the determination of traces of cobalt in sea water (109). The developed method was validated by analyzing two ocean water reference materials viz. CASS-2 and NASS-4. Galimowski et al. (110) have determined Co in sea water by CSV after complexation with α-benzyldioxine. The reported detection limit and RSD values were <2 ng/l and 5.6%. CSV was used for determining organic complexation of Co in sea water (111). High speed adsorptive CSV (ACSV) was developed for direct determination of Co in unpurged oceanic sea water (112). Saito and Moffett (113) have developed ACSV coupled with a competitive ligand exchange equilibria method for cobalt speciation. A direct (114) and sequential flow analysis (115) ACSV procedures were developed for the determination of traces of cobalt in sea water with a reagent system comprising of NaNO2 and 1,2-cyclohexanedione dioxime. The detection limit of the former procedure is 3 pM, the lowest reported so far for cobalt. An online preconcentration HPLC column switching technique was described for the determination of Co in sea water by formation of chelate with 2-(5-bromo-2-pyridylazo)-5(N-propyl-N-(3-sulphophenyl)-amino) phenol (116). The linear calibration range and detection limits are 0.2–10 nM and 40 pM Co respectively.

Nickel (Ni). Nickel(II) was preconcentrated by flotation after complexing with sodium diethyl dithiocarbamate in presence of oleic acid surfactant and determined by spectrophotometry or AAS (117). The detection limit was 0.05 μg per g of sea water. ETAAS is used for direct determination of Ni in sea water using multiple injection and Zeeman correction (118). Detection limits were 1, 0.2 and 0.1 μg/l for 20, 100 and 200 μl injection volumes respectively. The RSD were in the range 1.6–9.6%. An original online preconcentration system for the determination of nickel in sea water by ETAAS is achieved by replacing the sample tip of autosampler arm by a microcolumn packed with a silica gel chelating resin functionalized with 1-(di-2-pyridyl)methylene dithiocarbanohydrazide (119). The optimized method has two linear calibration ranges, between 0 to 1 ng/ml and between 1 and 5 ng/ml with a detection limit of 0.06 ng/ml and throughput of 36 samples/h for 1 min preconcentration time.

Copper (Cu). The salient features of various analytical procedures developed for the determination of copper in sea water are summarized in Table 4.

Zinc (Zn). A flow injection analysis with fluorimetric detection procedure was described for the determination of 0–500 nM of Zn with a detection limit of 0.01 nM (155). 1-(2-pyridylazo)-2-naphthol modified polymeric membranes were used for batch preconcentration and determination with FAAS (156). The analytical curve was linear upto 30 μg/l with a detection limit of 0.7 μg/l and a RSD of <2%. Zn levels in sea water was determined by ETAAS with a limit of detection of 0.25 μg/l and RSD of 1.67–2.5% (157). GFAAS was employed for the determination of as low as 0.1 and 0.02 μg/l in the absence and presence of chemical modifier via. NH4VO3 respectively (158). Zinc in sea water is preconcentrated by using methyl tricapryl ammonium chloride coated octadecyl silyl silica columns and determination by GFAAS (159). The detection limit was 2.4 ng/l based on a 125-fold concentration of 500 ml sample. A FI-ICPAES

TABLE 3
Salient features of analytical methodologies developed for iron in sea water during 1995–2004

Sl. No.	Distinct features	Analytical technique	Calibration range	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Ferrocene is used as colour forming reagent	Spectrophotometry	μM level	—	—	(74)
2	Ferrozine is used as colour forming reagent	Spectrophotometry	—	—	—	(75)
3	SPE preconcentration onto C18 cartridges, ferrozine is used as colour forming agent	Spectrophotometry	Upto 4 μg/ml	—	0.8	(76)
4	SPE preconcentration of Fe(II) ferrozine complex onto poly(chlorotrifluoro ethylene) resin	Spectrophotometry	Upto 1 μg/ml	0.088	—	(77)
5	Flow injection online preconcentration	Spectrophotometry	—	0.05	2.4–8.1	(78)
6	Flow injection online preconcentration	Spectrophotometry	75 mM	0.1 nM	—	(79)
7	Flow injection online preconcentration	Spectrophotometry	—	0.025 nM	2.5	(80)
8	Flow injection online preconcentration	Spectrophotometry	—	—	—	(81)
9	Flow injection online preconcentration	Catalytic spectrophotometry	—	0.016 nM	—	(83)
10	Sequential injection analysis	Spectrophotometry	—	—	3	(83)
11	Admixtures of Fe(II) & Fe(III)	Spectrophotometry/AAS	0.1–1 μM	—	—	(84)
12	Sensor	Spectrophotometric transducer	41–300 μg/l	41	4.9	(85)
13	—	ETAAS	—	—	—	(86)
	—	High resolution isotope dilution ICPMS	—	0.05 nM	—	(87)
	SPE using chelating resin disc	High resolution isotope dilution ICPMS	—	—	—	(88)
16	Luminol	Chemiluminescence	5–500 nM	0.06 nM	8	(89)
17	Shipboard analysis, online FIA, Luminol	Chemiluminescence	Upto 2 nM	0.021 nM	—	(90)
	Online FIA, oxine immobilized on vinyl copolymer	Chemiluminescence	0.04–10 nM	—	3.2	(91)
19	Online FIA, Luminol	Chemiluminescence	—	—	—	(92)
20	Fe(II) and Fe(total), online FIA		0.8–200 nM	0.3–0.8 nM	4	(93)
21	Chalcogenide glass	Ion selective electrode	10^{-22}–10^{-16}M	—	—	(94)
22	Chalcogenide glass	Ion selective electrode	10^{-10}–10^{-25} M Fe(III)	—	—	(95)
23	Amalgam sensor electrode	DPASV	—	—	—	(96)
24	1-Nitroso-2-naphthol	DC CSV	0–20 nM	—	—	(97)
25	2-(2-thiazolylazo)p-cresol, competitive ligand exchange	CSV	—	0.1 nM	—	(98)
26	Catalytic method	CSV	—	13 pM	—	(99)
27	Catalytic method	CSV	—	—	—	(100)
28	Catalytic method, Fe, Fe(III), and Fe(II)	CSV	—	0.08, 0.077, and 0.12 nM	—	(102)
29	Oxygenated sea water solutions	Adsorptive CSV	—	120 pM	—	(101)
30	Salicylaldoxime	Adsorptive CSV	—	—	—	(103)

TABLE 4
Salient features of analytical methodologies developed for copper in sea water during 1995–2004

S. No.	Salient features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Preconcentration using cation exchange column	UV spectrophotometry	5–100	0.5	0.85	(120)
2	Extraction of ion-association complex of dichlorocuprate(I) ion with ethyl violet	Spectrophotometry	—	31.8	0.90	(121)
3	Complexation with bathocuproine	Absorbance spectroscopy	—	0.4 nM	—	(122)
4	Catalytic effect of Cu(II) on the oxidation of cysteine by hexacyanoferrate(III)	Spectrophotometry	0–6.35	0.15	—	(123)
5	Acetyl salicyl-hydroxamic acid as colorimetric reagent	Spectrophotometry	5–120	1.0	0.64	(124)
6	Membrane filter using 5,10,15,20-tetraphenyl-21H 23H-porphine tetra sulphonic acid	Solid phase spectrophotometry	Upto 20 ng	0.15	1.8	(125)
7	Selective separation by flotation	FAAS	0.05–0.5mM	1000	—	(126)
8	Liquid membrane preconcentration	FAAS	2.5–5	—	0.33	(127)
9	Solid phase extraction preconcentration on octadecyl silica membrane discs modified with a new anthraquinone derivative	FAAS	—	0.1	—	(128)
10	FI online adsorption preconcentration	FAAS	0–10	—	1.7–3.6	(129)
11	FI online preconcentration	FAAS	—	—	—	(130)
12	FI online preconcentration	FAAS	—	0.06	1.2	(131)
13	Online solid phase extraction	FAAS	—	0.05	1.5	(132)
14	FI online sorbent preconcentration	FAAS	Upto 50	—	3.0	(133)
15	FI online preconcentration onto calmagite loaded Amberlite XAD-2	FAAS	0–20	0.15	2.7–6.0	(134)
16	FI online preconcentration RP-C18 material in presence of 1-nitroso-2-naphthol	FAAS	—	2.0	1.7	(135)
17	Chromotrope 2R immobilized on an anionic resin	GFAAS	2–10	—	—	(136)
18		GFAAS	—	5	4	(137)
19	FIA	Chemiluminescence	1–6 nM	—	<10	(138)
20	FIA	Chemiluminescence	—	—	—	(139)
21	Complexation with 1,2-dihydroxy anthraquinone-3-sulphonic acid	Adsorptive stripping voltammetry	Upto 50 nM	0.3 nM	—	(140)
22		Potentiometric stripping analysis (PSA)	Upto 15	0.8	2.8	(141)
23		Potentiometric stripping analysis (PSA)	Upto 5	6	6–10	(142)

(Continued on next page)

TABLE 4
Salient features of analytical methodologies developed for copper in sea water during 1995–2004 (*Continued*)

S. No.	Salient features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
24	Mercury film coated glassy carbon electrode	ASV	—	—	—	(143)
25		Adsorption cathodic stripping voltammetry/ASV	—	—	—	(144)
26	Gold electrode	ASV	—	—	—	(145)
27	Automated flow system	ASV	—	—	—	(144)
28	Gold disc electrode	Constant current stripping analysis	—	0.011	4	(147)
29		ISE/PSA	—	—	—	(148)
30		ISE	1 μM–0.1M	—	—	(149)
31		ISE	—	—	—	(150)
32	Jalpaite membrane	ISE	—	—	—	(151)
33	Jalpaite membrane	ISE	>1 μM	—	—	(152)
34	Jalpaite membrane	ISE	—	—	—	(153)
35	Continuous flow analysis	ISE	—	—	—	(154)

procedure was developed for the determination of traces of zinc in sea water (160). The method has a linear calibration range from 2–500 ng/ml with a detection limit of 1.7 ng/ml and a sample throughput of 40 samples/h using a 60 s preconcentration time.

4d-Transition Elements.

Zirconium (Zr). A method for preconcentrating Zr from large volumes of sea water using MnO_2^- impregnated fibres is described (141). The fibres are synthesized from poly(propylene) cartridge filters by a redox reaction between $KMnO_4$ and $MnCl_2$. The preconcentrated Zr was recovered from the fibres and measured by ICPAES.

Technetium (Tc). Technetium present in sea water was enriched onto Amberlite IRA-400 column and eluted with 10 M HNO_3 and determined by ICPMS with Rh as internal standard (162). The detection limit for 99Tc was 0.03 ng/l, which is very good.

Molybdenum (Mo). The distinct features of various analytical methodologies developed for the determination of traces of Mo in sea water since 1994 are summarized in Table 5.

