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Naphthols as Reagents for Solid Phase Preconcentrative Separation of Inorganics

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ABSTRACT

Solid phase extraction (SPE) has emerged as a powerful tool for separation/enrichment of inorganics, organics and biomolecules. The basic principle of SPE is the transfer of analytes from aqueous phase to the active sites of adjacent solid phase. The solid phase materials were prepared by sorption/chemical immobilization/coprecipitation of various chelating reagents or sorption of metal-chelating agents onto solid supports such as activated carbon, naphthalene, silica and silica gel, glassbeads, cellulose, polyurethane foam and polymer supports. This review highlights the salient features of SPE preconcentrative separation procedures developed so far for inorganics wherein naphthols are used as chelating reagents and evaluates them critically.

1. INTRODUCTION

A number of analytical techniques have been described for trace and ultra trace characterization of biological, geological, environmental and metallurgical samples. Direct determination is still difficult because of insufficient sensitivity, lack of selectivity, presence of complex matrix, poor precision and accuracy. Of the various pretreatment techniques used in conjunction with trace/ultra trace analytical techniques, preconcentration is widely employed by various researchers (Mizuike, 1983; Prasada Rao and Mary Gladis, 2001). Preconcentration is a process in which the ratio of the amount of a desired analyte to that of complex matrix is enhanced and usually separated from a host of other inorganics. Thus, preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitate the calibration. In general, it can be referred to as the enrichment process which involves separating the minor component (analyte) from complex matrix or extraction of particular analyte from one phase to other in which latter one is of less volume than first one.

Preconcentrative separation techniques adopted by various researchers are based on physical, physicochemical and chemical principles. These include liquid–liquid extraction, ion exchange, chemical immobilization, coprecipitation, flotation, adsorption, electrophoresis, ultracentrifugation and solid phase extraction. Hitherto, liquid–liquid extraction is most often used due to its simplicity, rapidity and ready adaptability to scale up and ease of recovery of analyte and extractant. Solid phase extraction (SPE) is replacing liquid–liquid extraction due to the following advantages offered by the former technique. These include (Junker-Buchheit and Witzenbacher, 1996; Mary Gladis et al., 2002; Pyrzynska and Trojanowicz, 1999)

1. Higher enrichment factors
2. Absence of emulsion
3. Safety with respect to hazardous samples
4. Minimal costs due to low consumption of reagents
5. Flexibility
6. Ease of automation and
7. Environmentally more friendly as large volumes of solvents are not used.

The basic principle of SPE is the transfer of analytes from aqueous phase to the active sites of the adjacent solid phase. This transfer is stimulated by the selection of appropriate operational conditions in the system of 3 major components, water (liquid phase)–sorbent analyte (Liska, 1993). The analyte after sorption on solid phase either desorbed with a suitable eluate or analyte along with sorbent is dissolved in suitable solvent and further analysed. Recently, Vlasankova and Sommer (1999) have reviewed SPE preconcentration procedures developed for noble metals present in environmental and biotic materials.

Naphthols form sparingly soluble precipitates with various inorganics. By proper control of pH of the solution or the use of masking/sequestering agents, a greater degree of selectivity is usually achieved. So naphthols, in addition to their use as spectrophotometric reagents (Onishi, 1986, 1989; Prasada Rao et al., 1998; Snell, 1978) have been widely used as chelating and/or sorbent extraction agents in analytical chemistry. This review deals with various preconcentrative separation methodologies coupled to atomic and molecular spectrometric techniques developed for various inorganics. The naphthol reagents employed include 1(2-Thioazolyl azo)2-naphthol (TAN), 1-(2-pyridylazo)2-napthol (PAN) and 1-nitroso-2-naphthol.

