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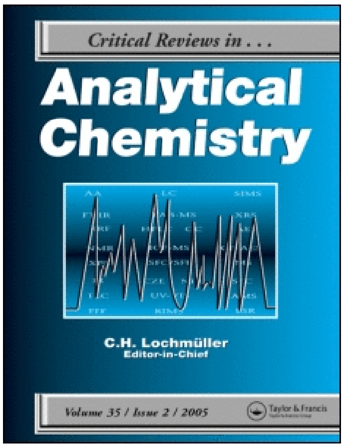

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Styrene-Divinyl Benzene Copolymers: Synthesis, Characterization, and Their Role in Inorganic Trace Analysis

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Styrene–Divinyl Benzene Copolymers: Synthesis, Characterization, and Their Role in Inorganic Trace Analysis

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Styrene–divinyl benzene copolymers are widely used in inorganic trace analysis for solid-phase extraction preconcentration as well as other fields of application. These include nascent, ionic, and chelate incorporated polymeric materials. Furthermore, the chelate incorporation usually is achieved by surface sorption or by grafting via chemical immobilization and in situ polymerization. This review covers various synthetic approaches adopted by various researchers since 1990. Again, the chemical and morphological characterizations of styrene–divinyl benzene copolymers are also discussed. Finally, a critical account of these polymers in trace analysis of various mono- and multielement analysis of inorganics is brought out in a nutshell.

Keywords inorganics, preconcentration, solid phase extraction, styrene-divinyl benzene copolymers

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The basic principle of solid-phase extraction (SPE) is the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase (1, 2). This transfer is stimulated by the selection of appropriate operational conditions in the system of three major components: water (liquid phase)–sorbent–analyte. The solid phase is then isolated from the sample, and the analytes are recovered by elution using a liquid or fluid and determined using suitable analytical technique (3–5). Thus, SPE method consists of three to four successive steps as shown in Figure 1. The mechanism involved in SPE depends on the nature of the sorbent and analyte. Thus, SPE is carried out by means of adsorption, ion exchange, chelation, ion pair formation, and so forth. The essential requirements of sorbents in SPE are (1) the possibility to extract selectively a large number of analytes over a wide pH range, (2) quantitative sorption and elution, (3) kinetically faster sorption and desorption mechanisms, (4) regenerability, (5) high retention capacity, (6) accessibility, and (7) mechanical and chemical stability. The sorbents employed can be broadly classified into inorganic based (inorganic oxides) and organic based (natural and synthetic polymer) sorbents (see Figure 2). The most important inorganic-based sorbents are silica gel, C_{18} bonded silica gel, modified silicas, alumina, florisil, diatomaceous earth, and other inorganic oxides. On the other hand, the popular organic-based sorbents are divided into polymeric and nonpolymeric sorbents. Even though a broad variety of functionalized SPE are available, the selective preconcentrative extraction of a particular analyte is still a challenging problem. Immunosorbents and ion-imprinted polymers (IIPs) are new types of SPEs that are almost specific for a particular analyte.

New polymeric sorbents have been synthesized either by direct polycondensation or polymerization of monomers containing chelating groups (6, 7), or by chemically bonding chelating groups to polymeric cross-linked chains (preformed polymers). The most widely used polymeric sorbents are styrene–divinyl benzene (DVB) copolymers that have a hydrophobic surface (3, 4). Thus macroporous hydrophobic resins of the Amberlite XAD series are good supports for developing chelate matrices with no ion exchange capacity. Due to the hydrophobic character of styrene–DVB polymers, the addition of a chelating ligand to the sample or functionalization by chemical immobilization/surface adsorption is essential in order to retain the inorganic analytes on such materials. Chemical modification of styrene–DVB copolymers were reviewed in the year 2000 (7). However, that review does not include surface adsorption

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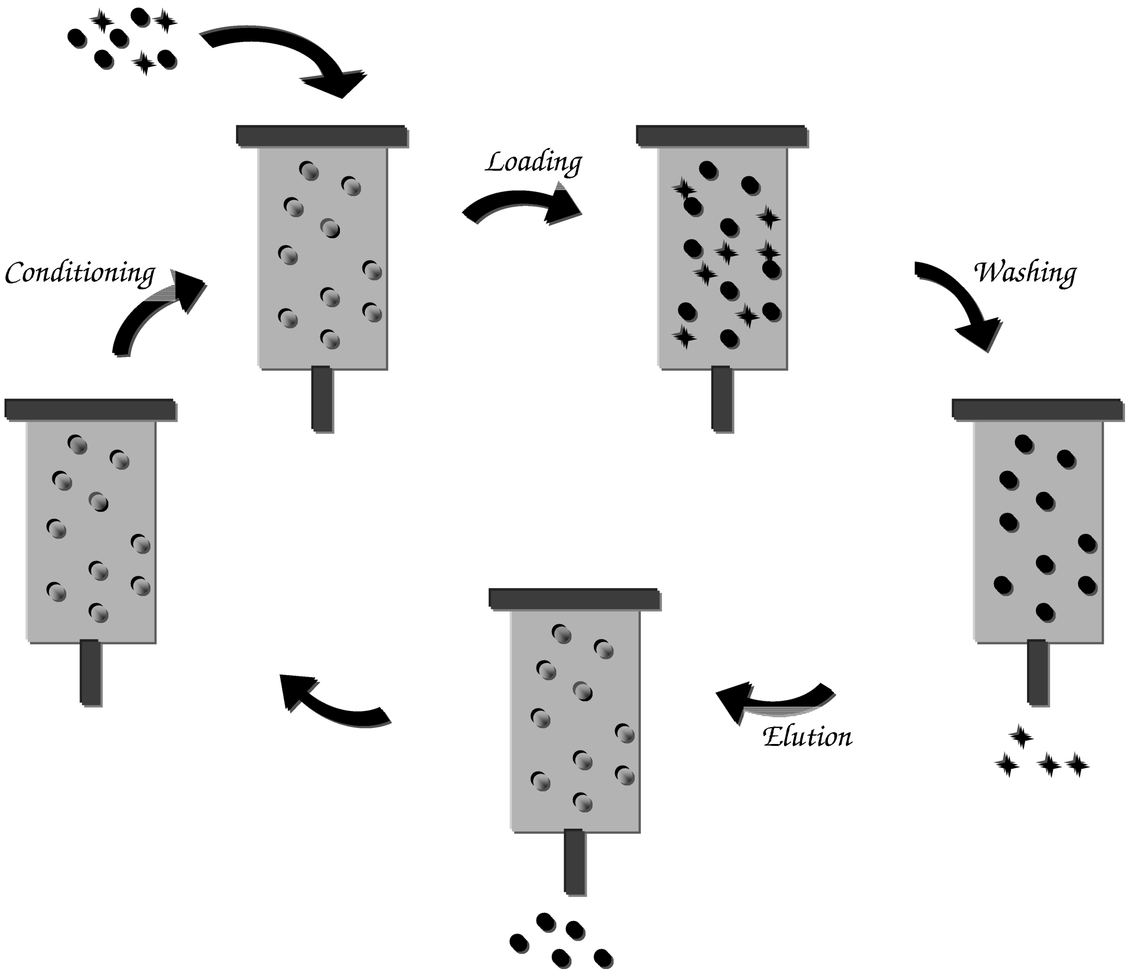

