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Speciation and Determination of Heavy Metals in Bera Lake Water by Atomic Absorption Spectrometry after Sorption on Amberlite XAD-16 Resin

Dissertation submitted in partial fulfillment for the
Degree of Bachelor Science (Health) in Forensic Science

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2006

CERTIFICATE

This is certify that the dissertation entitled

"Speciation and Determination of Heavy Metals in Bera Lake Water by Atomic Absorption Spectrometry after Soprtion on Amberlite XAD-16 Resin"

is the bonafide record of research work done by

Ms Nor Azreen Binti Zulkafli

during the period **January 2006** to **April 2006**

under my supervision.

Signature of supervisor: ____________________

Name and address of supervisor:

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Date: 11/05/06

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(Nor Azreen Binti Zulkafli)

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ABSTRACT

The concentration of some heavy metals in Bera Lake water samples collected in rainy and dry seasons has been determined by atomic absorption spectroscopy. The metals in free state, bound to humic substances; and suspended particles, were fractioned according to a scheme developed. The metals were pre-concentrated on columns (1 x 10 cm) packed with pre-purified Amberlite XAD-16 resin. The concentrations of the metals bound to humic substances and of free metal ions were determined after sorption-elution on the resin. The method optimized with sodium tetraborate reagent was used in determining the free metal ions. Meanwhile, the concentrations of metal bound to suspended particles were determined after filtration, dissolved in concentrated nitric acid, centrifugation, and evaporation.

The linearity of the detector response for the concentrations range of 0 – 2.0 ppm was excellent with a correlation coefficient ranging between 0.998 – 0.999. The recoveries ranged between 99.5 – 100% with a RSD of 0.5 – 1.5%. The concentration of elements found in Bera Lake water ranged: Cu (II), 0.001 ± 0.000 mg/L to 0.309 ± 0.002 mg/L; Cd (II), 0.067 ± 0.002 mg/L to 0.163 ± 0.002 mg/L; Pb (II), 2.613 ± 0.012 mg/L to 10.712 ± 0.025 mg/L; Ni (II), 0.012 ± 0.020 mg/L to 0.224 ± 0.007 mg/L; Cr (III), 0.002 ± 0.006 mg/L to 0.114 ± 0.002mg/L.

INTRODUCTION

Heavy metals in environment are generally a source of pollution. Every country and communities have their regulations on the levels of traces metal ions in the environment. The levels of heavy metals should be lower than the levels of the regulations of the relevant country. Because of those points, the accurate determinations of metal ions at trace concentrations are an important field of the analytical chemistry (Soylak *et al.*, 2005).

The trace heavy metals existing in fresh waters are present in various physicho-chemical forms, which include simple hydrated ions, hydroxo-complexes, inorganic and organic complexes, and colloidal particles. These psyciso-chemical forms can effectively change their bio-availabilities and toxicities, for example, chromium (III) is an essential element, whereas chromium (IV) is highly toxic and even carcinogenic; arsenic (III) is more toxic than arsenic (V). The heavy metal speciation, therefore, arouses substantial interest in water analyses because the geochemical behavior and biological effects of heavy metals depend greatly on their physico-chemical forms. The chemical speciation has been a topic of increasing research interest in geochemical, biological and environmental sciences, and waste water treatment processes.

Humic and fulvic acids are also known to interact with various metal ions, hydrated metal oxides, clay minerals and organic compounds. Humic substances, major organic constituents of natural waters, interact strongly with various heavy metals to form humic complexes and affect adsorption-desorption behavior of metals. Physico-chemical forms of metal-humic complexes, however, are complicated because they may exist alone or be absorbed on other colloidal particles. Up to now, methods such as co-precipitation, sorption on adsorbent resins and separation by ion-exchange resins have been used in determining metal ions both free and bound to humic substances present in natural waters. Among the trace element determination techniques, adsorption is one of the most widely used. For this purpose, commercially available Amberlite XAD copolymers (XAD-2, -4, -7, -8 and -16) have been widely used as adsorbents suitable for multi-element pre-concentration from different matrices, because of their purity, good adsorption properties (Tokalioglu *et. al.*, 2000).