2. NAPHTHOLS AS SOLID PHASE EXTRACTANTS

2.1 Transition Elements

2.1.1 TAN

Cloud point extraction has been used for the preconcentration of Mn (Teo and Chen, 2001) and Co and Ni (Chen and Teo, 2001) after the formation of complex with TAN and subsequent quantitation by flame atomic absorption spectrometry using octyl-phenoxy polyethoxy ethanol (Triton X-114) as surfactant. Under optimal conditions, above preconcentrative separation permitted the detection down to 0.28 μg/l of Mn, 0.24 μg/l of Co and 0.44 μg/l of Ni in water samples. The enrichment factors were 57.6, 57 and 65 for Mn, Co and Ni respectively which are quite good compared to liquid–liquid extraction preconcentration. The relative standard deviations for Co, Ni and Mn and 2.1, 2.6 and 2.8% indicate very good precision that can be obtainable by cloud point extraction compared to liquid–liquid extraction preconcentration. However, the developed procedures were applied to 1 sample each to tap, river and seawater and its wide applicability to different real samples has not been adequately tested.

2.1.2 PAN

PAN and PAN–capriquat loaded on naphthalene (Taher and Puri, 1995) and membrane filter (Mori et al., 1994) were used for preconcentrative separation of Fe from pH 5.0 solutions and subsequent determination by 3rd order derivative spectrophotometry. The former method is sufficiently selective to be applied directly to alloys and biological samples. The R.S.D. for latter procedure was 1.8% which is very good and recoveries of Fe from artificial waste water containing Fe(III), Cu(II), Al(III), Ca(II) [1:2:20:20] were satisfactory (95.4–106%).

PAN immobilized on surfactant coated alumina (Manjoor et al., 1999), silica gel (Ivanov et al., 1994) and membrane filter (Ohzeki et al., 1987) was used for preconcentrative separation of Co. The R.S.D.'s are 4 to 1.4% at 20–100 μg/ml, 1.8% (good precision) for 0.3 μg/ml for the first two procedures respectively. The detection limit and R.S.D. for the latter procedure was calculated to be 0.3 μg/10 ml of Co and 1.8% (quite good) respectively. This procedure has been successfully employed for determination of traces of cobalt(II) in white wines (2.5–4.4 μg/l) Differential pulse voltammetry using a carbon paste electrode constructed by incorporating PAN into a conventional carbon paste mixture composed of graphite powder and Nujol oil was developed for the determination of as low a 1.3×10^{-7} M of Co (Bae et al., 1996; Khan and Khoo, 1998). The calibration curve was linear over 2 ranges (1.7×10^{-6}–1.3×10^{-4} M and 2.0×10^{-7}–8.0×10^{-7} M) of Co and precision is not that good as it ranges from 2.8 to as high as 9.67%. Khan and Khoo (1998) have determined Co in human hair, pig liver and spinach samples. However, the recoveries were lower by 8% and authors have indicated the use of standard addition method for alleviating the matrix effect but has not been done in the present study.

Solid phase materials such as Amberlite XAD-2 (Ferreira et al., 1999) and naphthalene (Taher et al., 2000) loaded with PAN have been employed for the determination of 0.1–2.75 μg/l and 0.4–20 μg/ml of Ni using ICP-AES and AAS respectively. The R.S.D. values calculated for Amberlite XAD-2 SPE was found to be 3.9% (seven replicates of 0.20 $\mu g ml^{-1}$) which is quite good at the nickel concentration tested. The potential of the above developed procedures was seen from the analysis of saline matrices and standard alloys of biological samples for Ni. Polyurethane foam treated with tri-n-butyl phosphate solution containing PAN is used successfully for the quantitative retention and recovery of Ni and Bi from thiocyanate solutions by both batch and column extraction modes (Elnemma and Farag, 1994). The batch method with foam results in the determination of as low as 0.05 and 0.5 μg/ml of Ni and Bi (LOD's) respectively. A cloud point preconcentration procedure was developed for Ni and Zn using PAN as hydrophobic ligand and Triton X-114 as nonionic surfactant results in detection limits of 8 and 6 ng/ml (which are not achievable by other preconcentration techniques) of Zn and Ni respectively (Oliveros et al., 1998).