FIG. 1. Mechanism of solid-phase extraction.

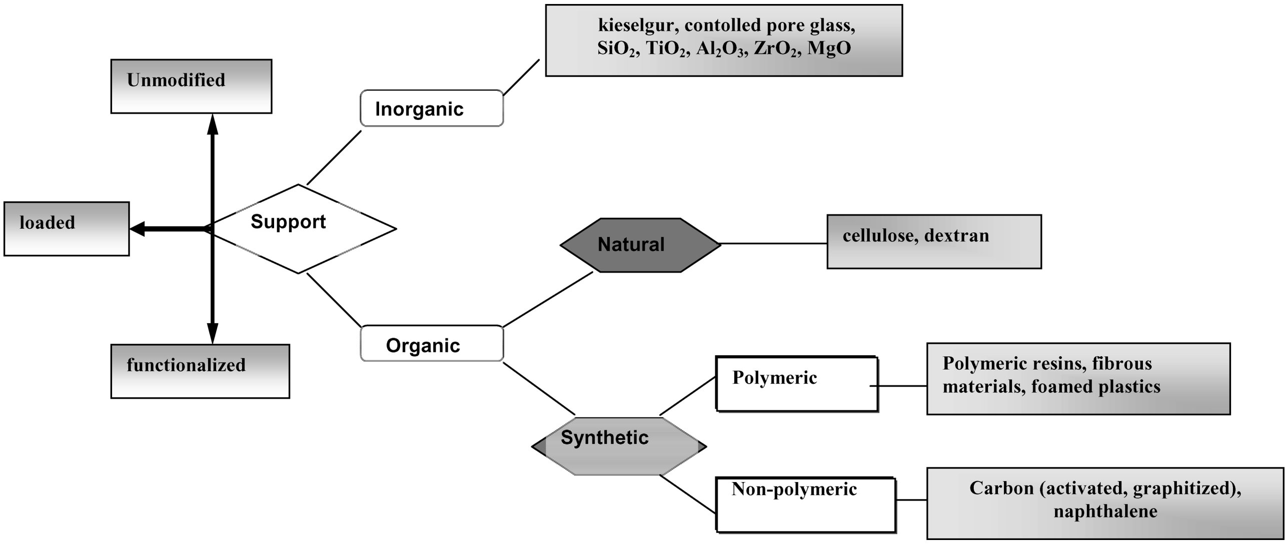

FIG. 2. Sorbents used in solid-phase extraction.

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and in situ polymerization. Hence, the scope of the present review is synthesis, characterization, and analytical applications of styrene–DVB-based polymeric sorbents used for trace enrichment of inorganic ions.

PRECONCENTRATION USING NASCENT-, CATIONIC-, AND CHELATE-INCORPORATED STYRENE–DIVINYL BENZENE COPOLYMERS

Nascent Polymeric Resins

Nascent styrene–DVB resins such as Amberlite XAD-1180 (8–10), XAD-4 (11), and XAD-16 (12–15) were used directly for enrichment of inorganics as their halide or thiocyanate complex.

Ion Exchange Resins

Various cationic styrene–DVB resins such as Amberlite IR-120 (16–18), IRA-400 (18), and IRA-410 (19) were used for enrichment of Sr, Co, Cr(VI), and Cr(III), and Se(IV) by ion exchange phenomenon.

Surface-Sorbed Chelating Resins

Amberlite XAD-2 resin modified by surface adsorption with oxime (20, 21) 1-(2-thiazolylazo)-2-naphthol (20, 24), pyrocatechol violet (20), 4-(2-pyridylazo) resorcinol (21), eriochrome blue black R (21), ammonium pyrollidine dithiocarbamate (APDC) (22), tropolone (23), 1-(2-pyridylazo)-2-naphthol (PAN) (25), 2-(2-thiazolylazo) *p*-cresol (26), calmagite (27, 28), and 2-(5-bromo-2-pyridylazo)-5-diethyl amino phenol (29) were used as solid phase extractant sorbents in off-line or online column preconcentration modes.