Amberlite XAD-16 (Rohm and Haas Co.) is a polymeric adsorbent based on polystyrene divinylbenzene-copolymer supplied as insoluble white beads. It is used in continuous filtration for adsorption of water-soluble substances. XAD-16 has excellent physical resistance, hydraulic characteristics and thermal stability. It is a non-ionic, hydrophobic, cross-linked polymer which derives it adsorptive properties from its patented macroreticular structure (containing both a continuous polymer phase and continuous pore phase), high surface area and the aromatic nature of its surface. In addition, it has high porosity, low polarity, and the largest surface area (800 m^2 g^{-1}) among the XAD series of Amberlite resins. Amberlite XAD-16 is used to absorb hydrophobic molecules from polar solvents and volatile organic compounds from vapor streams. The characteristic pore size distribution of Amberlite XAD-16 makes it polymeric adsorbent, an excellence choice for the adsorption of organic substances of relatively low to medium molecular weight. It can be used in column or batch preparation. Therefore, it was selected as an adsorbent resin, owing to these performance characteristics.

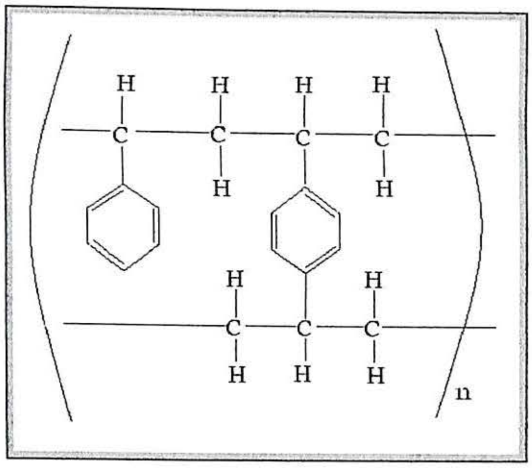

Fig. 1.1: Chemical structure of Amberlite XAD-16

One of the important instrumental techniques for the determination of traces heavy metals is flame atomic absorption spectrometry, due to its low-cost and easy usage. Enrichment-separation procedures for the traces metal ions in environmental samples including natural waters are necessity prior to their flame atomic absorption spectrometric (FAAS) determinations, due to their lower levels than the detection limits of FAAS and the interfering effects of the matrix constituents of the samples.

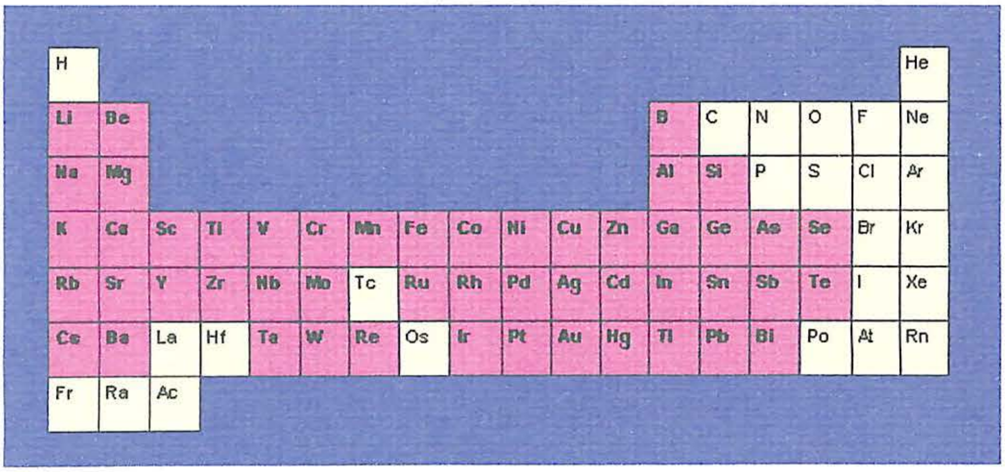

Fig. 1.2: Elements highlighted in pink are detectable by atomic absorption spectroscopy.

Flame atomic absorption is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use. Figure 1.2 shows elements which are commonly detected through atomic absorption. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve.