Pencil-core electrode modified with PAN was used for preconcentrative separation of 80 nM to 1.5 μM of Cu in human hair (Zhao and Wang, 1998) and determination by anodic stripping voltammetry. Amberlite XAD-4 impregnated with PAN was used for on-line flow injection preconcentration of Cu from sea water and subsequent determination by flow injection flame AAS (Yebra et al., 2001). The R.S.D., detection limits and enrichment factor of this procedure were found to be 1.2% for 2 μg/l, 0.06 μg/l and 30 respectively. The enrichment factor established by the authors is rather low compared to other solid phase extraction preconcentration FIA-AAS procedures which are generally to be ~ 100. On the other hand, the accuracy of the developed procedure was clearly brought out by analysing SLEW-3 and NASS-5 certified reference materials.

PAN modified naphthalene was used for preconcentrative separation of trace amounts of V (2–250 μg/5 ml) in standard Al-alloys, steels and environmental samples (Taher et al., 1999). The relative standard deviation and detection limits were 1.2% (very precise) and 0.1 μg/ml respectively.

2.1.3 1-Nitroso-2-naphthol

Zhang et al. (2000) have preconcentratively separated ultratrace amounts of Co in seawater after coprecipitative preconcentration with a combination Qunioline-8-ol and Ni as a carrier element and 1-nitroso-2-naphthol as an auxiliary complexing agent and subsequent determination by graphite furnace AAS using the solid sampling technique The enrichment factor by this coprecipitation reached about 33,000 (the highest reported so far for any preconcentration procedure) for 1 l of aqueous sample. The detection limit was calculated to be 1 ng/l of Co. Further, the accuracy of the developed preconcentration procedure was quite impressive as seen from the result obtained with NASS-4 (NRC sea water).

2.2 Toxic Heavy Metals

2.2.1 TAN

Traces of Zn in standard alloys, environmental and pharmaceutical samples were determined by derivative spectrophotometry after preconcentration of Zn–TAN complex on ammonium tetra phenyl borate (ATPB) supported on naphthalene via the formation Zn–TAN–TPB ion association complex (Bhalotra and Puri, 1999). The calibration graph was linear for 0.02–1.4 μg/ml of Zn and the detection limit was 9.5 μg/ml. The developed procedure was quite precise as the R.S.D. at 1 μg/ml Zn level was found to be 1.1%. The tolerance limits of various anions and cations were quite high as seen from the data compiled in this paper. 400 Times of salts and >15 times in case of most cations do not interfere. However, Cu(III), Fe(III), Co(II) and Ni(II) could be tolerated and higher levels by masking with sodium thiosulphate–thiourea, sodium fluoride or ascorbic acid and dimethyl glyoxime respectively. Separation by adsorption of Zn–TAN complex on Seppak C_{18} cartridges resulted in trace determination of Zn in copper base alloys (Teixeira et al., 1998). ICP-AES was used for monitoring zinc with detection limit of 16 μg/l. Though, high concentration of Copper could be tolerated by separation of zinc–TAN complex from Cu–TAN complex in presence of ascorbic acid and thiosulphate, the R.S.D. for 10 different aliquots was 5.7% and average recovery found for zinc was 96% which are not that impressive. Zn and Ni (Oliviera et al., 2000) were determined by flow injection spectrophotometry after adsorption of their TAN complexes on a C_{18} bonded silica from pH 6 solutions. This enables the determination of 43 samples/hour in the range 0.3–1.0 μg/ml with a R.S.D. value of 5% (which is quite high). Cu and Zn were preconcentratively separated from natural water samples based on the complexation by TAN and sorption onto Amberlite XAD-2 resin (Ferreira et al., 1998). The above preconcentration procedure resulted in an enrichment factor of ~ 80 (reasonably good) in the concentration range 0.10–100 μg/400 ml of sample solution.