Surface adsorption of Amberlite XAD-4 resin beads with oxine (30–33), APDC (30, 31), 2[[2-(5-chloropyridyl)azo]-5-dimethyl amino phenol (5-ClDMPAP) (32, 33) butane–2,3-dione bis(N-pyridinoacetyl hydrazone) (34), 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol (5-Br PADAP) (35–37), 5-phenyl azo-8-quinolinol (38), 1-nitroso-2-napthol (39), and sodium diethyl dithiocarbamate (NaDDTC) (40) were used as solid-phase extractants for the trace determination of inorganics using a variety of detection techniques which include spectral and X-ray techniques.

Traces of inorganics were enriched on Amberlite XAD-16 resin beads after surface adsorption with a variety of chelates, namely, PAN (41), NaDDTC (42, 45), 4-(2-thiazoylazo) resorcinol (43, 44), N,N′-dibutyl-N′-benzoyl thiourea (DBBT) (46), and di-(2-ethyl hexyl phosphoric acid (D2EHPA) (47).

Grafted Chelating Resins

Grafting by Chemical Immobilization

Amberlite XAD-2. Singh et al. chemically immobilized Amberlite XAD-2 with Alizarin Red S (48), Tiron (49), catechol (56), thiosalicylic acid (51), *o*-aminophenol (52), chromotropic acid (53), catechol violet (54), salicylic acid (55), and pyrogallol (56) via four-step synthesis. Nitrated Amberlite XAD-2 was obtained by stirring the resin with the nitrating mixture. The nitrated resin was filtered, repeatedly washed with water until free from acid, mixed with $SnCl_2$, concentrated HCl, and ethanol and refluxed for 10 h at 90°C. The amino polymer was filtered off and washed with water and 2 M NaOH which released the free aminopolymer. The aminopolymer was treated with HCl, washed with water to remove excess HCl, and suspended in ice water and mixed with HCl-$NaNO_2$ solution until the reaction mixture began to give a permanent blue colour with starch-iodide paper. The diazotized polymer was filtered, washed with cold water, and reacted with chelating ligands mentioned above after dissolving chelate in diluted acetic acid at 0°–3°C for 24 h. The synthesis of chelate-grafted Amberlite XAD-2 is shown schematically in Scheme 1.

A similar synthetic scheme was employed by Jain et al. (57, 58) to chemically immobilize *o*-vanilline thiosemicarbazone on to Amberlite XAD-2 resin. Dogutan et al. (59) synthesized palmitoyol-8-hydroxyquinoline functionalized Amberlite XAD-2 by a modified procedure described by Suebert et al. (60) via Scheme 2.

Amberlite XAD-2 was first chloromethylated and then stirred with 5-palmitoyl oxine chloride and heated at 70°C for 72 h. At the end of this period, nitrobenzene was removed by filtration and the product was washed twice with 1:1 HCl, $CHCl_3$, alcohol, and ether. The resultant product was heated in ethanol for 2 h, filtered, and dried in vacuum to yield palmitoyl hydroxyquinoline immobilized Amberlite XAD-2. In 1992, Trojanowicz group (61) chemically immobilized Eriochrome blue black R onto Amberlite XAD-2. Yuan and Shuttler (62) immobilized quinoline-8-ol onto Amberlite XAD-2 and controlled poreglass, and reported higher enrichment factors with the former as it gave higher flow rates during quantitation of aluminum by FIA-ETAAS.

Amberlite XAD-4. Scheme 1 was used for synthesis of *o*-aminobenzoic acid grafted Amberlite XAD-4 resin by Cekic et al. (63). Amberlite XAD-4 was functionalized with N-hydroxy ethyl ethylene diamine by Hirata et al. (64) as per the synthesis procedure described by Dev and Rao (65). The resin was first acylated and treated with alkaline permanganate for 1 h. The carboxylic acid resin thus formed was refluxed with thionyl chloride at 60°C for 0.5 h. The intermediate resin was refluxed with N-hydroxy ethyl ethylene diamine and sodium ethoxide in toluene at 100°C for 8 h to obtain the desired chelating resin (see Scheme 3).

Scheme 4 shows the grafting of acid chloride onto Amberlite XAD-4 (66). Subsequently acid chloride resin was grafted with salicylic acid as per Scheme 5.

Yakin and Apak (67) immobilized maleic acid by electrophilic substitution of the Amberlite XAD-4 resin with maleic anhydride by a Friedel-Crafts reaction (see Scheme 6). Dev et al. (68, 69) synthesized bicine functionalized Amberlite XAD-4 according to Scheme 7.