Silver (Ag). Dithizone was used as a complexing agent in cloud point extraction and applied to the selective preconcentration of trace amounts of Ag (176). The analyte in the aqueous solution was acidified with H_2SO_4 and Triton X-114 was added as a surfactant. After phase separation, based on the cloud point separation of the mixture, the surfactant rich phase was diluted with THF and the analyte in the enriched solution was determined by FAAS. The calibration graph was linear in the range 3–200 ng/ml and the limit of detection was 0.56 ng/ml. As low as 6 pM of Ag in sea water was determined by GFAAS in conjunction with the extractive preconcentration into CH2Cl2 in presence of diethyldithiocarbamate as complexing agent (177). An on-line flow injection preconcentration using minicolumn packed with 50 μl of Dowex 1-X8 anion exchange resin followed by isotope dilution—ICPMS determination (178). The detection limit estimated at 0.06 pg/ml is superior to previously published methods. Traces of Ag present in sea water was analysed by FI-differential impulse voltammetry, using a chemically modified graphite powder composition indicator electrode and SCE as reference (179). As low as 0.05 nM of Ag was determined with RSD values in the range 3.7–9.4%. Poly(8-mercaptoquinoline) film modified GCE was used for highly selective and sensitive determination of Ag(I) (180).

Laser-excited atomic fluorescence spectrometry with a novel diffusive graphite tube electrothermal atomizer was used for the direct determination of silver in sea water (181). A very low detection limits of 40 and 90 fg of Ag in H_2O and 1:1 diluted sea water, respectively were reported by these authors. Bermejo-Barrera et al. (182) have studied the influence of modifiers to increase the charring temperature and avoid losses of silver during ETA-AAS analysis of silver. The best results were obtained with reduced Pd samples. Under these conditions a detection limit of 0.1 μg/l was reported when 0.4 ml of sample was taken and 40 μl of the diluted solution was injected. The precision of the procedure is also quite good as it lies in the range 1.4–3.4%.

Cadmium (Cd). The significant features of various analytical procedures developed for the determination of trace and ultratrace amounts of cadmium in sea water since 1994 are compiled in Table 6.

TABLE 5
Distinct features of various analytical methodologies developed for the determination of Mo in sea water since 1994

S. No.	Distinct features	Analytical technique	Calibration range (mg/l)	Detection limit (mg/l)	Precision (% RSD)	Ref.
1	Membrane filter extraction of Mo-phenyl fluorine complex	Solid phase spectrophotometry	0–0.06 and 0.08–0.14 μg	8 ng	—	(163)
2	Bronopyrogallol red-cetyl trimethylammonium bromide colour system	Spectrophotometry	60–800	25	0.92	(164)
3	Online FIA preconcentration onto C18 bonded silica gel in presence of quinoline-8-ol	FAAS				(165)
4	Online preconcentration using anion-exchange column (AGI-X8)	ICPAES	—	0.7	—	(166)
5	Preconcentration using diethylene triamine tetraacetic acid functionalized polysiloxane	ICPAES	—	0.7	3	(167)
6	Preconcentration of Mo as its thiocyanate complex onto polyurethane foam	ICPAES	—	1.5	1.8	(168)
7	Preconcentration of Mo as its calmagite complex onto activated carbon	ICPAES	—	0.75	2.21	(169)
8	Quinoline-8-ol extraction of Mo from high matrix samples	ID/MIPMS	—	—	1.0	(170)
9	On-column and precolumn derivatization with quinoline-ol	HPLC-UV detection	1–200 and 0.5–200	0.2	4.8	(171)
10	Coprecipitative preconcentration using ammonium pyrollidine dithiocarbamate and thioanilide	NAA	—	1.0	6.6	(172)
11	2-(2′-thiazolylazo)-*p*-cresol as chelate	Catalytic adsorptive stripping voltammetry	Upto 12	11 pM	—	(173)
12	Complexing agents such as chloroanilic acid, oxine, tropolone and cupferron	Flow through adsorptive stripping voltammetry	—	—	—	(174)
13	In presence of quinoline-8-ol complexing agent	Adsorption cathodic stripping square-wave voltammetry	Upto 150	0.1	—	(175)

5d-Transition Elements

Tungsten (W). A highly sensitive and selective fluorescence quenching method was developed for the determination of trace amounts of W in environmental samples using dibromohydroxy phenyl fluorone (199). The decrease in fluorescence of the reagent solution (ΔF) was linear for 0–0.9 μg of W(VI) in 25 ml of solution with a limit of detection of 0.012 ng/ml.

Rhenium (Re). In order to determine Re in sea water samples by ICPMS, a prior separation on an extraction chromatography resin was employed. A very low detection limit of 0.2 ng/ml was reported by Tagami and Uchida (200).

Gold (Au). Chen et al. (201) have determined gold in sea water by AAS after preconcentration onto 2-hydroxybenzal rhodamine loaded resin column. A low cost flame AAS procedure was described for the determination of gold in sea water after ammonium diethyl dithiophosphate as a complexing reagent (202). The reported detection limit was 2.9 ng/l. Au in river and sea waters were determined by ET-AAS with preconcentration on a W rod (203). The detection limit is 1.6 pg/ml of Au with a RSD of 3.2% (at 250 ng/ml of Au). Ultratrace amounts of gold in sea water was determined by GFAAS or ICPMS after ion exchange preconcentration or by evaporation, respectively (204). Sato and Veda (205) have determined gold by GFAAS

TABLE 6
Significant features of various analytical procedures developed rot the determination of cadmium in sea water since 1995

S. No.	Significant features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Online preconcentration in presence of anthryl azamacrocycle	Fluorescence	—	35 pM	—	(183)
2	Adsorption of Cd-4-(2-pyridyl)azoresorcinol (PAR) complex onto activated carbon	FAAS	—	—	—	(184)
3	Cloud point extraction preconcentration	FAAS	0.5–50	0.4	—	(185)
4	FI online preconcentration using knotted reactor & diethyldithiocarbamate as chelating agent	FAAS	—	3.44	—	(186)
5	Field flow preconcentration onto microcolumn packed with PAN coated Amberlite XAD-4 resin	FAAS	—	3.8	—	(187)
6	Field flow preconcentration onto minicolumn packed with PAR coated Amberlite XAD-4 resin	FAAS	0.05–0.7	—	—	(188)
7	Online FI sorbent extraction with PAR or 2-(2- pyridylazo)-5-dimethylaminophenol as chelating agents	ETAAS	Up to 1.0	4.0 or 1.7	2.7–15 or 12.8	(189)
8	Automatic online column preconcentration	ETAAS	—	—	—	(190)
9	Dynamically coated column of quaternary ammonium salt on C18 bonded silica gel	GFAAS	—	0.002	1.8	(191)
10		GFAAS	—	—	—	(192)
11	FI cold vapour generation	ETAAS	—	0.004	1.6–4.2	(193)
12	Automated online preconcentration	GFAAS	—	42 pM	3.2	(194)
13	Speciation	DPASV	—	0.1	—	(195)
14	In presence of 5-fluorouracil	CSV	—	90 pM	—	(196)
15	Complexation with 2-acetyl pyridine salicyloyl hydrazone	DP adsorptive CSV	—	0.06 nM	—	(197)
16	Pertains to study of Cd complexation in sea water	DP ASV	—	—	—	(198)

after coprecipitative preconcentration with nickel ethyldithiocarbamate from pH 9 solutions. Au in sea water was preconcentrated onto Mg-W cell (described in detail) and determined subsequently by ET-AAs by Itoh et al. (206). The detection limit was 0.02 μg/l, which is lower than that obtained by ETAAS or ICPMS. The calibration graph was linear upto 0.1 mM – Ag(I) with a very low detection limit of 27 pM.

Mercury (Hg). The salient features of various analytical determinations reported for mercury in sea water since 1994 are summarized in Table 7.

p-Block Metal Ions.

Aluminium (Al). Aluminium present in sea water was determined spectrophotometrically in neutral solutions with pyrocatechol violet (244). The detection limit is 2 μg/l for a 25 ml sample with a very good precision of 1%. Salicylaldehyde picolinoyl hydrazone was used as a selective regent for the direct fluorimetric determination of dissolved Al in sea water (245). The detection limit was 9.8 nM – Al and the RSD for 0.166 μM of Al was 1.85%. Ren et al. (246) presented a modification of the Al-lumogallion fluorescence measurement in the presence

TABLE 7
Salient features of various analytical determinations reported for mercury in sea water since 1995

S. No.	Salient features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Thiamine reagent	Fluorescence optosensing	10–150	3	3	(207)
2	6-Mercapto purine	Fluorimetry	Up to 1200	1.4	1.3	(208)
3	Comparative study of $Mg(NO_3)_2$, $Pd(NO_3)_2$ and reduced Pd modifiers	ETAAS	—	—	—	(209)
4	FI preconcentration onto coated graphite tubes	ETAAS	—	0.09	—	(210)
5	Preconcentration with baker's yeast immobilized on silica gel for speciation of Hg	CVAAS	—	—	—	(211)
6	Sequential injection using automated flow manifold	CVAAS	—	0.1	2	(212)
7	Online flow system device	CVAAS	—	0.0005	3.8	(213)
8	Online flow manifold, Au amalgam preconcentration	CVAAS	—	0.0001	2.7	(214)
9	Karachi coastal waters	CVAAS	—	—	—	(215)
10	Capillary cold trap for Hg speciation	Microwave-induced plasma AAS	—	0.0013	—	(216)
11	Hg speciation	CVAAS	—	0.1	—	(217)
12	New sampler	HGAFS	—	0.06 ng/l	—	(218)
13	FI with online oxidation	AFS	Up to 200	0.025	—	(219)
14		AFS	0.0035–0.0195	0.002	7.2–17	(220)
15		AFS	Up to 0.05	0.0012	—	(221)
16	Speciation	AFS	—	—	—	(222)
17	Continuous flow LLE	ICPAES	Up to 105	2	5	(223)
18	Preconcentration onto silica functionalized with methyl thiosalicylate	ICPAES	Up to 1000	5	0.8-2.1	(224)
19	Head space SPME, Speciation	GC-MIPAES	—	—	—	(225)
20	Online preconcentration onto C18 immobilized on silica microcolumn in presence of ammonium salt of O,O′-diethyldithiophosphoric acid	ICPMS	—	0.0005	—	(226)
21	In situ nebulizer vapour generator speciation of Hg, methylethyl Hg	LC-ICPMS	—	0.03–0.1	1.6–3.3	(227)

(*Continued on next page*)

TABLE 7
Salient features of various analytical determinations reported for mercury in sea water since 1995 (*Continued*)