2.2.2 PAN

Zn is determined in alloys and biological samples by AAS after batch and column preconcentrative separation of its PAN complex onto microcrystalline naphthalene in the pH range 3.5–7.5 (Taher, 2000a). The calibration curve is linear in the range 0.1–6.5 ng/ml in DMF solution with a R.S.D. of 1.5% which shows that the developed procedure enables very high precision. The separation and enrichment procedure for traces of Pb in alkali metal salt with Nickel–PAN as coprecipitant and subsequent AAS determination was developed (Su et al., 1998). The detection limit and R.S.D. values were calculated to be 15 μg/l and $< 4\%$ (poor precision). Dan et al. (1998) enriched Pb and Cd by adsorption of their PAN complexes onto activated carbon and subsequent determination by derivative polarography. Polythene powder impregnated with PAN was used for column separation and enrichment of Cd, Cu, Zn and Pb from high salt matrices for subsequent determination by ET-AAS (Bohrer et al., 1999). The recoveries of Cu, Cd, Pb and Zn in presence of salts and glucose were found to vary over a wide range 81–112%. So, the method finds application for the analysis of different saline concentrates meant for haemodialysis. The results obtained agree well with those obtained by anodic stripping voltammetry.

PAN immobilized on silica (Ponce et al., 1996) has been used to preconcentrate Pb(II) in aqueous samples for its determination using Energy Dispersive X-ray Fluorescence Spectrometry. Taher and Puri (1999a) determined Pb and Cd in standard alloys and biological samples after selective adsorption of their PAN complexes onto microcrystalline naphthalene. The calibration graphs obtained by subsequent Differential pulse polarographic determination are linear over the range 0.1–150 μg/ml for Cd and 0.1–300 μg/ml for Pb with detection limits of 0.07 and 0.1 μg/ml of Cd and Pb respectively. Cloud point methodology has been successfully used for the preconcentration of trace amounts of Cd as a prior step to its determination by flame AAS (Pinto et al., 1996). Cd–PAN complex is used for the enrichment of Cd in a surfactant rich phase of

Triton X-114 with enrichment factor of 120. Zolotov et al. (1995) have suggested a flow system including a microcolumn or a capillary tube for the determination of Cd, Co, Cu and Fe(III) by FIA-spectrophotometry in the range 8×10^{-8}–3×10^{-5} M. The preconcentration factors are upto 9 for the microcolumns and upto 19 for the capillary tubes which are quite low. On the other hand, the throughput of the samples is quite good (30–60 per hour). The accuracy of the procedure was also good as seen from the analysis of the certified reference samples of standard soil extract and swamp water containing all the metals. A chemically modified chloromethylated polystyrene–PAN was synthesized and used for preconcentration and separation of total Hg (Hafez et al., 2001). The metal complex formed between ion exchanger and mercury was characterized by IR spectroscopy, pH metric titration and thermal analysis. In conjunction with the above preconcentration procedure cold vapour AAS determination allows ng/ml of Hg present in natural waters, milk and urine. The R.S.D. was found to be in the range of 0.6–6.0% indicating that the developed method is quite precise and does not subject to random error. The detection limits are very impressive as 2 pg/ml of Hg(II) could be determined by the developed method.

A chemically modified electrode (CME) containing PAN is evaluated for its suitability to preconcentrate Bi(III) prior to its quantification by voltammetry (Dong et al., 1991). The CME approach is shown to be sufficiently sensitive for sub-nanomolar concentrations to be determinable after chemical deposition for 60 s and sensitivity is significantly better than conventional stripping analysis. The results obtained for Bi(III) in an NBS reference solution agrees well with the recommended value. Taher and Puri (1999b) have developed batch and column preconcentration methods for Bi(III) based on its PAN complex prior to its determination by differential pulse polarography (DPP). The above preconcentration methods enable the determination of Bi(III) concentrations down to 20ng/ml in industrial alloys and environmental samples and can be used as an alternative to ICP-AES/ICP-MS.

As low as 0.2 μg/ml of In was determined by DPP after column preconcentration with PAN–naphthalene adsorbent or its complex on microcrystalline naphthalene (Taher, 2000b). Linear calibration graph was obtained in the concentration range 0.8–125 μg/ml with a detection limit of 0.2 μg/ml. The precision was quite impressive as the relative standard deviation was ±0.96%. The method was successfully tested for the determination traces of indium in a number of standard alloys and biological reference materials. A chelatic sorbent obtained by adsorption of PAN on Amberlite XAD-2 (Bermejobarrera et al., 2001) was used for preconcentration of Ga and In. A peristaltic pump was used to adjust the flow rate of sample solution and optimum sorption conditions for these metals were established under dynamic conditions. PAN and 1-nitroso-2-naphthol in aqueous 1.25 mg/ml of Na_2CO_3 were equilibrated with 1 g portions of polymer resin (XAD-4, XAD-7 or Dowex) for 3 h and washed with water (Malcick et al., 1998). The resulting optodes were mounted in a flow cell, solution of heavy metal ions [Zn(II), Cd(II), Pb(II), Hg(II), Fe(II), Cu(II), Co(II)] of pH 4–9 were passed through the flow cell and the reflectances were measured. Calibration graphs were linear and the detection limits were in the range 0.1–1.0 μg/ml. The response times were 1–5 min and the optodes were regenerated with 0.1 M HCl in 1–15 min.