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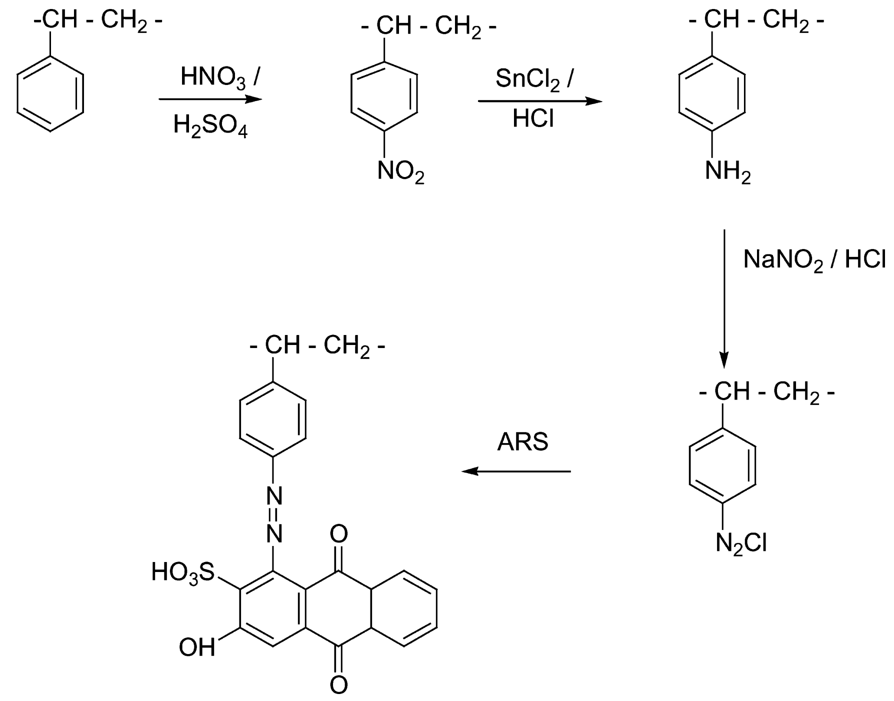

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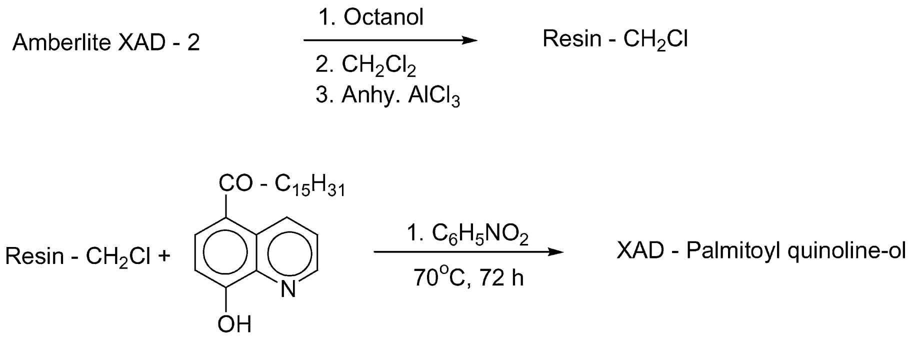

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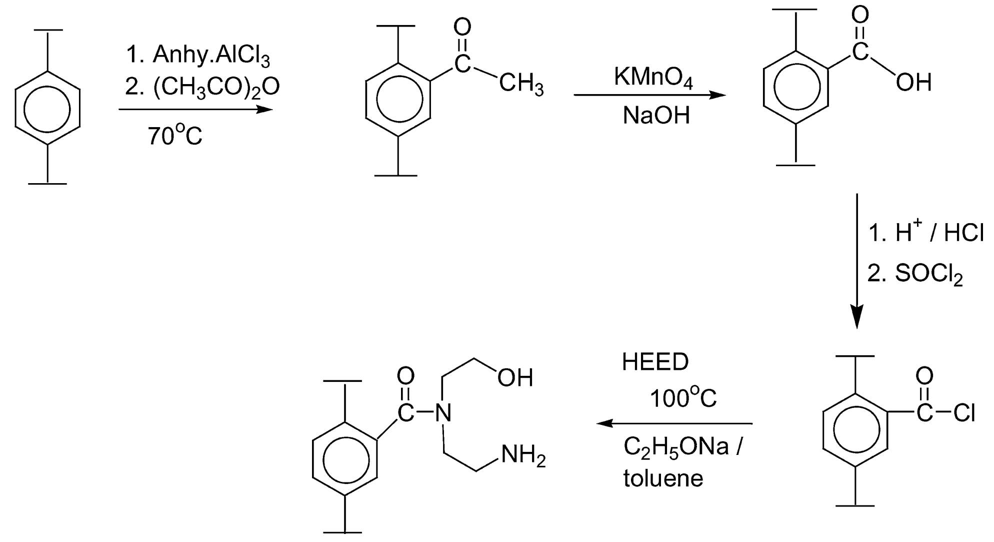

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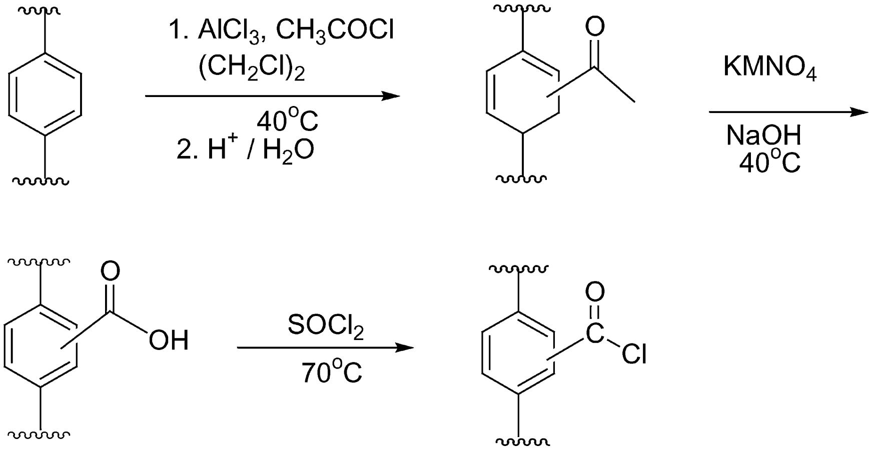