S. No.	Salient features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
22	CH_3 Hg and $HgCl_2$	LC-ICPMS	20–100	16 and 17	—	(228)
23	preconcentration by amalgamation on a gold–Pt gauge	ICPMS	—	0.2 ng/l	0.9	(229)
24	Hg total	AAS/AES/AFS/NAA	—	—	—	(230)
25	Speciation, online SPE of Hg-DDTC complex CH_3Hg, C_2H_5Hg & C_6H_5Hg	HPLC	Up to 500	1, 1.2 and 1.2	—	(231)
26	CH_3Hg, C_2H_5Hg, C_6H_5Hg and Hg(II) speciation	HPLC	—	0.25, 0.21, 0.19 and 0.72 ng	3–3.7	(232)
27		Sensor	Up to 100	0.3	3.9	(233)
28	Chalcogenide glass memberane	ISE	—	—	—	(234)
29		ISE	—	—	—	(235)
30		ISE	—	—	—	(236)
31	Screen printed electrodes	DP voltammetry	—	12 pM	—	(237)
32	CME	ASV	1.5–12 pM	—	3.3	(238)
33	GCE modified with polycationic ionomers	LS or DP-ASV	—	0.4 and 0.04 nM	—	(239)
34	Dithizone modified GCE	ASV	2.5–750 nM	0.5 nM	2.9	(240)
35	Poly(4-vinylpyridine) gold film electrode	SWV	—	—	—	(241)
36	FIA with gold electrodes	PSA	0.5–100	0.25	1.9	(242)
37	Au electrode	Stripping chronopotentiometry	—	—	—	(243)

of non-ionic surfactant Triton X-100. The detection limit for dissolved Al in sea water is 0.7 nM with a RSD of 3.6% at an Al level of 5.0 nM. A flow through analytical method was described for the determination of Al in sea water with the use of lumogallion fluorimetric detection (247). Fe was removed by passing through quinoline-8-ol immobilized chelating resin column. The detection limit and RSD were 0.17 nM and 2.7% (at 2 nM Al). Electrothermal AAs (248) and ET atomization-laser excited AFS (249) techniques were employed for the determination of nanomolar levels of Al in sea water. The former method allows to reach a detection limit of 30 ng/l which is approximately 8 fold lower than that reported previsouly. High scan performance adsorptive CSV involving stair case modulation was used to determine Al in sea water after complexation with 1,2-dihydroxy anthraquinone-3-sulphonic acid (250). The method is especially suited for the determination of Al conducted on board oceanographic vessels.

Gallium (Ga). Traces of Ga present in sea water was preconcentratively separated from other metal ions using Muromac A-1 ion exchange resin (251) and activated carbon impregnated with quinoline-8-ol (252) and determined by GFAAS. The latter procedure offers a linear calibration range up to 2.5 μg with detection limit and RSD of 0.1 μg/100 ml and 3.2%.

Indium (In). ETAAS was used for the determination of traces of In in sea water after a coprecipitative preconcentration onto gallium phosphate (253). The calibration graph was linear for 0.02–0.3 μg/ml of In(III) with a detection limit of 0.3 ng/ml for a 500 ml sample and RSD of 1.3% for 5 μg of In(III). Murakami and Takada (254) have preconcentrated In(III) in sea water with bis(2-ethylhexyl) hydrogen phosphate loaded porous PTFE filter tube. A very good precision of 1.4% was reported by these authors.

Thallium (Tl). A spectrofluorimetric procedure based on the extraction of Tl—cryptand 2,2,1-eosine ternary complex into 1,2-dichloroethane (255). The detection limit for Tl was 0.9 ng/ml and the linear working range extended upto 150 ng/ml of Tl. The RSD was found to be 2.0% at the 100 ng/ml level. Nanogram per litre levels of Tl was determined by GFAAS after selective extraction of its diethyl dithiocarbamate complex with benzene and subsequent elution with HNO3 (256). The limit of detection and RSD were 0.86 ng/l and 3.3% (for 20 ng/l). A DPASV procedure was developed by Cai and Khoo (257) for determination of Tl in sea water by using quinoline-8-ol modified carbon paste electrode in Britton-Robinson buffer of pH 4.56. The calibration graph was linear from 0.5–10 nM and also from 0.08-10 μM of Tl(III) were 2.8 and 4.8%, respectively. Becker-Ross et al. (258) have described a flash lamp continuum AA. A device comprising a Xe flash lamp modified for end on observation with power supply and ignition triggering unit, a GFAAS instrument and autosampler, an echelle spectrometer in tetrahedral mounting and a linear-away charge-coupled device detector and has been evaluated for the determination of Tl in sea water with Pd as a modifier (258).

Germanium (Ge). An isotope dilution HG-ICP MS based procedure was described for the trace determination of Ge in sea water (259). The absolute detection limit was ~400 fg.

Tin (Sn). Sequential titrimetric and spectrophotometric determination of trace amounts of Sn(II) and Sn(IV) in sea water was described based on amplification procedure based on periodata, molybdate and KI (260). Tin was preconcentrated by passing through a catechol violet—capriquat loaded silica gel column and analysed by ETAAS (261). Khoo and Ye (262) have determined traces of tin in flow systems at an epoxy—carbon powder—quinoline-8-ol composite electrode using DPASV method. Under optimized conditions, the calibration plot was linear from 5 nM to 1 μM and a detection limit of 0.46 nM was found.

Lead (Pb). The salient features of various analytical procedures developed for the determination of trace levels of lead in sea water since 1994 are summarized in Table 8.

Antimony (Sb). Speciative determination procedures described for Sb(III), Sb(V) and organoantimony were reviewed by Russeva and Havezov (285). The limits of detection varied widely from 100 μg/l for spectrophotometry with cationic dyes to 1 ng/l for ICP-MS. Hybrid generation of AAS procedures were described for the determination of traces of Sb in sea water (286, 287). The latter procedure offers detection limits of 10 and 5 ng/l for Sb(V) and Sb(III), respectively. Kubota et al. (288) have described a GFAAS procedure in conjunction with the preconcentration of Sb(III)—pyrogallol complex onto activated carbon. Speciative preconcentration procedures were developed for Sb(III) and Sb(V) onto activated alumina (289) and continuous tandem on-line separation device (290) in connection with GFAAS and ICP-AES methods respectively. Yan et al. (291) have described a flow injection on-line sorption preconcentration in a Knotted reactor coupled with ETAAS. The calibration graph was linear from 0.1–2 μg/l of Sb(III) and the limit of detection and RSD were 0.021 μg/l and 2.9% respectively. The method was applied to sea water.

Quentel et al. (292) have described a DPASV procedure for the trace determination of Sb(III)/Sb(V) in sea water. Under optimized conditions a detection limit of 11 ng/l is obtained for 10 min deposition time.

Bismuth (Bi). Bi at μg levels was determined by spectrophotometry in conjunction with sequential chemical-amplification reactions using periodate, molybdate and KI (293). The detection limit and RSD were 0.1 μg/ml and 1.3—1.7% respectively. Zen and Chung (294) have described square wave voltammetric stripping analytical procedure for Bi(III) at a poly(4-vinyl pyridine)/Hg film electrode. The calibration graph was linear upto 60 μg/l of Bi(III), the detection limit was 0.12 μg/l and RSD for 10 μg/l Bi(III) was 3.7%. A co-precipitative preconcentration of Bi onto zirconium hydroxide at a pH ~9.0 and determination by DPASV procedure (295).

Noble Metals

Ruthenium (Ru). Activated carbon impregnated with 2,4,6-tri-2-pyridyl-1,3,5-triazine was used for enrichment of ruthenium present in sea water from pH 7 phosphate buffered solutions (296). The carbon is then collected on a membrane filter and dispersed in 5 ml of H_2O and 10 μl of resulting suspension is subjected to GFAAS. The calibration graph is linear upto 2.5 μg of Ru in 100 ml of aqueous phase and the detection limit is 0.08 μg in 100 ml.

Rhodium (Rh). Rhodium present in sea water was preconcentrated in a galvanic electrodeposition cell by dipping Mg and W sheet electrodes connected by wire, which was stirred for 120 s (297). The W cathode was washed with water and inserted into the W tube atomizer of ETAAS instrument for analysis of Rh. The limit of detection and RSD are 13 ng/ml and 4.1% (for 500 ng/l of Rh).

Palladium (Pd). Pd present in sea water was floated using sulphur containing reagent (4-phenyl thiosemicarbazide) and oleic acid as surfactant (298). The absorbance of the floated complex was determined spectrophotometrically and obeys Beer's law in the range 2–14.5 μg/ml. Pd as its ternary complex with 5-[chloro-2-pyridylazo] 2,4-diaminotoluene-sodium dodecylbenzene sulphate was preconcentrated onto a nitrocellulose membrane filter (299). The filter is then dissolved in H2SO4 and subjected to GFAAS determination of palladium present in sea water. The calibration graph for palladium was linear from 4.69 pM–6.09 nM of Pd with a detection limit of 1.78 pM. Pd was preconcentrated by galvanic electrodeposition onto W cathode as described above in case of Rh and determined by ETAAS (300). The calibration graph was linear upto 25 ng/ml with a detection limit and RSD of 0.37 ng/ml and 3.8–6.4% respectively.

Lanthanides

Biju and Rao (301) have determined traces of erbium present in sea water based on the quenching of fluorescence intensity of Rhodamine 6G during extraction of ternary complex Er-5,7-diiodoquinoline-8-ol-Rhodamine 6G into xylene. Chelation ion

TABLE 8
Salient features various analytical procedures developed for lead in sea water since 1995

S. No.	Salient features	Analytical technique	Calibration range (μg/l)	Detection limit (μg/l)	Precision (% RSD)	Ref.
1	Preconcentration on chelex 100 ion exchange resin	Spectrophotometry	—	—	—	(263)
2	FI online exchange	FAAS	Up to 40	0.3	2.5	(264)
3	3-Methyl-1-phenyl-4-stearoyl-2-pyrazolin-5-one loaded on porous polymer adsorbent	FAAS	—	—	—	(265)
4	FI-online preconcentration	FAAS	Up to 300	2.9	1–1.4	(266)
5	Field flow preconcentration on Amberlite XAD-4/PAN	FIFAAS	0.05–0.2	0.005	3.1–4.0	(267)
6	FI in lead hydride generation	FAAS	—	0.8–4.0	—	(268)
7	Coprecipitation onto iron(III) hydroxide	FI-ETAAS	—	0.38	—	(269)
8	Coupling a laser with an optical parametric oscillator	ETA-LEAF	—	0.3	—	(270)
9	Online FI preconcentration on C18 bonded silica gel	ETAAS	—	0.0045	—	(271)
10	FI sorption preconcentration on a knotted reactor	ETAAS	0.1–2	—	2.9–4.9	(272)
11	Pd/Mg$(NO_3)_2$ as modifier	ETAAS	—	0.5	—	(273)
12	Pd-Sr$(NO_3)_2$ as modifier	ETAAS	—	—	—	(274)
13	Crystand (222B) modified polymer column	ETAAS	—	—	—	(275)
14	Speciative preconcentration using chelex resin	ETAAS	—	0.1	—	(276)
15	Electrothermal vaporization and capacitively coupled plasma atomization, oxalic acid/HCl as modifier	ETAAS	1–100	0.2	—	(277)
16	Coprecipitated naphthalene alizarin red	ICPAES	—	53	1.8–4.6	(278)
17	Isotope dilution coupled with FI	ICPMS	—	0.204	—	(279)
18	Extraction with 0.001% dithizone in $CHCl_3$	IDMS	—	0.5	—	(280)
19	Isotope dilution, Quinoline-8-ol functionalized chelating resin	ICPMS	—	0.22	—	(281)
20	Collection on C18 microcolumn in presence of ammonium diethyldithiophosphate	ICPMS	—	0.16 ng/l	—	(282)
21	Partially quaternized poly(4-vinyl pyridine)/Hg film electrode	SWASV	—	1.0	—	(283)
22	Xylenol orange	Adsorptive SV	Up to 7	0.006	—	(284)

chromatographic method was developed for determining lanthanides in sea water using α-aminobutyrohydroamate or its N-methyl derivative for on-line preconcentration and separation from alkali and alkaline earth metals (302). The calibration graphs were linear upto 16 μg/l and limit of detection was 2.5 μg/l. Rare earth elements (REE) were preconcentrated onto activated carbon and determined by ICPAES (303). The detection limit and precision were 0.3 ng/l and 10% (at 0.3 ng/l). REE in sea water were preconcentrated on-line onto homemade columns of commercially available iminodiacetate resin, Monomac A-1 (304) and determined by ICPMS. The detection limits of REE are in the range 0.04–0.25 ng/l.