As for as this research is concerned, Bera Lake has been chosen for sampling and subsequent studies. Bera Lake is one of the two major natural bodies of fresh water in Malaysia. Located in the south-eastern part of Temerloh, north and south of Datok Village, State of Pahang, Bera Lake is situated in the saddle of the main and eastern mountain ranges of Peninsula Malaysia. This natural freshwater lake system is the largest freshwater swamp in Peninsula Malaysia, extending 34.6 km long and 25 km wide, drainings into the Pahang River via the Bera River. The Bera River originates east of the swamp watershed and passes very close to the main channel of the swamp near its outlet near Tanjong Kuin. The area of the Bera Lake Nature Reserve Park is about 26,500 hectares.

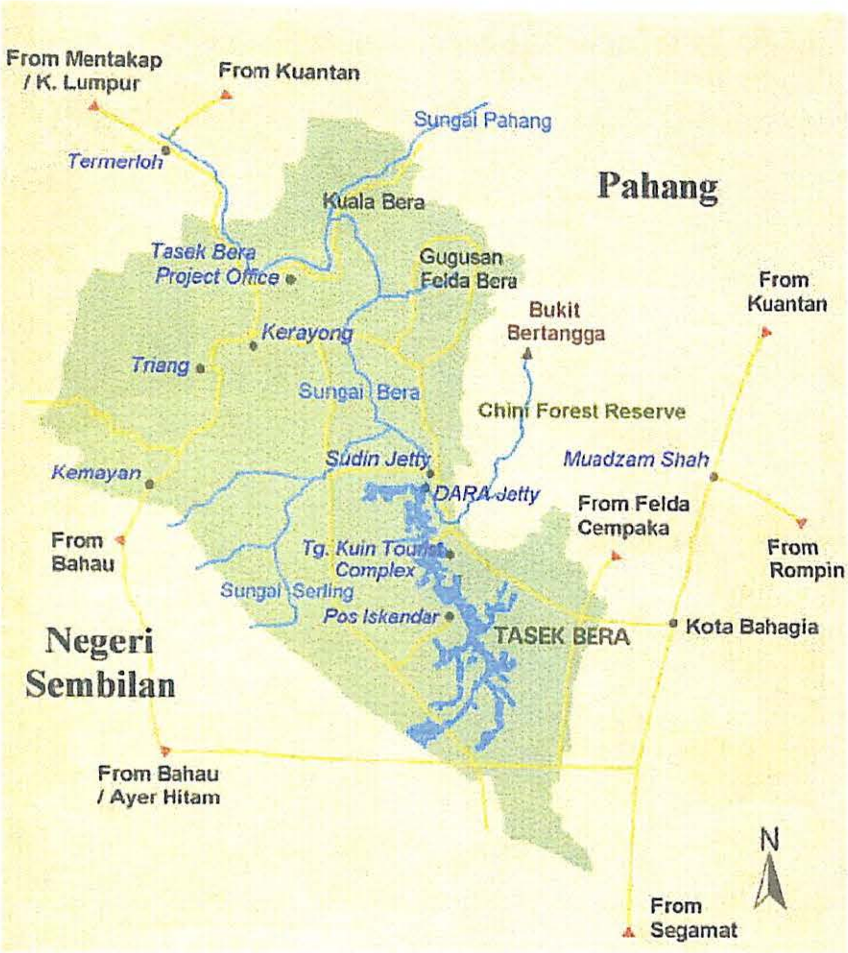

Fig. 1.3: Location of Bera Lake in the district map.

Disturbances and threats includes shifting cultivation by Semelai natives, possible pollution from the river systems through reverse-flow during flood conditions during the northeast monsoon, agriculture activities, forest destruction in the watershed leading to an increase in erosional load, mining activities (iron extraction) causing siltation, disturbance from a network of logging roads surrounding the lake and from several trails reaching to or near the shoreline in the south and west, and alteration in the local drainage patterns and increased siltation in tributaries to the west, caused by logging operations, especially road construction.

The aim of this research is to determine the concentration of heavy metals in several areas of Bera Lake between two seasons, which are rainy season (September-January) and dry season (February-March).