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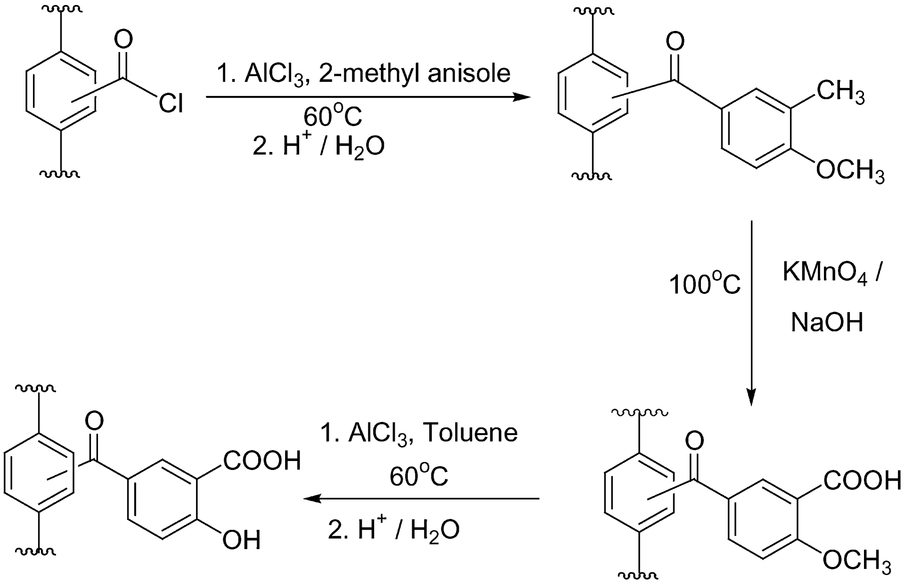

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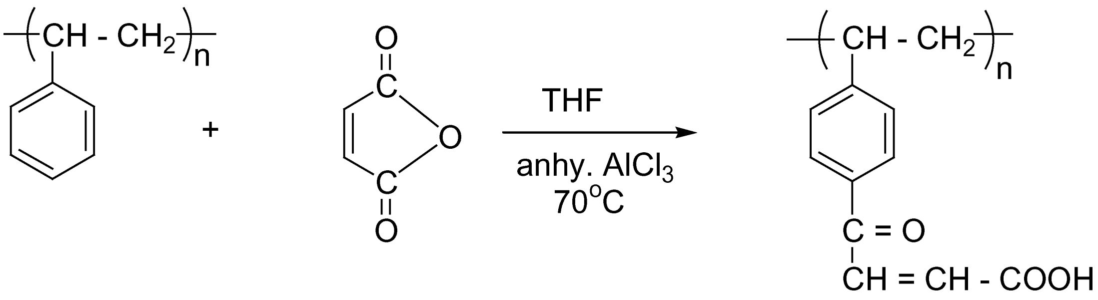

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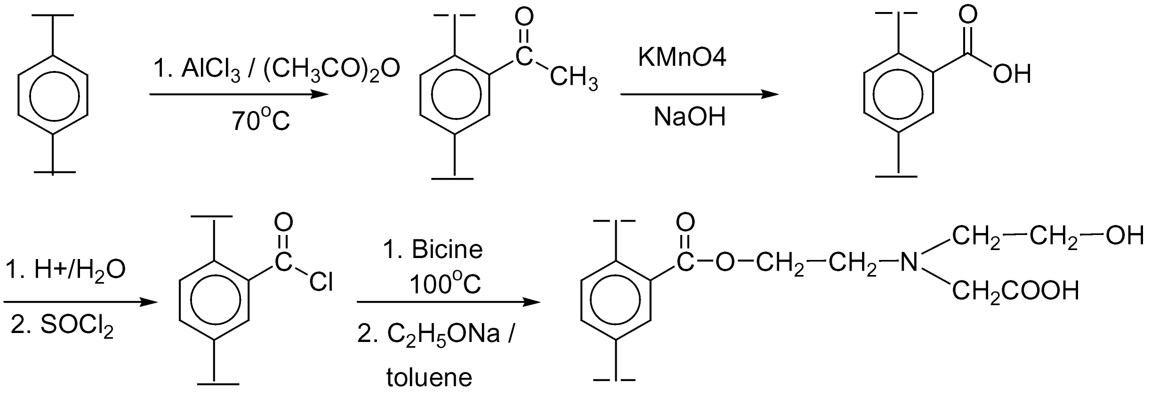
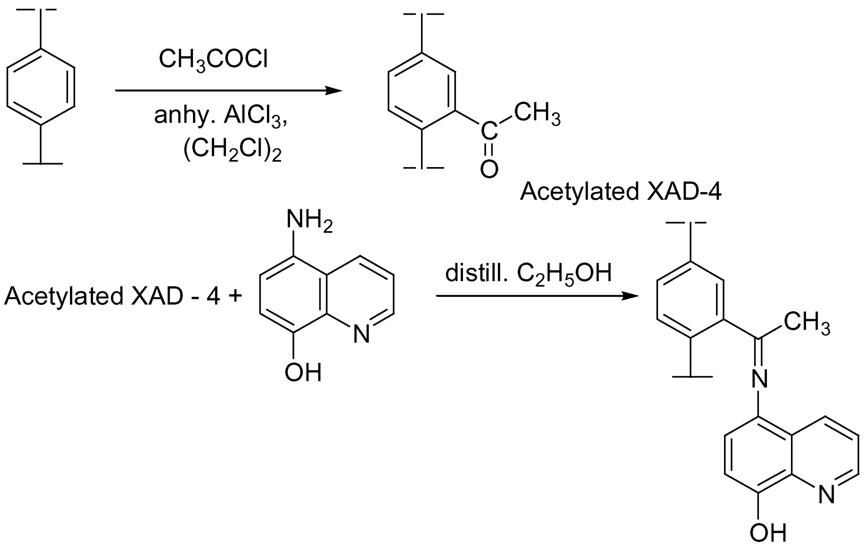


SCHEME 7.