A simple method of simultaneous preconcentration and matrix reduction based on coprecipitation with $Mg(OH)_2$ was developed for the determination of REE in sea water and groundwater by isotope dilution ICPMS (305). The calculated detection limits ranged from 0.1 pg/g for light REE to 0.02 pg/g for heavy REE. The REE were preconcentrated on-line, by a method based on their separation from brine by adsorption on a microcolumn of oxine immobilized silica and determined by ICPMS (306). Detection limits are ranged from 0.06 ng/l for Tb and Ho to 0.6 ng/l for Ce and Nd. REE were preconcentrated from harbour water onto SPE cartridge, eluted with HNO3 and determined by ICPMS (307). Calibration graphs for 15 REE were linear for 1–50 pg/ml with detection limits of 0.03–0.4 ng/l. Ultratrace amounts of REE in seawater were preconcentrated into polyacrylonitrile hollow fibre membrane, eluted with HNO3 and determined by ICPMS (308). The detection limits and RSD values are 0.21–2.7 ng/l and <5%, respectively. Zhang et al. (309) preconcentrated REE in sea water with poly(acrylaminophosphonic dithiocarbamate) chelating fibre prior to determination by ICPMS. The detection limits were 0.2–2 ng/l and with RSD of <5%. REE as their oxine complexes were preconcentrated online by passing through Amberlite XAD-7 resin, eluted with HNO3 and determined by ICPMS (310). The calibration graphs were linear upto 1 ng/ml and limits of detection lie in the range 0.0017–0.016 ng/l. For 2 ng/ml of the REE, the RSD were in the range 1.2–2.3%. Trace REE in sea water were preconcentrated with quinoline-8-ol-5-sulphonic acid-cellulose microcolumn prior to determination by ICP-MS (311). IC-ICPMS procedure was developed for the determination of 1–10 μg/l of REE added to sea water (312). The detection limits and RSD were 1–10 ng/l and 0.5–3.5% at 1 μg/l respectively.

Actinides

Thorium (Th). A method for the liquid-liquid extraction, separation and preconcentration of trace amounts of thorium from sea water with N-phenylbenzo-18-crown-6-hydroxamic acid into dichloromethane is described (313). The extract was directly injected into plasma for ICPAES measurement of Th. A similar procedure was reported by Shivslar et al. (314) by extraction with 2,3′-ethylene dioxydiethylene-diimino-dipropianohydroxamic acid into CHCl3 and subsequent determination by ICP-AES/spectrophotometry. With ICPAES, the calibration graph is linear upto 150 μg/l with a detection limit of 5 μg/l.

Uranium (U). The liquid-liquid extraction of U was based on the ion-pair phase separation of perfluorooctonate ion with tetrabutyl ammonium ion from pH 4 aqueous acetate solutions (315). The extract was analysed for U(VI) by spectrophotometry. The calibration graph was linear for 0.033–2.7 μM of U(VI) and the detection limit was 0.6 nM. The precision is also quite good, i.e., 1.4%. The method was applied to determine U(VI) in the sea water. Katragadda et al. (316) have determined U(VI) spectrophotometrically after a prior preconcentration with phenylphosphonic acid-embedded polyurethane foam. The calibration graph was linear for 1–10 ppm of U. Venkatesh and Maithi (317) have preconcentratively separated U(VI) from sea water solutions with dibenzodimethane (DBM) quinoline-8-ol or tri-n-octylphosphine oxide (TOPO) impregnated on XAD-4 resin. The preconcentrated U could be eluted with dilute mineral acid in case of DBM or oxine and ammonium bicarbonate with TOPO and determined spectrophotometrically using Arsenazo III as reagent. Uranium in sea water samples was preconcentrated using chelating resin disc and determined by ICPAES (318). Chou and Moffatt (319) determined U in sea water by ICP-MS after coprecipitation with iron(III) hydroxide. The accuracy of the method was tested by analyzing NAAS-4 CRM. Electrochemical pretreatment of anodically conditioned glass carbon coupled online with ICPMS was used for preconcentration and determination of U in sea water (320). Dadafarnia and McLead (321) have developed FI online trace enrichment followed by determination with ICPMS. The calibration graph was linear from 0.01–10 μg/l of U and the RSD for determination of 50 μg/l was 4.5% and the detection limit was 4 ng/l. The method was applied to sea water. Syndibenzo-16-crown-5-oxyhydroxamic acid in $CHCl_3$ was used to extract U for the determination of U in sea water by NAA (322). Radiometric determination of U in sea water samples was described after preconcentrative separation using chelex cationic exchange resin and liquid-liquid extraction with TBP followed by electrodeposition on stainless-steel discs (323). By employing high resolution α-particle spectrometry the measured activity of 238U and 234U radioisotopes were found to be ~7 and 35 μg/l for ground water and sea water samples, respectively. The U traces present in sea water was preconcentrated by SPE using C18 artridges followed by DPP determination in CHCl3 eluate (324). The precision for 0.2 μg/ml of U was 1.6%. The dissolved U(VI) traces in sea water was directly determined by CSV with a detection limit of 2.4 nM and RSD of 8.5% (325). Uranium(VI) along with various other metals in sea water were adsorbed onto amidoxime fibre either by immersing for several weeks or by pumping through a packed column for 7 days at a rate of 3 dm^3/min and determined by ICPAES (326).

Uranium(VI) and Thorium(IV). A method was developed for the determination of thorium(IV) and uranyl ions involving precolumn complexation with mandelate and preconcentration on a short C18 column (327). The adsorbed metals are eluted with α-hydroxy isobutyric acid as mobile phase and post column detection with Arsenazo III at 658 nm. The detection limits were reported to be at the sub-ppb level.

Plutonium (Pu). Pu in sea water was preconcentratively separated by coprecipitation with iron(III) hydroxide and determined by ICPMS with ultrasonic nebulization (328). The detection limit for 239Pu is 5 fg/l which is the lowest reported so far.

Miscellaneous Species/Parameters

Sedjil and Lu (329) have described the development of a colorimetric detector with a buried double p-n junction (BDJ) structure which provides two photocurrents whose ratio is sensitive to spectral changes. Samples containing bromophenol blue were illuminated with monochromatic sources or LEDs (330) and the obtained current ratio was used to determine the pH. The above proposed system enables the development of miniaturized and inexpensive pH sensors. Hopkins et al. (331) have utilized thymol blue indicator calibration and its equilibria at atmospheric pressure enabled them in-situ spectrophotometric measurements of sea after pH throughput the oceanic water column. A high precision sulphone phthaline indicator based online automated marine pH sensor was developed by Bellerby et al. (332). The method has an online precision of better than 0.001 pH units and an estimated accuracy of better than 0.004 pH units. The instrument is compact, portable and has a measurement frequency of 20 samples/h. Bellerby et al. (333) have described a procedure wherein the shipboard flow injection based measurement of sea water pH with spectrophotometric detection using phenol red indicator. Over the temperature range of 18–27°C an error of + 0.001 pH/°C was estimated. The feasibility was investigated of performing automated sea water pH measurements by means of a flow measurement technique involving the use of a pH ISFET microsensor (334). Matrix interference effects were compensated by the use of saline buffers and the measurement precision thus obtained was 0.01 pH units. Ammonium ion in sea water was determined based on the indophenol reaction with *o*-phenylphenol (335). Calibration graphs were linear upto 20 μM ammonium ion with RSD of 0–1%.

The salinity of sea water was determined by UV-spectroscopic measurements (336) or by an optical sensor (337). In the former method, the results for 4 samples of sea water were close to values obtained by the Mohr Kundsen and conductivity method based on decrease in absorbance of bromophenol blue at 590 nm with alkalinity was described by Sarazin et al. (338). This method of pH measurements for estimating alkalinity gives results within 1% of those given by Gran's potentiometric titration but requires only 1–2 ml of samples and is relatively rapid. Zhao and Liao (339) have developed a novel optical fibre sensor for simultaneous measurement of temperature and salinity. Temperature measurement employs the principle of temperature dependent semiconductor absorption at the band edge. And the sensor exploits beam deviation caused by refraction due to salinity of water.

MULTIMETAL MIXTURES

Multimetal mixtures in sea water were determined by adopting several analytical techniques based on spectral, electrochemical, X-ray and chromatographic principles. The details of these techniques in analysis of sea water for multimetal mixtures are discussed in the following pages.

Spectrophotometry/Spectrofluorimetry

U(VI), Zr(IV) and Th(IV) mixtures were extracted from perchlorate solutions with 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (PC-88a) in toluene and stripped with 4 M HCl, 2.5 M NaF and 8 M HCl respectively. The method was applied to the determination of U(VI) in sea water by using simple spectrophometer and the results obtained are in good agreement with those by AAS (341). First derivative spectra of U(VI) and V(V), 4(2-pyridylazo resorcinol)-cetylpyridinium chloride solutions enable sequential determination of the above metals in saline waters, based on the measurements at 563 and 600 nm with detection limits of 0.25 and 3.0 μg/ml respectively (341). A rapid screening spectrophotometric method was developed based on reaction with non-selective reagent such as 4-(2-pyridylazo-resorcinol) for simultaneous determination of heavy metal pollutants (Cd, Cu, Pb, and Zn) and natural and elevated Ca and Mg metals in sea water (342). In this method, a sea water sample was diluted with an equal volume of 0.12 nM – PAR of pH 9. After 15 min, the absorption spectrum was recorded between the wavelength range 190–600 nm. Calibration was carried out by partial least squares regression using standards. Worsfold et al. (343) described an integrated luminometer which can perform fluorescence, room temperature phosphorescence and chemiluminescence measurements together with flow injection manifolds on sea water samples. The analytical figures of merit are given for each manifold during the determination of few trace metals in sea water.