REVIEW OF LITERATURE

Tokalioglu et al., (2000) determined heavy metals (Pb, Cu, Cd, Ni and Cr) in lake waters by atomic absorption spectrometry after sorption on Amberlite XAD-16 resin. A column packed with Amberlite XAD-16 resin was used for preconcentration and determination of chemical forms of heavy metals such as Cr, Ni, Cu, Cd and Pb in lake water samples. The concentrations of the metals bound to humic substances and of free metal ions were determined after sorption-elution on the resin. The method optimized with sodium tetraborate reagent was used in determining the free metal ions. Flame atomic absorption spectrometry was used to determine the metals in lake water sample.

Tokalioglu et al., (2000) also determined the heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. A four-stage sequential extraction procedure for determination of the speciation of extractable heavy metals, proposed by the Commission of the European Communities Bureau of Reference (BCR) as a mean of comparison of data of extractable heavy metals, has been applied to lake sediments collected from the lakes of a water-laden area of Sultansazligi, Kayseri, Turkey. The determination of extractable heavy metals such as chromium, cobalt, nickel, copper, zinc, cadmium (below the detection limit), lead, manganese and iron in the sediment samples was carried out by flame atomic absorption spectrometry (FAAS) using an injection method. Acetic acid, hydroxyl ammonium chloride, hydrogen peroxide plus ammonium acetate, and aqua regia stages of the sequential extraction procedure were applied to the sediment samples, respectively. Recoveries were quantitative (>95%). The accuracy, obtained by comparing the pseudo-total metal concentrations with the sum of the four extraction stages, was found to be satisfactory.

Tokman et al., (2004) reported the determination of lead, copper and manganese by graphite furnace atomic absorption spectrometry after separation/ concentration using a water-soluble polymer. In his study, a water-soluble polymer, polyvinylpyrrolidinone (PVP) having chelating functionalities was used for the preconcentration and separation of traces of Pb, Cu, Ve and Mn prior to their determination by graphite furnace atomic absorption spectrometry. For this purpose, the sample and the PVP solutions were mixed and the metal bound polymer was precipitated by adding the mixture onto acetone. The precipitate was separated by decantation and dissolved with water. By increasing the ratio of the volumes of sample to water used in dissolving the precipitate, the analyte elements were concentrated as needed. The concentration of trace elements was determined using graphite furnace atomic absorption spectrometry. The analyte elements in matrix free aqueous solutions were quantitatively recovered. The validity of the proposed method was checked with a standard reference material (NIST SRM 1577b bovine liver) and spiked fruit juice, sea water and mineral water samples. The analytical results were found to be in good agreement with certified and added values. Detection limits were 1.7, 3.6 and 4.1μg/l for Pb, Cu and Mn, respectively, using 10 μl of sample volume. The method is novel and can be characterized by rapidity, simplicity, quantitative recovery and high reproducibility.

Guo et al., (2004) reported a method for the preconcentration of trace metals with 2-(methylthio)aniline-functionalized XAD-2 and their determination by flame atomic absorption spectrometry. In his research, 2-(Methylthio)aniline-modified Amberlite XAD-2 has been synthesized by coupling it through a –N=N–NH– group. The resulting chelating resin, characterized by elemental analysis, thermogravimetric analysis and infrared spectra, was used to preconcentrate Cd, Hg, Ni, Co, Cu and Zn ions. Several parameters, such as the distribution coefficient and sorption capacity of the chelating resin, pH and flow rates of uptake and stripping, and volume of sample and eluent, were evaluated. He also investigated the effect of electrolytes and cations on the preconcentration. The recoveries were >96%. The procedure was validated by standard addition and analysis of a standard river sediment material (GBW 08301, China). The developed method was utilized for preconcentration and determination of Cd, Hg, Ni, Co, Cu and Zn in tap water and river water samples by flame atomic absorption spectrometry with satisfactory results.

Vicente de la Riva et al., (2001) employed spectrofluorimetric method for the rapid screening of toxic heavy metals in water samples. They developed about a fast and inexpensive test for recognizing potential wastewater contamination by the presence of highly toxic heavy metals. The test is based on the reaction of the toxic heavy metals Hg (II), Cd (II), Pb (II) and Ag (I) with 6-mercaptopurine (6-MP) to produce highly fluorescent complexes. The fluorescence emitted by the complexes was measured at 380 nm and 540 nm for excitation and emission wavelength, respectively.