2.3 Lanthanides and Actinides

2.3.1 TAN

Sc has been preconcentrated from a large volume of its aqueous solution after solid phase extraction of its TAN chelate onto ammonium tetraphenylborate–naphthalene adsorbent in the pH range 4.0–5.8 (Bhalotra and Puri, 2000). The solid mass consisting of metal complex along with the adsorbent was dissolved in 5 ml of DMF and quantified by second derivative spectrophotometry. The calibration graph is linear in the concentration range 0.08–2.8 μg/ml and has been used for the analysis of standard biological and synthetic samples.

2.3.2 PAN

A method has been described for the simultaneous multielement determination of Y and lanthanides at μg level based on the preconcentration onto PAN modified naphthalene (Bhagavathy et al., 1991). The quantitation of rare earths in Xenotime samples was carried out in an Energy dispersive X-ray fluorescence analyser, employing ^{241}Am annular source via their characteristic-X-rays. A liquid solid extraction procedure for Pr, Nd, Sm and Y mixtures and subsequent determination by EDXRF is described (Cornejoponce et al., 1998). The preconcentration procedure which involves the use of silica modified with PAN, permits complete recovery of rare earths and significant sensitivity enhancement in comparison with direct determination in the aqueous phase. The detection limits lie in the range 0.06–0.6 μg/ml with R.S.D.'s lower than 5% were obtained which are comparable to the results reported in the previous works.

The preconcentration of U(VI) was carried out using modified and unmodified Amberlite XAD-4 sorbent packed into columns and subsequent quantitation by spectrophotometry (Vacha and Sommer, 1993). The use of micellar enhanced ultrafiltration for the preconcentrative separation in presence of PAN and removal of UO_2^{2+} ion from aqueous acid solutions was investigated (Pramuro et al., 1996a). Cloud point extraction has been used for the preconcentration of U prior to its determination by flow injection spectrophotometry in tap and river waters from Salamanca (Laespada et al., 1993). The limit of detection was 1.1 μg/l and the R.S.D. were quite impressive as it is 5.1% in view of the low uranyl concentrations involved ($\sim 1.5 \times 10^{-7}$ mol/l). The non-ionic surfactant employed was Triton X-114 and the reagent chosen to form hydrophobic chelate of U was PAN. A similar micellar enhanced ultrafiltration with complexing micellar aggregates composed of Triton X-100 and PAN as hydrophobic ligand resulted in selective separation UO_2^{2+} ion from acid samples containing Sr(II) and Cd(II) (Pramauro et al., 1996b).

2.4 Noble Metals

2.4.1 TAN

Silica gel modified with TAN was used to enrich as low as 3 ng/ml of Pd (Ivanov et al., 1991). The method was applied for the determination of Pd in catalysts. A new chelating silica for high pressure liquid stationary phase was prepared by immobilizing 2-(2-thiazoyl-azo)5-aminoanisole on 3-chloropropyl silyl silica (Sutthivaiyakit et al., 1998). This stationary phase, whose capacity is about 50 μM/g, possess selectivity for Pd(II), Pt(IV) and Au(III).