Flame Atomic Absorption Spectrometry (FAAS)

Simultaneous determination of total and free metal ion (Cd and Mn) concentration was possible by sorption on iminodiacetate resin by batch method at constant acidity. The procedure was validated by sorption on chelex-100 resin. The sorbed metal ion concentrations were measured by FAAS. The procedure was applied to the determination of the total concentration of metal ion present in solution and the ratio of total to free metal ion concentrations of Mn(II) and Cd(II) in simulated seawater (344). Kenaway and Hafez (345) have preconcentrated 0.1 to <10 μg/ml of Cd, Cr, Cu, Fe, Ni, Pb, Sn, Y and Zn onto cellulose from weakly alkaline (pH $\sim$9.0) in presence of sodium sulphide and thiourea and determined by AAS. The detection limits are 1–30 ppb excepting V which are quite good. The developed method was applied to various water samples including sea water. The limits of RSD were 0.8–4%, which is reasonable in view of the concentrations involved. Elci et al. (346) have developed similar preconcentration with cellulose and FAAS determination during the determination of multimetal mixtures of Cu, Fe, Pb, Mn, Zn, Cd, Ni, Bi, and Cr. The RSD and detection limits are in the range 3.5–6.9% and 4-64 μg/l, which are inferior to the procedure developed by Kenaway and Hafez (345).

An online preconcentration of Cu and Mo onto Muromac A-1 chelating resin followed by AAS allowed the determination of as low as 0.05 and 3 ppb, respectively. The results obtained for the above metals in 2 sea water standard reference materials agreed with the certified values (347). The physicochemical distribution of Cu, Pb, Cd, and Hg in sea water was studied by isolating fractions representing particulate metal, metal adsorbed on particulate inorganic matter, total dissolved metal and dissolved labile metal (348). The fractionation involved various processes including filtration through a 0.45 mm pore size filter, UV-irradiation to destroy organic matter, and metal preconcentration by SPE using chelamine column and 2 M HNO_3 as eluent. The analyses were performed by FAAS or cold vapour generation-AAS for Hg. The method was applied to sea water samples collected at oporto coast, Protugal during the period January to March 1996. Soylak and Elci (349) have preconcentrated trace metal ions (Fe, Ni, Cu, Zn, Cd, and Co) from surface sea water as their NaDDTC chelate complexes onto Amberlite XAD-16. After elution with 1 M HNO3, the trace metal ions were determined by FAAS. The detection limits were 14 Cd and 51 ng/l Ni with a sample volume of 100 ml which are quite good. Heavy metals viz. Cu, Ni & Cd as their APDC complexes were collected onto a thermally reversible polymer (350). The accuracy and precision were assessed using CRMs .

Aheva et al. (351) have similarly preconcentated trace metal—APDC chelates onto Whatmann QM-Aquartz microfibre filter and determined by FAAS and ETAAS. The results are in close agreement between the two techniques. A flow injection and atom trapping AAS procedure was developed for the determination of Cd, Cu, Pb and Mn in saline waters (352). The RSD were 1.69, 4.30, 2.76 and 3.16%, respectively, which are quite high. Tony et al. (353) have described a flow injection online FAAS procedure based on the enrichment of Fe, Co, Ni, Mn and Zn present in sea water as their 5,7-dichloroquinoline-8-ol chelates onto C18 bonded silica gel column. Unlike the above method, the RSD values are <2% for all metals. Abollino et al. (354) have described an apparatus consisting of 3 columns packed with different substrates namely an anion exchange resin, a reversed phase sorbent and a chelating ion exchange resin. The retention of Cd, Cu, and Pb present in sea water onto the substrates at different pH conditions was investigated. In an aim to distinguish among species with different charge or chemical behaviour, experiments were performed with free metal ions, their anionic complexes with EDTA and quinoline-8-ol sulphonic acid and their neutral complexes with quinoline-8-ol. A cloud point extraction preconcentration-FAAS procedure was developed for Ni and Zn in sea water in presence of PAN reagent. The detection limits and RSD were 6 and 8 ppb and 1.9 and 1.4%, respectively, which are quite impressive (355).

Chen and Teo (356) have determined Cd, Cu, Pb and Zn in sea water samples after cloud point extraction with TAN and Triton X-114. The detection limits are 0.099, 0.27 and 0.095 ng/ml, respectively, which are quite good. Bravo-Sanchez et al. (357) have developed FI-online AAS determination of Pd and Hg in sea water by using Kelex-100 adsorbed on Bondapack C18, oxine immobilized on vinyl copolymer Toyopart gel and commercial polystyrene-DVB ion exchange resin with paired iminodiacetate groups. Narin et al. (358) have employed Amberlite XAD-2000 resin packed column to preconcentrate Cr, Cu, Ni & Pb as their PAN complexes prior to determination by FAAS. The procedure was applied to sea water samples collected from Mersin Bay—Mediterranean sea with satisfactory results.

Thioglycollic (359) or 4-amino-3-hydroxy-2-(2-chlorobenzene)azo-1-naphthalene sulphonic acid (360) was bound physically and also chemically (via.1 step direct synthetic route on the surface of active silica gel) and resultant SPEs were used for selective removal of some heavy metal ions viz. (i) Cu, Zn, and Hg (359), (ii) Cr, Ni, Cu, Zn, Cd, and Pb (360) from natural sea water samples. The presence of higher concentrations of Na, K, Ca, and Mg have no matrix effect on extraction process of the above mentioned heavy metal ions. Mohmoud (361) have compared metal sorption properties of 1-aminoanthraquinone sorbed physically and chemically immobilized N or O-atom of chelate onto better preconcentration results during extraction of Cu and Cr^{3+} from natural sea water samples.

Akman et al. (362) have employed a syringe mountable filter resin technique for the separation and enrichment of Pb and Cd prior to determination by FAAS as a substitute for batch and column techniques. The proposed method was compared with the column technique with respective to ease of use, speed, reproducibility, simplicity, recovery and risk of contamination. The housing of a syringe-mountable membrane filter was filled with Dowex HCR cation exchange resin and mounted on the tip of a plastic syringe. The sample solution was drawn into the syringe, passing through the resin and discharged manually. The sorbed metals (Pb and Cd) were then eluted by drawing and discharging 2.5 M HCl as the eluent. Pb and Cd present in sea water samples could be concentrated by drawing and discharging several portions of sample successively but eluting only once. The proposed method is inexpensive, simple and precise. The risk of contamination is less than with the column technique. In addition, the method is faster, easier and more practical than the column technique. The SPE of Pb and Cu from sea water with acidic, neutral and basic alumina was either unmodified or contained adsorbed 2-mercaptonicotinic acid was studied (363).

In general, modified alumina had better selectivity for Pb and Cu compared to other metals, e.g., Cd, Cr, and Zn. Micorcolumns containing 100 mg of modified aluminas were used for SPE of 1 ng/ml of Pb(II) or Cu(II) from1 l of sea water at 10 ml/min. After elution with conc. HNO_3, Cu and Pb were determined by FAAS. Yamini et al. (364) have preconcentrated Ni, Bi, Cd, Fe(III), Pb, Zn, and Co present in sea water onto Sep Pak C18 cartridge conditioned with NaDDTC. The detection limits were in the range 0.4–5.0 ppb for above mentioned metals. APDC complexes of Bi, Cd, Co, Cu, Fe, Ni, and Pb have been preconcentrated onto a short column of chromosorb 102 resin and eluted with acetone (365). The recoveries were >95%. The 3μ detection limits for Cd, Cu, Fe, Ni, and Pb were found to be as 0.10, 0.44, 11, 3.6, and 10 μg/l respectively. A cloud point extraction using dithizone and Triton X-14 was developed for preconcentrative separation of Cd and Ni from sea water prior to determination by FAAS (366). Detection limits of 0.31 and 1.2 μg/l were obtained for Cd and Ni, respectively. Tuzen and

Soylak (367) have preconcentrated Cu, Co, Fe, Pb, Ni, and Zn from sea water as their dithizone complexes onto Diaxion HP −2 MG adsorbent prior to FAAS determination. The detection limits of the metals was varied from 0.08 μg/l Cd to 0.25 μg/l Pb. The RSD were found to be <9% chitosan is functionalized with quinoline-8-ol via diazotization reaction and is used as a column material during FI-FAAS determination of Cd and Cu (368). The detection limits and RSD were 0.1 and 0.4 μg/l 1.5 and 0.7%, respectively, which are quite impressive.

Graphite Furnace AAS (GFAAS)

Cr, Cu, and Mn in sea water were determined using transversely heated GFAAS with longitudinal Zeeman background correction (369). The reported detection limits are 42, 75, and 26 ng/l with a 20 μl sample, which are reasonably good. Zhuang et al. (370) have developed flow injection online Co-ammonium pyrollidine dithiocarbamate coprecipitation preconcentration and determination of Pb and Cu in sea water with GFAAS. This procedure involves drying the coprecipitatate after preconcentration and then dissolution in a 50 μl IBMK by stirring with air stream which result in low recoveries viz. ∼94%. As, Cd, and Pb were determined using pyrolitic graphite-coated wall and totally pyrolitic graphiteplatform and probe atomization techniques in conjunction with aqueous $Mg(NO_3)_2$, $Pd(NO_3)_2$ or elemental Pd as chemical modifier (371). Optimium performance was obtained using totally pyrolitic graphite platforms inserted within pyrolitic coated graphite tubes. For As, the modifier was injected with the sample while for Cd & Pb, the modifier was initially reduced in situ by thermal decomposition of Pd. Quantitative recoveries were obtained over the ranges of 30–90, 2–10, and 10–50 μg/l of As, Cd, and Pb respectively.

The influence on various organic matrix modifiers viz. tartaric, ascorbic and citric acids was studied on the investigation of sea water matrix interference during GFAAS determination of Cd, Co, Cr, Cu, Mn, Mo, Ni, and Pb (372). The recoveries and the detection limits lies in the range 95–107% (rather poor) and 0.02–0.2 μg/l. Zhang and Davison (373) have determined Cd, Fe, Mn, and Cu in coastal and sea water by forming resin gel thin films for their in situ measurement by Zeeman furnace AAS. Though the measurements were independent in the range 5–8.3 and in the presence of 10 nM–1 M NaNO3, the recoveries are very poor (70–80%). Huang et al. (374) have directly determined Mo, Cr and Mn in sea water by GFAAS in presence of $Pd(NO_3)_2$, $PdCl_2$–$Mg(NO_3)_2$ and $PdCl_2$-Hydroxyl amine hydrochlorides as modifiers, respectively.