SCHEME 8.

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Quinoline-8-ol functionalized Amberlite XAD-4 resin was synthesized by Gladis and Rao (70) by a two step reaction. This involved the preparation of acetylated XAD-4 resin, and then subsequently coupling it with 5-aminoquinoline-8-ol (refer to Scheme 8). Jain et al. (71) employed a synthetic scheme similar to Scheme 1 for functionalizing Amberlite XAD-4 with *o*-vanilline-semicarbazone.

Amberlite IRA-400/IRA-410. Two novel chelating ion exchange resins were synthesized by functionalizing chromotrope 2R (72,73) and arsenazo III (74) on Amberlite IRA-400 and Amberlite IRA-410 resins, respectively.

Merrifield Chloromethylated Resin. The Merrifield chloromethylated resin was functionalized with thenoyl trifluoro acetone under anhydrous conditions using sodium hydride in dry tetrahydrofuran and refluxing at 60°C for 12 h. The resin matrix was washed with excess of THF, filtered, and washed with water to bring down to the neutral pH.

Styrene–DVB Resins. Macroreticular chelating resins containing amidoxime groups were prepared from styrene–(divinyl-type compound) copolymer beads (76). DVB and ethylene dimethacrylate were used as divinyl monomers. The chelating resins with various porous structures were prepared by changing the monomer ratio of each monomer in feed and the amount of diluent. A new chelating resin has been synthesized by introducing N-benzoyl phenyl hydroxylamine group into styrene–DVB copolymer beads (77). The resin is stable in fairly strong acids, but not in alkali.

Grafting by In Situ Polymerization

Dysprosium(III) ion-imprinted polymer particles were prepared by grafting of dysprosium(III)-5,7-dichloroquinoline-8-ol-4-vinyl pyridine complex in polymer matrix by copolymerization of styrene (monomer), divinyl benzene (cross-linker) in presence of 2,2′-azobisisobutyronitrile (AIBN) as initiator (78, 79). The synthesis was carried out via thermal polymerization at ~60°C using 2-methoxy ethanol as porogen. Subsequent leaching with mineral acid resulted in leached IIP particles which now selectively bind dysprosium(III) ion in presence of closely related lanthanides. Gopikrishna et al. (80) synthesized neodymium(III) IIP particles under similar experimental conditions mentioned for dysprosium IIP particles. Lemaire et al. (81) synthesized a series of gadolinium triacrylate-divinyl benzene styrene copolymers varying from 14/24/62 to 15/85/0 by keeping gadolinium cation to diluent ratio constant and modifying the proportion of the cross-linking agent. The blank or control polymers do not fix any cation independent of the DVB/(DVB + styrene) ratio and the number of washing steps.

Gladis and Rao (82) patented a process for synthesizing uranyl ion-imprinted polymer particles by grafting uranyl ion-quinoline-8-ol and its derivatives (dichloro-, dibromo-, and diiodoquinoline-8-ol)-4-vinyl pyridine ternary complex in copolymer of styrene and divinyl benzene with methanol as porogen. Uranyl IIP particles thus obtained selectively enrich uranium(VI) from dilute aqueous and seawater solutions in presence of thorium, lanthanum, europium, and various transition metals. A general schematic diagram depicting the synthesis of IIP particles is shown in Figure 3. Gladis and Rao (83) developed a preconcentration procedure using uranyl IIP particles in conjunction with simple instrument UV-visible spectrophotometer. The accuracy of this method was tested by analyzing marine sediment reference material. The influence of porogen was systematically studied and it was found that medium polar porogens like 2-methoxy ethanol offer higher retention capacities for uranyl ion and higher $S_{U/Th}$ values (84). Metilda et al. (85) embedded/grafted binary uranyl-5,7-dichloroquinoline-8-ol (DCQ) or 4-vinylpyridine (VP) and ternary uranyl-DCQ-VP complexes in a styrene–DVB copolymer matrix in the presence of 2-methoxy ethanol and AIBN as porogen and initiator, respectively. These studies showed that uranyl IIP particles obtained with ternary complex alone gave quantitative enrichment of traces of uranium from dilute aqueous solutions.

Uranyl ion-vinyl benzoate binary ion imprinting complex was grafted by in situ polymerization using styrene as the matrix monomer and DVB as the cross-linking monomer (86). The synthesis was carried out in a screw-cap vial using pyridine as porogen and AIBN as initiator, and sonicated in an ultrasonic bath for about 4 h after N_2 purging and keeping it in an oven at 60°C overnight to complete polymerization. The polymerized product was removed from the vial and placed in a fume hood to allow the bulk of the porogen to evaporate. The dry pellet of polymer thus obtained was ground into fine powder and washed with 1 M HNO_3 and deionized water to obtain leached uranyl ion-imprinted polymer particles. Subsequently, Murray et al. (87) prepared membranes using uranyl-vinyl benzoate as ion-imprinting complex, and styrene and DVB as matrix and cross-linking monomers. Membrane synthesis was carried out in a screw-cap vial by dissolving uranyl-vinyl benzoate in 2-methoxy ethanol in presence of nitrophenyl octyl ether as plasticizer and polyester prepared from diglycollic acid and 1,6-hexane diol. AIBN was added to the above solution and placed in a sonicator at 60°C until it became viscous. The resulting viscous solution was poured into a Teflon mold, kept in a sealed container, and placed in an oven at 60°C for 18 h to complete the polymerization. The membranes thus formed had a thickness of 100 microns. The uranyl ion template and