2.4.2 PAN

Pd was determined in nonferrous metallurgical materials by passing through a glass column packed with PTFE inpregnated PAN (Basova et al., 1996). The Pd–PAN complex was eluted with $CHCl_3$:isopentyl alcohol (2:1) and determined by spectrophotometry. A solid chelating material, PAN supported on naphthalene provides a rapid and highly selective means of preconcentrating Pd from large aqueous volume of its synthetic samples (Taher et al., 1998). The solid mass consisting of the adsorbent along with the metal complex is dissolved out of the column with 5 ml of DMF and Pd was determined by first derivative spectrophotometry. The calibration curve is linear over the concentration range 0.3–200 μg of Pd present in 5 ml of DMF with a detection limit of 0.04 μg/ml. The analytical data reported shown that the developed procedure can be used as an alternate to sophisticated ICP-AES/ICP-MS. Taher and Puri (1999c) described a highly selective, sensitive, rapid and economical method using spectrophotometry for the determination of trace amounts of Rh in various synthetic samples after adsorption of its PAN complex onto microcrystalline naphthalene. The calibration curve is linear over the concentration range 0.1–25 μg/ml with a detection limit of 30 ng/ml which is quite good for this element. Silica gel bonded by aminopropyl-benzoylazo-1-(2-pyridylazo)2-naphthol (ABPN.SG) is stable in solutions between 6 M HCl and pH 9.0 (Liu et al., 1995). After separation and preconcentration using an ABPN.SG column, ng/ml of Pd(II) and Pt(IV) in artificial water samples can be measured by spectrophotometry. Pt(II) and Ru(III) were determined by interfacial deposition as their complexes with PAN onto a hanging mercury drop electrode and subsequent measurement by differential pulse cathodic stripping voltammetry (Elshawi et al., 1994). Calibration graphs were linear from 0.32–64 nM of Pt(II) and from 0.41 to 51 nM of Ru(III) with RSD of 2.4% and 1.6% respectively. Complexes of Pd(II), Pt(II) and Rh(III) with PAN are separated by HPLC on a steel column (Bolshova et al., 1987). Basova et al. (1986) separated after extraction of Pt group–PAN complexes into $CHCl_3$ by thin layer chromatography on silufol R plates. Pd, Rh and Pt complexes with PAN were formed by heating and the complexed metals were concentrated by extraction into $CHCl_3$ (Basova et al., 1986). The above metals were simultaneously separated and determined in the extract on a Silasorb-600 column with detection limits of 120 (Pd), 50 (Rh) and 140 (Pt) ng/μl.

2.5 Miscellaneous

2.5.1 TAN

Trace metal ions in Antarctic sea water (Ross Bay) has been determined by ICP-AES after adsorption of their TAN complexes used in conjunction with Amberlite XAD-2 (Mentasti et al., 1991). Coprecipitative preconcentration of trace metals present in sea water, drinking water and biological materials was carried out as their TAN complexes and subsequent quantitation by Neutron activation analysis (Rao and Chatt, 1993). The detection limits are in the ng/ml range.

2.5.2 1-Nitroso-2-naphthol

Pd is quantitatively retained by disodium-1-nitroso-2-naphthol-3,6-disulphonate and tetradecyldimethylbenzylammonium chloride supported on microcrystallne naphthalene in the pH range 2.0–6.5 from a large volume of aqueous solutions of various samples (Taher, 2000c). The detection limit is 0.3 μg/ml and the calibration curves is linear from 0.4–3.7 μg/ml in

DMF solution. Eight replicated determinations of 30 μg of Pd in 5 ml of DMF solution gave an RSD value of ± 1.3% which indicate that the developed procedure is quite precise.

3. CONCLUSIONS

Naphthols particularly PAN and to some extent TAN are versatile organic reagents and reacts with several inorganics as they have basic nitrogen or sulphur and a phenolic OH group. Consequently naphthols have been widely used for preconcentrative separation of inorganics prior to their quantitation by molecular, atomic, X-ray and radiochemical methods. Barring a few, most of the procedures involve 1) preconcentrative separation of 1 or 2 elements and 2) quantitation by singular analytical techniques. Multielement preconcentrative separation from complex metallurgical, geological and biological materials and multielement determination by XRF, NAA, ICP-AES and ICP-MS are rare and future lies in the development of such preconcentrative separation and determination methodologies. Further, increased use of validation of the developed methods will be adopted by analysing certified reference materials and comparing with certified values.

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