Good agreement with certified values was obtained by these authors. Polyorgs XXIV (a cellulose-polyacrylonitrite copolymer containing hydrazide groups) in the hydroxyl form was used for sorption of trace metals viz Cd, Pb, Cu, Zn, and Ni (375). These trace metals were desorbed from the sorbent with 2 × 5 ml of 2M HNO_3 for 15 min. At the μg/l level, the RSD were <0.15%, which are quite impressive. Cd and Cu from sea water were electrodeposited on a graphite disc electrode and was placed in a graphite tube atomizer of ETAAS by an automatic sampler (376). The sensitivity increased linearly with deposition time, the detection limits were 5.9 ng/l for Cd (after 10 min deposition) and 100 ng/l (after 4 min deposition). The RSD were quite high viz., 7.8 for 0.17 μg/l for Cd2+ and 7.2% for 6.7 μg/l of Cu^{2+}.

Itoh et al. (377) have preconcentrated Cu, Ni, Co and Cd from sea water on a micromembrane filter with use of a pulverized chelate resin and subjected to determination by GFAAS via direct ashing. The detection limits for the cited metals were 45, 95, 30, and 0.5 ng/l respectively. Pb and Cd in sea water were determined directly by Zeeman effect GFAAS with nitric acid as modifier (378). The recoveries and RSD at ng/ml levels are 97 and 103% and 3.8 and 1.9%, respectively, which are quite good.

An improved dithiocarbamate-oxine solvent extraction method was developed for the preconcentration of heavy metals and shaken with 1 ml 0.01% Hg solution for metal-exchange back extraction (379). The resulting aqueous phase was used for the GFAAS determination of heavy metals. This method offers quite high enrichment factors rapidly. Ohta et al. (380) have employed a novel Mg-W cell for preconcentration of Ag, Au, Cu, Pd, Pt, and Rh and determined by ETAAS. However, the authors predicted possible determination in sea water only. Cd and Pb in sea water were preconcentrated on a chelating resin microcolumn placed in the injection tip of GF autosampler (381). A time-based computer-controlled FI-manifold is used for column conditioning, preconcentration and washing steps.

Elution is performed in a single step by the programmable GF autosampler and offers detection limits and RSD's of 0.9 and 8 ng/l and 2.7–4% for Cd and Pb in sea water respectively which are quite good. A similar automated online preconcentration systemfor ETAAS allows the diction of 0.009 and 0.06 μg/l of Cu and Mo, respectively (382). The results agree well with certified values of sea water standard reference materials. Ivanova et al. (383) have described FI online sorption preconcentration procedure in a knotted reactor coupled to ETAAS during the determination of Cu, Ni, and Mn in sea water. The linear response ranges, detection limits and RSD for Cu, Ni, and Mn were 0.05–0.5, 0.05–0.5, and 0.1–1.0 μg/l, 6, 8 and 29 ng/l and 1.5 and 2.5% at 0.2 μg/l and 2.9% at 0.4 mg/l, respectively.

Cu and Mn were determined directly and simultaneously in sea water by a multielement ETAAS with use of either Pd or a mixture of Pd and Mg as matrix modifier (384). The detection limits were 0.06–0.15 and 0.04–0.14 mg/l of Cu and Mn, respectively, and RSD were <10 V. Results for Cu and Mn in standard reference materials were in good agreement with certified values. Mo and V in sea water were determined by multielement ETAAS in presence of chemical modifiers (385). Detection limits were 0.35–0.60 and 0.32–0.51 μg/l for Mo and V, respectively. RSD were <11%, which are very poor.

A fullerene minicolumn was used for online preconcentrative separation of Cu, Pb and Ni in sea water prior to determination by W coil AAS (386). Quite impressive detection limits of 2.2, 23 and 75 ng/l respectively were reported by these authors.

Madrid et al. (387) have biosorbed Sb and Cr in sea water by Spirulina platensis and phaseolus for 2 min at room temperature prior to determination by ETAAS. The detection limits were in the range 0.05–0.9 μg/l. The recoveries vary widely as they lie in the range 90–107%. Ag, As, Cd, Cr, Hg, Ni and Pb in sea water were determined by ETAAS after addition of chemical modifiers $Pd(NO_3)_2$—ascorbic acid, $Pd(NO_3)_2$ or $CaCl_2$ (388).

The use of chemical modification and background eliminated the interference from saline matrix excepting Pb. Biological and chemical quality assurance tests were carried out by Lussier et al. (389) to measure the ratios of dissolved to total metal concentrations (As(III) and Se(IV)) in sea water. Cu, Cd, Pb, Ni, and Cr in sea water can be preconcentratively separated by electrodeposition on a graphite ridge probe at a controlled potential and subsequently determined by ETAAS (390). The detection limits were 16, 1, 6, 64, 14, and 17 ng/l for Cu, Cd, Pb, Ni, Cr(III), and Cr(VI), respectively. The determination of Bi, In and Pb in spiked synthetic and natural sea water by ETAAS with Zeeman effect background correction was investigated using W containing chemical modifier and tartaric acid as reducing agent (391). The respective lowest detection limits of 8.5, 4 and 1.3 μg/l were reported by these authors. An online separation, preconcentration system coupled to ETAAS was developed for Ni in sea water samples (392). The RSD and detection limit were $<5\%$ and 62 ng/l.

Chen et al. (393) reported a direct and simultaneous procedure for the determination of Cu, Mn, and Mo in sea water with a multielement GFAAS in presence of a mixture of Pd $(NO_3)_2$ and $Mg(NO_3)_3$ as chemical modifier. The RSD's are in the range 2–12% and the detection limits were 0.42, 0.68 and 1.2 μg/l of Cu, Mn, and Mo, respectively. The accuracy of the method was confirmed by the analysis of certified reference saline waters. A preconcentration system for multielement ETAAS was developed with a microcolumn packed with a chelating resin (394). The proposed method was applied successfully to the simultaneous determination of Co, Ni, and Cu in sea water. The detection limit and RSD of this method were 1.5×10^{-4}, 4.8×10^{-4}, and 1.2×10^{-3} μg/l and 4.3, 4.8, and 9.9% for Co, Ni, and Cu, respectively. The accuracy of the method was confirmed by the analysis of two certified reference saline waters.

A SPE preconcentration of trace metals from sea water onto iminodiacetate resin do not remove completely alkali and alkaline earths prior to determination by ETAAS (395). To reduce the interfering effects, two different approaches viz. chemical modification and matrix separation by pre-elution with ammonium acetate for analysis of Cd, Pb, Cu, Fe, and Mn in sea water reference materials CASS-3 and NASS-5. Cabon (396) has employed HF as a chemical modifier during the determination of Cd and Pb in sea water by GFAAS. The experimental detection limits are 0.007 and 0.25 μg/l for a 15 μl sea water sample. Good agreement with certified values of CASS-2 was claimed in this paper. Anhydrous Mg mineral sepiolite was used for preconcentrative separation of Co, Ni, Cu, Cd and Pb prior to determination by GFAAS (397). The sorbed metals were eluted with 2 M HCl and good RSD values of 1.55–2.00% were reported by these authors.

A water-in-oil type emulsion containing quinoline-8-ol was used for preconcentration of heavy metals from sea water prior to the determination by ETAAS (398). The emulsion used was prepared by dissolving 40 mg of uinoline-8-ol and 60 mg of sorbitan monoleate in 3.0 ml of toluene and vigorously mixing with 0.70 ml of 1.5 M HCl by ultrasonication. Due to the highly efficient concentration (100-fold), the heavy metals were determined at sub-ng/ml levels in sea water with satisfactory accuracy and precision. Colloidal Pd modifier was used during the determination of As, Sb and Pb in a spiked seawater by ETAAS (399). The detection limits were 5.4, 3.6 and 1.1 ng/ml, respectively. The recoveries vary widely in the range 98–112%. Tokman et al. (400, 401) have filled syringe with 3-aminopropyl triethoxy silane loaded silica gel for preconcentrative separation of Cu, Cd and Cr and Bi, Pb and Ni prior to GFAAS determination in sea water. The recoveries were quite good (96–98%) and detection limits were 6.6, 7.5 and 6.0 μg/l, respectively. Same authors (402, 403) have determined Pb and Ni and Bi and Cd in sea water after sorbing on chromosorb-107 filled in a syringe prior to their determination by ETAAS. The sample solution was treated with or without ammonium pyrollidine dithiocarbamate. The precision is quite good as the RSD value is $+2\%$. Tokmann et al. (404) have determined Pb, Cu and Mn ion sea water by GFAAS after preconcentrative separation using water soluble polymer, polyvinyl pyrrolidone. Reported detection limits were 1.7, 3.6, and 4.1 μg/l, respectively using a 10 μl of sample volume. This method is novel and characterized by rapidity, simplicity, quantitative recovery, and high reproducibility.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES)

Rare metals such as U, Nb, Ta, Zr, and Hf were preconcentrated onto poly(dithiocarbamate) chelating resin in column mode and then determined by ICP-AES after dissolution of resin in HNO_3-H_2O_2 mixture (405). The method though applicable to sea water analysis, the recoveries are very poor as they lie in the range 81–94%. The metals such as Co, Cu, Mo, Mn, Fe, Ti, and V (406) and Sb, Pb, and Tl (407) in sea water samples were preconcentrated via diantipyrylmethane-iodide third phase formation prior to determination by ICP-AES. Again, in both procedures the recoveries were very poor, viz. 90–110%. A coprecipitation carrier such as palladium was added to preconcentrate Cu, Pb, and Cd in synthetic water and sea water prior to determination by ICPAES (408). A 50-fold enrichment of analytes was achieved and the calibration graphs were linear in the range 0–500 ng/ml. The recoveries of μg/l level of Cu, Cd and Pb from sea water are 95, 103, and 100%, which are quite reasonable. EDTA cellulose column method was developed to preconcentrate Mo and V in sea water and eluted with 3 M HNO_3 and the eluate was analysed by ICPAES (409). The corresponding recoveries were 92–104% and 98–112% and the RSD were 8.2 and 4.9%, which are rather poor. High surface zirconium oxide was used to preconcentrate 18 trace elements prior to determination by FI online ICPAES (410). The preconcentration system was evaluated for several synthetic mixtures, standard water samples and synthetic sea water only. V and Cu present in sea water samples collected in Salvador City, Brazil was preconcentrated as their PAN complexes onto active carbon prior to ICPAES determination (411). The developed procedure offer detection limits of 73 and 94 ng/l, respectively, which are reasonably good. A rapid and simple method is described for the preconcentration and determination between the organic fraction and the labile fraction of the metals Mn, Cd, Cu, Zn, V, Ni, Pb, and Fe from sea water using oxine, which forms neutral complexes with these metals, followed by adsorption on C-18 chemically bonded silica gel (412). The results obtained in conjunction with ICPAES determination are comparable to certified values of SLEW-3, CASS-3 and NASS-3, which have different ionic strengths.

ICP-Mass Spectrometry (ICPMS)

The salient features of various analytical procedures for multimetal analysis using ICP-MS detection are summarized in Table 9.