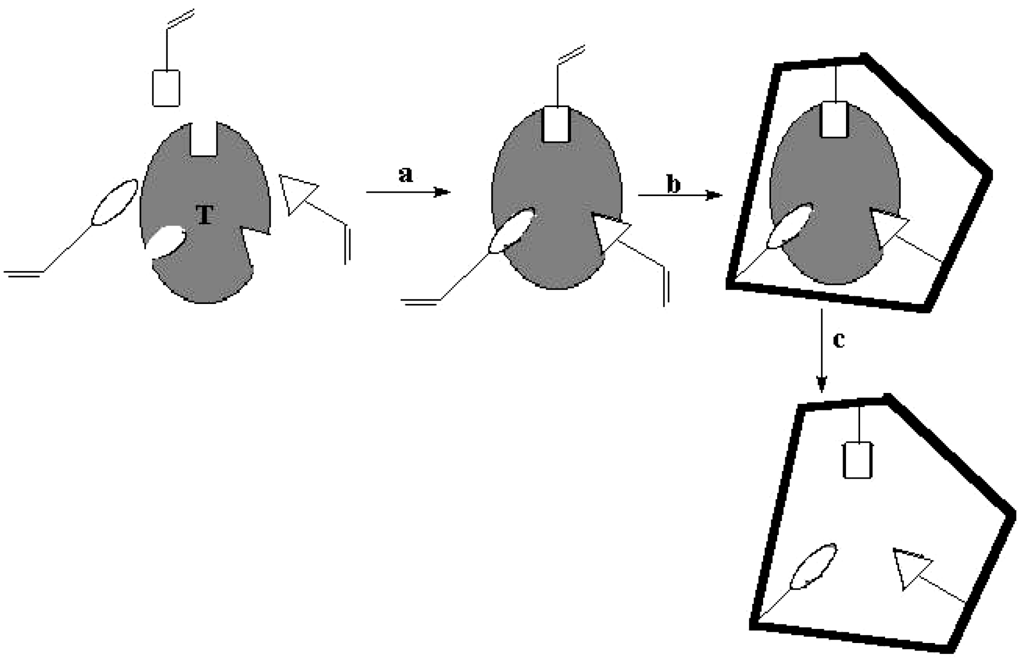

FIG. 3. Schematic representation of the imprinting process: T, template; a, complexation; b, polymerization; c, leaching.

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the polyester were removed using 0.1 M acetic acid solution followed by 5% HNO_3 and deionized water. This membrane allows specific separation of uranyl ion from nickel, zinc, and copper ions.

Ion-imprinted polymer materials with nanopores were prepared by grafting palladium-dimethyl glyoxime-4-vinylpyridine ternary complex in styrene–DVB copolymer using cyclohexanol and AIBN as porogen and initiator, respectively (88). The effect of the role of porogen during synthesis and postirradiation of palladium IIP particles on percent enrichment of palladium was also investigated.

CHARACTERIZATION OF STYRENE–DVB COPOLYMERS

Macroscopic network polymers are notoriously difficult to characterize, largely on account of their insoluble and intractable nature (89). First, it should be established that the polymerization has proceeded to the full conversion of the monomers and, ideally, the regularity and structure of the primary chains should be studied. It is also important to determine the accessibility and microenvironment of the functional groups and binding sites (90). Thus, one can distinguish between two levels of characterization, namely, (1) chemical and (2) morphological characterization. A brief consideration of chemical and morphological aspects will be briefly discussed by listing a few principle techniques available at the disposal of the analyst and the information that can be extracted.

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Chemical Characterization

In view of the insoluble and intractable nature of the styrene–DVB copolymers, they are not amenable to the characterization methods involving solution state, for example, solution-state nuclear magnetic resonance (NMR). Conventional methods that can be used with solid samples to good effect include those mentioned below.

Elemental Microanalysis

Elemental microanalysis can be used in a routine manner to measure the percentage by mass of carbon, hydrogen, nitrogen, chlorine, and so forth in samples. When this technique is applied to the analysis of styrene–DVB copolymers, the chemical composition information obtained often can be used to calculate the comonomer composition of the polymer. An exact match between the theoretical composition, calculated assuming a quantitative yield of polymerization and the analytical results, indicates that the polymerization has incorporated all monomers stoichiometrically in high yield (91). Reactions with the polymer, for instance, addition of a functional group, can easily be detected when the added species contain an element such as nitrogen, halogen, sulfur, or phosphorus. Elemental microanalysis has been used by several authors (48–58, 66, 70) to characterize styrene–DVB copolymers.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of insoluble polymers can easily be obtained from KBr pellets of the polymer (92). By first comparing bands of the monomers to those of the polymer, the extent of incorporation of monomers can be established. The method is of particular value when the different chemical environments of the sample (e.g., those arising from the incorporation of a functional group or metal-ligand complex along with the monomer and cross-linker) give rise to well-resolved and diagnostic signals. Several authors have utilized the FTIR technique for evaluation of styrene–DVB copolymers (48–58, 66).