Brach-Papa et al., (2002) proposed a selective procedure for the spectrofluorimetric determination of aluminium in drinking water by sequential injection analysis. The analytical procedure is based on the complex formation between Al^{3+} and 8-hydroxyquilnoline-5-sulfonic acid (HQS) and on fluorimetric detection of the complex. The reaction was carried out in the presence of thioglycolic acid as a masking agent. This procedure has been adapted to a sequential injection analysis (SIA) system. Operative conditions both for batch and SIA procedures were investigated including reagent concentration, volumes, pH and wavelengths used for the fluorimetric detection.

Sutherland et al., (2002) determined Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. In his study, the optimized BCR three-step sequential extraction procedure is applied to five certified reference materials (SRM 2710, SRM 2711, CRM 483, CRM 601 and CW 7). Four fractions are reported, acid extractable, reducible, oxidizable, residual for Al, Cu, Fe, Mn, Pb and Zn. The objectives of their studies were to characterize experimental precision and/or accuracy and to establish baseline data of fraction-specific element concentrations for future studies applying the optimized BCR three-step extraction procedure. The optimized procedure was found to be precise (typically <5%) for all metals in all fractions.

Kenawy et al., (2000) determined some trace heavy metal ions in natural and biological samples by AAS after their preconcentration using a chemically modified chloromethylated polystyrene-PAN ion-exchanger. He described about the use of chemically modified chloromethylated polystyrene-PAN, CMPS-PAN ion-exchanger for the separation of Au(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), Pd(II) and Zn(II) from aqueous solution. After preconcentration, the heavy cations under investigation were determined using atomic absorption spectrometry (AAS). The chelates formed between CMPS-PAN ion-exchanger and the investigated metal ions were characterized by FT-IR spectrometry, potentiometry and thermal analysis. They carried out the analytical applications for the preconcentration and separation using the modified CMPS-PAN ion-exchanger and the determination of the studied metal ions in tap, Nile, waste and sea water samples, human urine, milk (synthetic and natural) and some ores.

Okumura et al., (2002) developed a simple and rapid *in situ* preconcentration method using solid phase extraction for the determination of dissolved manganese in Brackish lake water samples. Manganese in water samples, which was taken into a graduated syringe to easily perform the operation for collecting manganese at sampling sites, was converted into a stable complex with 4-(2-pyridylazo)resorcinol (PAR) at pH 10 immediately after sample collection. The formed Mn-PAR complex was collected by a Sep-Pak C18 cartridge, which was packed with C18-bonded silica. The complex was stable in the Sep-Pak C18 cartridge for at least one month. The retained complex was quantitatively eluted with 0.5 M hydrochloric acid. The manganese was determined by graphite furnace AAS.

Vassileva et al., (1996) performed column solid-phase extraction of heavy metal ions on a high surface area CeO_2 as a preconcentration method for trace determination. The adsorption of heavy metal cations on two CeO_2 samples, (C-1, 209 m^2 g^{-1}, prepared by hydrolysis of $Ce(NH_4)_2(NO_3)_6$, and C-2, 123 m^2g^{-1}, synthesized by hydrolysis-oxidation of $Ce(NH_3)_3$, has been investigated. They also studied adsorption kinetics, pH curves, adsorption isotherms, adsorption capacities and the nature of the sorption sites. Quantitative sorption of $Cd^{2+,}$ $Co^{2+,}$ $Cu^{2+,}$ $Mn^{2+,}$ $Pb^{2+,}$ and $Zn^{2+,}$ has been detected at pH>7. On the basis of IR spectra of adsorbed CO, it has been concluded that the adsorption sites represent coordinatively unsaturated Ce^{4+}-O^{2-}, pairs at the ceria surface. All of the adsorbed ions may be eluted by HNO_3 and EDTA and the CeO_2 sample preserves its sorption properties after this procedure. A column system for preconcentration is developed. They also established the conditions for quantitative and reproducible elution and subsequent atomic absorption spectrometry. He tested the system with some analytes of particular environmental importance (Cd, Co, Cu and Pb) in river and waste waters.