Electrochemical Techniques

Various electrochemical techniques based on anodic/cathodic stripping voltammetry, square wave voltammetry, adsorptive stripping voltammetry, stripping potentiometry and sensors have been reported for the determination of metal ions in sea water. The significant features of these procedures are compiled in Table 10.

X-ray Techniques

Energy dispersive X-ray fluorescence spectrometric technique in conjunction with coprecipitative preconcentration onto iron(III) hydroxide was used for simultaneous determination of Pb and As (504). Linear calibration was achieved upto $\sim 80\ \mu$g/l with detection limits of 0.63 and 0.21 μg/l of Pb and As in sea water, respectively. The precision of the method is quite good as the RSD values are in the range 0.5–5%. Trace metals in sea water were preconcentrated on a SPE work station prior to determination by total reflection XRF (505). The results obtained on analyzing NASS-4 CRM for V, Mn, Fe, Ni, Cu, Zn, Se, Pb, and U were in good agreement with certified values. The precision is very poor as the reported RSD values are in the range 4.3–33%. Total reflection of XRF is preferred over radioisotope excited XRF after precipitation with ammonium pyrollidine-1-carbodithioate for the determination of traces of heavy metals in estuarine waters of Barbacoas Bay, Columbia (506). The detection limits were ranged from 0.06 mg/l for As to 0.28 mg/l for Ti. Knoth et al. (507) have developed a total reflection of XRF spectrometer that uses double multilayer arrangement as a tunable monochromator over the energy range 4–40 KeV together with an X-ray tube with an Mo-W alloy anode. Very good detection limits of 0.4, 0.6, and 8 pg of Ni, Pb, and Cd were achieved using WLβ, MoK α and 35 KeV band pass excitation respectively.

Radiochemical Techniques

Speciation of Co, Zn and Hg in sea water was investigated via. tracer method by equilibrating 0.25 g of solid or liquid ion exchange resin in batch mode with 10 ml of artificial or real sea water (508). Furthermore, column chromatographic studies were also carried out using 1 g of ion exchanger in a small column. Co species were found to be be present mainly as the Co^{2+} ion with an appreciable concentration of cobalt sulphate complexes. Zn exists partly in the cationic, anionic and hydrolysed forms which exists in labile equilibrium. Hg was found to exist mainly as anionic chloro complexes, hydrolysed and organically bound. The general speciation of metals in artificial and real sea water is governed by anions like Cl^-, SO_4^{2-}, CO_3^{2-} and OH^- present in sea water. Lo et al. (509) preconcentrated trace metals by using precipitated hydrous MgO and determined by neutron activation analysis. The method was applied to the analysis of sea water samples collected from the Taiwan straight. Trace metals like Co, Zn, Mo, La, Ce, U, and Fe were detected at levels of 0.04–41 μg/l.

Chromatographic Techniques

Mixed micelles obtained from mixing sodium dodecyl sulphate and Zwittergent-3-14 were used as dynamic stationary phases in ion chromatography for simultaneously separating inorganic anions and cations (510). Anions were detected directly by UV absorption at 253 nm and cations were detected indirectly by the use of Ce^{3+} ion as mobile phase. The method was applied to sea water. γ-aminobutyrohydroxamate resins and its derivatives were evaluated for the concentration and separation of trace metals from sea water (511). Linear calibration curves were obtained for 0.5–10 ng/ml of Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) and 2–40 ng/ml of Cd(II) with detection limits of 0.3–1.2 ng/ml. Nesterenko and Jones (512) have devised single column method for the preconcentration and separation of trace transition metals from sea water. Mobile phases were pumped at 0.8 ml/min and eluate was mixed with 4-(2-pyridylazo)resorcinol at pH 10.2 and subsequent detection at 495 nm. Alkali metals were not retained.

Alkaline earth metals and Mn(II) were eluted with tartaric acid for further 20 min. Good retention of the transition metals was noticed even in high chloride solutions. Chelation ion chromatography and online detection with ICP-MS was used for the determination of V, Mo and W spiked in artificial sea water (513). Fe(III), Fe(II), Ni(II) and Cu(II) were separated by ion chromatography as their 4,7-diphenyl-1,10-phenanthroline chelates (514). Calibration graph is linear over 0.05–0.5, 0.25–2 and 0.25–4 μg/ml for Fe, Ni, Cu respectively with a precision of 3.11, 5.81, and 7.61% while determination in sea water. A three-column system of C18, Dowex anion exchange resin and chelamine chelating resin connected in series is described for the

TABLE 9
Salient features of analytical methodologies developed for the determination of multimetal mixtures in sea water by ICP MS

S. No.	Analytes	Preconcentration mode	Calibration range (μg/l)	Detection limit (μg/l)	R.S.D. (%)	Application	Ref.
1	Mn, Co, Cu, Zn, and Cd	Online	Up to 10	—	1.37–3.19	CRMs of sea water	(413)
2	REE	Offline	—	Ppt or sub-ppt	—	Sea water	(414)
3	Mn, Co, Cu, Zn, and Pb	Online	—	—	2.3–6.9	Open ocean	(415)
4	Mo	Online	—	—	—	Sea water	(416)
5	25 elements	Online	—	—	—	CRMs of sea water	(417)
6	17 elements	Offline	—	—	—	Sea water	(418)
7	Transition metal, U and Pb	Online	—	—	<5	Sea water	(419)
8	Trace elements	Online	—	0.002–0.32	—	Synthetic sea water	(420)
9	V, Mn, Co, Ni, and Cu	—	—	0.003–0.18	—	Sea water	(421)
10	Cd, Co, Cu, Ni, Pb, U, Y, and REE	Offline	—	—	7–26	CRMs estuarine and sea water	(422)
11	8 metals	Online	—	0.005–0.06	—	CRMs of water	(423)
12	Ti and V	Online	0.001–2	—	2.8–4.4	River & sea water	(424)
13	Hg and Bi	In situ	Up to 5	0.015 and 0.003	<7.2	CRMs of sea water	(425)
14	Cd, Cu, Cr, Ba, Ca, and Sr	Bioaccumulation	—	—	—	Sea water	(426)
15	Pb, Cu, and Cd		—	1.3, 5, and 39 nM	—	Ocean waters	(427)
16	Cd, Co, Cu, Mn, and Pb	Online	—	19, 24, 56, 17 and 23	4.4–7.7	CRMs of sea water	(428)
17	Trace metals		—	0.002–0.329	—	Sea water	(429)
18	Trace metals	Online	0.5–5	0.7–4.0	—	CRM of sea water	(430)
19	Cu, Cd, Pb, Bi, and Se(IV)	Online	0.0025–0.6	—	<10	CRMs of sea water	(431)
20	B, Ba, Mg, Pb, Co, U, Cd, and In	—	—	—	—	Undiluted sea water	(432)
21	As, Pb, Sb, Sn, and Tl		—	—	—	Sea water	(433)
22	Trace elements	Offline	—	—	<10	Antarctic sea water	(434)
23	Li, Sc, Co, Y, In, Tb, Tl, and Th		—	—	—	CRM of riverine water	(435)
24	U, Mn, Mo, Pb and Cd		—	0.1, 0.7, 1.4, 0.0008, and 0.0041	—	CRM of open ocean sea water	(436)

(Continued on next page)

TABLE 9
Salient features of analytical methodologies developed for the determination of multimetal mixtures in sea water by ICP MS (*Continued*)

S. No.	Analytes	Preconcentration mode	Calibration range (μg/l)	Detection limit (μg/l)	R.S.D. (%)	Application	Ref.
25	Zr and Hf		—	0.21 and 0.03 pmol/g	2.5–7.0 and 9–22	Sea water	(437)
26	Bioactive trace metals	Offline	—	0.3–5.5 pM	—	Sea water	(438)
27	Mn, Zn, and Fe	Online	—	8×10^{-5}–0.016	6, 8, 9	CRMs of water	(439)
28	Mn, Co, Ni, Cu, Zn, Cd, and Pb	Online	—	—	3–5	CRMs of sea water	(440)
29	Trace heavy metals	Offline	—	—	—	Sea water	(441)
30	Tl	Online	—	0.01	—	CRMs and real sea water	(442)
31	Trace elements	Offline	—	0.007–100	—	CRM of sea water	(443)
32	Trace elements	Offline	0.01–5	—	1–7.2	High salinity waters	(444)
33	Trace metals	Online	0.05–10	—	—	Estuarine and sea waters	(445)
34	Be, Bi, Co, Ga, Ag, Pb, Cd, Cu, Mn, and In	Offline	—	—	—	Coastal sea water	(446)
35	Cu, Ni, Sb, Co, Ag, Cd, Mo, In and Pb	Online	—	0.0002–0.026	<5	CRMs of sea water	(447)
36	Transition and REE	Offline	—	—	—	Open ocean sea water	(448)
37	V, Cr, Mn, As, Se, Y, Mo, Sn, Sb, W, Bi, and U	Offline	—	—	—	CRMs of sea water	(449)
38	Trace metals	Offline	—	0.1–6.6	1.6–7.8	Sea water	(450)
39	Mn, Ni, C, Cd, and Pb	Onlne	—	0.06–1.1	—	CRMs of sea water	(451)
40	Cd, Pb, Co, Ni, and Zn	Online	—	0.03–0.3	0.5–6.8	Sea water	(452)
41	Al, V, Mn, Co, Ni, Cu, Zn, Mo, Pb, and U	Online	—	0.001–0.076	<5.4	CRMs of sea water	(453)
42	Trace elements	Offline	—	0.001–0.012	0.3–3.4	Coastal waters	(454)
43	Trace elements	Offline	—	—	—	Seawater	(455)
44	Trace elements	Online	—	—	10	CRMs of sea water	(456)
45	Ge, In, Re, and Tl	Offline	—	—	—	CRMs of open sea water	(457)
46	V, Ni, Mn, Cu, Zn, Cd, Pb, and U	Online and offline	—	0.001–0.17	—	Coastal sea water	(458)

(Continued on next page)

TABLE 9
Salient features of analytical methodologies developed for the determination of multimetal mixtures in sea water by ICP MS (*Continued*)

S. No.	Analytes	Preconcentration mode	Calibration range (μg/l)	Detection limit (μg/l)	R.S.D. (%)	Application	Ref.
47	Trace elements	Offline	—	—	—	Surface sea water	(459)
48	Transition and REE	Online	—	20–50 pg/l	5–6	Sea water	(460)
49	Co, Cu, Fe, Ni, Zn, and Mn	Offline	—	—	—	CRMs of nearshore sewater	(461)
50	Inorganic and methylated species of Ge, Sb, and As	Online and offline	—	0.001–0.07 nM	2–8	Marine waters	(462)
51	Mn, Cr, As, Mo, Ba, and U	Online	—	—	—	CRMs of sea water	(463)
52	V, Cr, and Mn		—	0.02–0.3	—	CRMs of sea water	(464)
53	Al, As, Co, Cu, Mn, Mo, Ni, Pb, and V	Online	—	—	1.2–7.1	CRMs of sea water	(465)
54	U, Fe, and As		—	0.003–0.02	—	Sea water	(466)
55	Trace metals	Offline	—	—	—	CRMs of sea water	(467)
56	Al, V, and Th	Online	—	—	—	Deep sea water	(468)
57	As and Mo		—	—	—	Sea water	(469)
58	Trace metals and REE	Online	—	—	—	CRMs of sea water	(470)

simultaneous preconcentration and differentiation between neutral hydrophobic organic metal complexes, anionic complexes and free ion concentration of the transition metals in sea water (515).

Shijo et al. (516) have determined trace amounts of Cu, Ni and V in sea water by HPLC after extraction with Capriquat in xylene and back extraction with aqueous 50% methanolic 2 M NaClO4 containing 10 mM acetate buffer of pH 4. Calibration graphs were linear for 0.5–5 μg/l of Cu, Ni & V with detection limits of 47, 90 & 26 ng/l, which are quite good. The precision is also quite good as RSD lies between 3.5–4.1%. The results obtained agreed with those obtained by ETAAS. Mo and Mn as their 8-hydroxyquinoline chelates in sea water were determined by using reversed phase HPLC (517). Calibration curves were linear from 0.5–200 mg/l for both metals with a detection limits of 0.2 and 0.4 μg/l of Mn(II) and Mo(IV), respectively. Results agreed well with previous studies which employ GFAAS.

Multiquantitation Techniques

A highly sensitive atomic absorption/atomic fluorescence method was proposed for the determination of Ag, Bi, Cd, Pb, and Tl(III) in sea water (518). The detection limits ranged from 0.3–1 ng/l for Ag and Cd and from 2–10 ng/l for Bi, Pb, and Tl. Flame or ETAAS was used for the determination of heavy metal ions in sea water after SPE preconcentration onto a high surface area TiO_2 (519). The sorbed metal ions were eluted with 0.1 M – EDTA followed by 1 M HNO3. A column preconcentration procedure employing the chelating ion exchange resin chelex-100 is described for the determination of Cd, Pb, Zn, Sn, Fe, and Cr(III) in sea water by flame AAS and ICP-AES (520). Detection limits for the metals were in the range 0.7–12 μg/l. Kasahara et al. (521) have synthesized xanthurenic acid functionalized silica gel for determination of Cu, Pb, and Zn in sea water by using ETAAS or ICP-AES and compared with quinoline-8-ol functionalized silica gel. Dithiocarbamate loaded polyurethane foam preconcentration method was employed for enriching As,

TABLE 10
Significant features of various electrochemical procedures reported for the determination of multimetal mixtures in sea water

S. No.	Analytes	Electro chemical technique	Electrode	Detection limit (mM)	R.S.D. (%)	Application	Ref.
1	Cd, Pb, and Cu	DP ASV	—	—	—	—	(471)
2	Cu and Pb	ASV	MFGCE	—	—	Acidified sea water	(472)
3	Pb and Cu	ASV	MFGCE	—	—	Sea water	(473)
4	Cu, Pb, Cd, and Zn	ASV	SMDE	5.92, 2.37, 0.83, and 4.48 ng/l	—	Sea water	(474)
5	Cd and Pb	DPASV	MFGCE	—	—	Antarctic coastal sea water	(475)
6	Co	ASV	DME	5.4	6	Nonpolluted sea water	(476)
7	Trace metals	DPASV	—	—	—	Sea water	(477)
8	Pb and Cd	DPASV	MFGCE	—	—	Antarctic surface sea water	(478)
9	Fe and Mn	LSV	Au(Hg)	—	—	Sea water	(479)
10	Cd, Cu, and Pb	ASV		—	—	Sea water	(480)
11	Ni and Cd	DPASV	MFGCE	—	—	Sea water	(481)
12	Cd, Cu, and Pb	ASV		0.23, 1.13 and 0.023 nM	—	Estuarine and coastal waters	(482)
13	Zn, Cd, Pb, and Cu	ASV	MFC paste E	—	—	Sea water	(483)
14	Cd	DPASV	DME	20	0.7–3.5	Sea water	(484)
15	Cu, Pb, Cd, and Zn	DPASV		—	<5	Sea water	(485)
16	Trace metals	DPASV	—	—	—	Western media terranian sea	(486)
17	Cd, Pb, and Cu	DPASV	GCE	μg/l to ng/l	—	CRM of CASS-2	(487)
18	Hg, Cu, Cd, Pb, and Zn	DPASV	RDE	—	—	Fresh and sea waters	(487)
19	Ni, Co, Mn, and Cu	DPAds. CSV	MFRDE	—	—	Baltic sea water	(488)
20	Cd, Pb, and Cu	SWASV	MFGCE	13, 30, and 200 ng/l	—	Sea water	(489)
21	As, Se, Cu, Pb, Cd, Zn, and Mn	DPCSV/DPASV		1×10^4	<5	CRMs of sea water	(490)
22	Cu, Pb, Cd, Ni, Co, and Zn	CSV	HMDE	0.3, 0.2, 0.1, 0.4, 0.6, and 0.02 nM	—	Sea water	(491)
23	Ni and Co	Ads. CSV	HMDE	2 and 0.05 nM	—	Sea water	(492)
24	Cu, Pb, and Zn	Ads CSV/ASV		28, 4, and 63 nM	—	Natural waters	(493)
25	Ni, Co, Cd, Pb, and Cu	DP Ads. SV	HMDE	0.06–1.22 μg/l	2.7–5.2	Sea water and ground water	(494)
26	Mo, U, Sb, Sn, and V	DP Ads. SV		24, 21, 210, 560, 23, and 21 ng/l	—	Sea water	(495)

(Continued on next page)

TABLE 10
Significant features of various electrochemical procedures reported for the determination of multimetal mixtures in sea water

S. No.	Analytes	Electro chemical technique	Electrode	Detection limit (mM)	R.S.D. (%)	Application	Ref.
27	Cu, Pb, and Cd	Ads. CSV	HMDE	480, 48, and 36	0.16, 16, and 12	NASS-4 reference sea water	(496)
28	Cu, Zn, Ni, and Co	Ads. CSV		—	—	Gulf of Cadiz water	(497)
29	Cd, Pb, and Cu	SWASV	MFE	—	—	Sea water	(498)
30	Ni and Co	Constant current PSA	MFGCE	0.03 and 0.01 μg/l	—	Sea water and waste water	(499)
31	Cd, Pb, and Cu	PSA	MFGCE	1, 3, and 44 ng/l	3.4, 5, and 2	Mediterranean sea water	(500)
32	Ni and Co	PSA	MFGCE		—	CRMs of sea water	(501)
33	Fe^{3+}	Fibre optic		—	0.05	Simulated sea water	(502)
35	Cu, Hg, Pb, and Se	Remote sensor		—	—	Shipboard sea water	(503)

Sb, Hg, Bi, Se, and Sn in sea water followed by simultaneous determination by ETAAS and ICP-AES (522). The detection limits for the above elements are 0.12–8 and 0.06–0.3 μg/l for ICP-AES & ET-AAS, respectively. The precision is also quite good as RSD values lies in the range 3–7%. The distribution of major to ultratrace elements into natural salt from coastal sea water in a salt preparation process was investigated by ICP-AES and ICP-MS with preconcentration using a chelating resin (523). Sawatari et al. (524) have described a combined system of ICP-MS and ICP-AES which has been used for the determination of various elements in rocks and sea water. Subsequently, same authors determined 37 elements in sea water by using combined ICP-MS-ICPAES system after coprecipitative preconcentration ont Al(OH)3 (525). Trace elements in sea water were determined by ion chromatography-ICP-MS (526). Detection limits were 1–123 ng/l with RSD in the range 0.5–3% and 5–10% for rare earth and transition elements,respectively.

Howard et al. (527) have compared poly(L-crysteine) and quinoline-8-ol functionalized control pore glass for the extraction and recovery of trace amounts of Cd, Pb, and Cu from synthetic and reference sea water samples. Poly(L-cysteine) immobilized support exhibited high selectivity for Cd & Pb in the presence of a 10,000-fold excess of Co or Ni. Sea water was analysed for Cd, Cu, Fe, Ni, and Zn by adsorptive cathodic stripping voltammetry and GFAAS coupled with online preconcentration (528). Johansson et al. (529) performed speciation of alkyl and inorganic forms of lead and mercury by using GC-AAS and GC-microwave induced plasma AES by pumping sea water through a chelating column packed with dithiocarbamate resin. The best recoveries for alkyl and inorganic Pb were obtained at pH ~7 whereas for alkyl and inorganic Hg compounds, the recoveries were independent of pH.

SUMMARY

From 1995 to till the end of 2004, more than 500 scientific publications have appeared dealing with some aspects or other of the determination of metal species in sea water. This review attempts to critically look into various reports based on criteria like selectivity, sensitivity, precision etc. We now provide a synopsis of some of the interesting areas and trends.

Singular or bivalent metal determinations of metallic species in sea water was attempted by several authors. These determinations were critically evaluated by categorizing them into alkali and alkaline earth elements, transition elements (3d, 4d, and 5d), p-block metal ions, noble metals, lanthanides, actinides and miscellaneous species/parameters. Subsequently, the determination of multimetallic mixtures in sea water are discussed based on the analytical techniques employed. These include spectral, electrochemical, X-ray, radiochemical, chromatographic, and multiquantitation techniques.

Spectral techniques especially inductively coupled plasma atomic emission/mass spectrometry constitute the major chunk of these reports. In view of the high salt content of sea water, most of the reports deals with either offline-online preconcentration. Coprecipitation of analytes of interests from sea water matrix, is not that popular in recent times as the determination procedure has to be applicable in the presence of large amounts of coprecipitant. Ion exchange and liquid-liquid extraction (LLE) still find increasing use. The main drawback of the former technique is the need for frequent replacement of ion-exchange resins required for preconcentration. LLE is simple and rapid and has drawbacks such as low enrichment factors, emulsion formation necessitating the use of modifiers, etc. On the other hand, solid phase extraction eliminates the drawbacks of the above techniques during preconcentration of metals either singularly or in mixtures.

The use of online flow injection preconcentration is often preferred over offline techniques wherever applicable as the number of samples that can be analysed per hour is as high as ∼30 with 1 min loading time and offer good precision as these are computer controlled. In view of the above-mentioned points, flow injection analysis has taken a prominent place in sea water analysis for metals.

Hyphenated techniques are rarely used to date for sea water analysis and will be the most sought after in near future for both routine measurement/speciation. Another area that is increasingly popular in sea water analysis is use of reference materials for validation of developed analytical procedures. However, certified reference materials of sea water for rare earth elements are yet to be prepared and made available to the scientific community. The advances in the determination of metals in sea water matrix will certainly lead to the recovery of valuable and strategic materials from sea water in the not so distant future.

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