Hiraide et al., (1995) performed coprecipitation with tin (IV) hydroxide followed by removal of tin carrier for the determination of trace heavy metals by graphite-furnace atomic absorption spectrometry. Nanogram amounts of trace heavy metals were quantitatively coprecipitated with tin (IV) hydroxide at pH 5-6. After centrifugation, the precipitate is dissolved in nitric acid and the solution is allowed to stand overnight to form stannic acid. More than 90% of tin is precipitated, leaving trace heavy metals in the solution. The formation of stannic acid is highly accelerated by heating at 50°C. The trace heavy metals were successfully determined by graphite-furnace atomic absorption spectrometry without any interference from tin. The proposed method has been applied to the analysis of high-purity magnesium metal and river water.

Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples had been perfomed by Soylak et al., (2005). Trace amounts of copper, manganese, cobalt, chromium, iron and lead were quantitatively coprecipitated with erbium hydroxide using 0.05M NaOH medium. The coprecipitant could be easily dissolved with 1M nitric acid. The presence of up to 15 g/l of erbium ions did not interfere with the atomic absorption spectrometric determination of analyte ions. The recovery values for analyte ions were higher than 95%. The concentration factor was 25-fold. They also discussed about the coprecipitation parameters including reagent amounts and matrix effects. The relative standard deviations of the determinations were below 9%. The time required for the coprecipitation was about 30 min. The proposed method was successfully applied for the determination of trace amounts of analyte ions in urine, soil and sediment, natural water samples.

Dressler et al., (1998) determined heavy metals by inductively coupled plasma mass spectrometry after on-line separation and preconcentration. A method for the determination of Cu, As, Se, Cd, In, Hg, Tl, Pb and Bi in water and in biological materials by inductively coupled plasma mass spectrometry, after an on-line separation, has been described. The matrix separation and analyte preconcentration was accomplished by retention of the analytes complexed with the ammonium salt of O,O-diethyl dithiophosphoric acid in a HNO_3 solution using C_{18} immobilized on silica in a minicolumn. Methanol, as eluent, was introduced in the conventional pneumatic nebulizer of the instrument. In order to use the best compromise conditions, concerning the ligand and acid concentrations, the analytes were determined in two separate groups. The enrichment factors were in the range from 5 to 61, depending on the analyte. The limits of detection varied from 0.43 ng L^{-1} for Bi to 33 ng L^{-1} for Cu. The sample consumption is only 2.3 mL for each group and the sampling frequency is 21 h^{-1}. The accuracy was tested by analysing five certified reference materials: water, riverine water, urine, bovine muscle and bovine liver. The agreement between concentrations found was very good, except for As. The relatively small volume of methanol, used as eluent, minimizes the problems produced by the introduction of organic solvent into the plasma.

Vasconcelos et al., (1997) reported the method for speciation of Cu, Pb, Cd and Hg in waters of the Oporto coast in Portugal using pre-concentration in a Chelamine resin column. They collected the sea water monthly between January and March 1996 from the shore of the Oporto coast at three different representative sampling points and speciation of Cu, Pb, Cd and Hg were carried out. For the purpose, total particulate (retained on a 0.45 μm pore-size filter), particulate sorbed to inorganic matter, total dissolved, and dissolved and operationally labile metal was discriminated. The filters were digested by microwaves. The filtered water was pre-concentrated on a microcolumn of Chelamine, eluted with 5 ml of 2 mol L^{-1} HNO_3 and analyzed by flame atomic absorption spectrometry (F-AAS) or mercury cold vapour (MCV-AAS) for Hg. The organic matter (OM) destruction was performed by UV photolysis. For quality control of the results, determination of Cu, Pb and Cd total dissolved concentration by differential pulse anodic stripping voltammetry was also performed; for Hg only the pre-concentration in the column was changed to partial evaporation of the sea water, followed by MCV-AAS. Online pre-concentration with Chelamine showed to be effective for extraction of the heavy metals in coastal waters.

Jankowski et al., (2005) reported the multielement determination of heavy metals in water samples by continuous powder introduction microwave-induced plasma atomic emission spectrometry after preconcentration on activated carbon. In his research, a novel continuous powder introduction microwave-induced plasma atomic emission spectrometry method (CPI-MIP-AES) has been developed for trace determination of metals in ground and tap water samples after preconcentration on activated carbon. The experimental setup consisted of integrated rectangular cavity TE101 and vertically positioned plasma torch. The technical arrangement of the sample introduction system has been designed based on the fluidized bed concept. The satisfactory signal stability required for sequential analysis was attained owing to the vertical plasma configuration, as well as the plasma gas flow rate compatibility with sample introduction flow rate. The elements of interest (Cd, Cu, Cr, Fe, Mn, Pb, Zn) were preconcentrated in a batch procedure at pH 8–8.5 after addition of activated carbon and then, after filtering and drying of the activated carbon suspension, introduced to the MIP by the CPI system. An enrichment factor of about 1000-fold for a sample volume of 1 L was obtained. The detection limit values for the proposed method were 17–250 ng L^{-1}. The proposed method was validated by analyzing the certified reference materials: SRW bWartaQ Synthetic River Water and BCR CRM 399 major elements in freshwater. The method was successfully applied to the determination of the heavy metals in tap water samples.

Bolormaa et al., (2006) employed PIXE analysis of heavy metals in water samples from a mining area in Mongolia. The present paper deals with chemical analysis of the Boroo River water samples collected in mining area of Mongolia focusing the determination of heavy metal contents by particle induced X-ray emission (PIXE) technique. The samples were prepared by preconcentration method (water samples treated to form metal–dibenzyldithiocarbamate (DBDTC) complexes and collected on a nuclepore track-etch membrane filter) and irradiated by 2.5 MeV proton beam from the single-end type Van de

Graaff accelerator. The accuracy of the results was proved by using certified river water samples. The total dispersions of experimental procedure were evaluated by variance analysis.

Akl et al., (2004) employed organically modified silica gel and flame atomic absorption spectrometry for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems. A 5-formyl-3-(1'-carboxyphenylazo) salicylic acid-bonded silica gel (FCPASASG) chelating adsorbent was synthesized according to a very simple and rapid one step reaction between aminopropyl silica gel (APSG) and 5-formyl-3-(1'-carboxyphenylazo) salicylic acid (FCPASA) and its adsorption characteristics were studied in details. Nine trace metals viz.: Cd (II), Zn (II), Fe (III), Cu (II), Pb (II), Mn (II), Cr (III), Co (II) and Ni (II) can be quantitatively adsorbed by the adsorbent from natural aqueous systems at pH 7.0–8.0. The adsorbed metal ions can be readily desorbed with 1 M HNO_3 or 0.05M Na_2EDTA. The distribution coefficient,$_{Kd}$ and the percentage concentration of the investigated metal ions on the adsorbent at equilibrium, $C_{M,eqm}$ % (Recovery, R%) were studied as a function of experimental parameters. The logarithmic values of the distribution coefficient, $\log_{Kd}$, are 3.7–6.4. Some foreign ions caused little interference in the preconcentration and determination of the investigated nine metals by flame atomic absorption spectrometry (AAS).The adsorption capacity of FCPASASG was 0.32–0.43 meq g^{-1}. C and N elemental analyses of the adsorbent (FCPASASG) allowed us to calculate a surface converge of 0.82 mmol g^{-1}. This value compares well with the best values reported for the azo compounds. The adsorbent and its formed metal chelates were characterized by IR (absorbance and/or reflectance) and UV spectrometry, potentiometric titrations and thermogravimetric analysis (TGA and DTG). The mode of chelation between the FCPASASG adsorbent and the investigated metal ions is proposed to be due to reaction of those metal ions with the salicylic and/ or the carboxyphenylazo chelation centers of the FCPASASG adsorbent. Nanogram concentrations (0.07–0.14 ng ml^{-1}) of Cd (II), Zn (II), Fe (III), Pb (II), Cr (III), Mn (II), Cu (II), Co (II) and Ni (II) can be determined reliably with a preconcentration factor of 100.