X-ray Diffraction (XRD)

The X-ray diffraction pattern gives an overall idea regarding the nature of the polymers, namely, amorphous or crystalline. Also from the 2θ values in the XRD patterns, one can distinguish the nature of metal-ligand complexes in the polymer backbone. Thus, the presence or absence of characteristic peaks in the XRD patterns of polymers indicates the presence or absence of metal ions in the ion-imprinted polymer network (See Figure 4) (88).

Energy Dispersive Spectrometric Analysis (EDS)

The energy dispersive spectrum of various materials including imprinted polymers gives the elemental composition (At% and Wt%) of different constituents present in the bulk matrix. Again, analysis of the compositions in different regions of the same sample gives an idea regarding homogenous or heterogeneous distribution of the metal-ligand complex in ion imprinted polymer (IIP) materials. Figure 5 shows the EDS spectra of unleached and leached uranyl IIP particles from which it is clear that (1) the uranyl ion present in the unleached sample is absent in the leached polymer and (2) the chlorine peak arising from incorporation of 5,7-dichloroquinoline-8-ol in the styrene–DVB copolymer is intact even after leaching with mineral acid (84).

Thermal Analysis

When a polymer undergoes a physical or chemical change, a corresponding change in enthalpy is observed. Measurement of associated heat released or taken up by the polymers and the change in mass form the basis of differential scanning colorimetry (DSC) and thermogravimetric analysis (TGA), respectively (93). Figure 6 shows TGA patterns of unleached and leached dysprosium IIP particles which indicate rigidity of leached IIP particles over unleached particles as the former show decomposition at 300°C while the latter start decomposing even at 150°C. This observation is possibly due to the decomposition of the dysprosium-DCQ complex which is present only in case of unleached IIP particles (78).

Solid-State NMR

Solid-state NMR techniques circumvent the need to work in solution and therefore enable the NMR spectra of insoluble materials to be acquired. For network polymers, insight into

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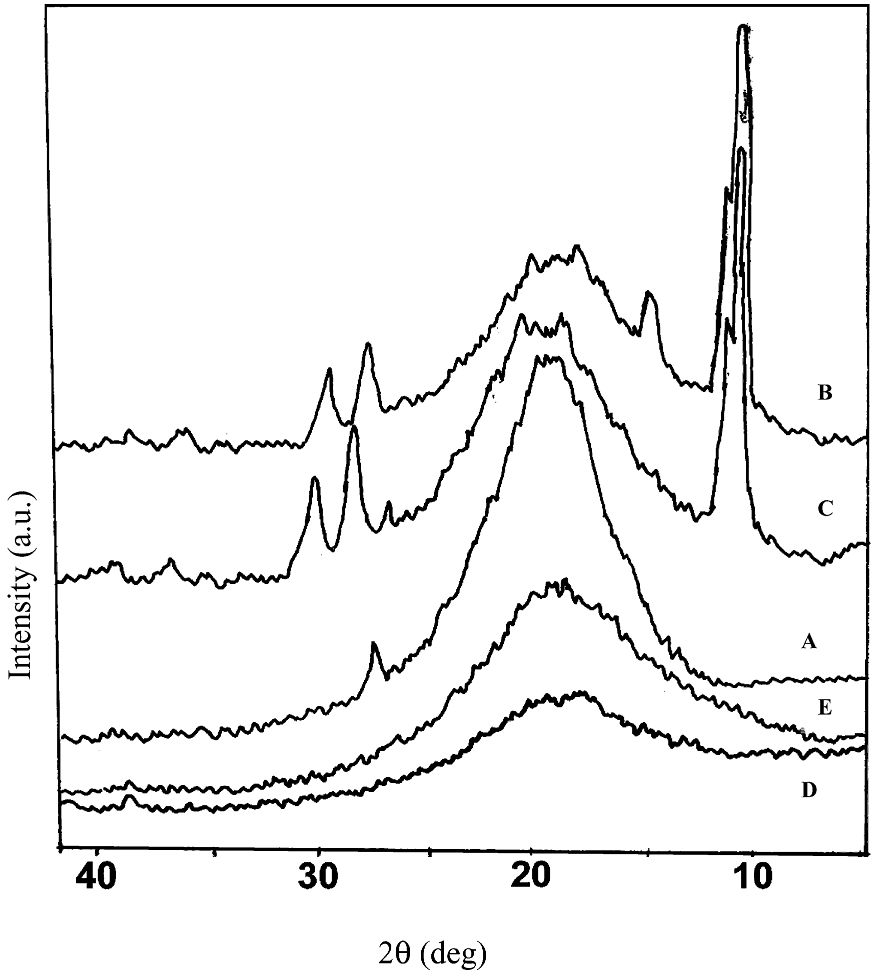

FIG. 4. X-ray diffraction patterns of ion recognition (curve A), unleached (curves B and C), and leached (curves D and E) palladium ion-imprinted polymer materials with and without irradiation.

the different chemical environments present in the sample and information on the degree of chemical cure can be obtained. The solid-state NMR has been relatively under exploited to date for characterization of styrene–DVB copolymers.

Morphological Characterization

It is possible to probe the morphology of styrene–DVB copolymers in much the same way as one is able to do with most porous solids. Depending on the method of analysis, useful information may be obtained on the specific surface area, specific pore volumes, pore sizes, and pore size distributions. Suitable analytical methods include those mentioned below.

Solvent Uptake Experiments

Macroporous polymers are permanently porous even in the dry state and solvent can be used to access the pore network. By measuring the amount of solvent uptake by a polymer, an estimate can be made of the specific pore volume (mL/g).

N_2 Sorption Porosimetry

N_2 sorption porosimetry involves a fixed mass of dry polymer exposed to a gas (usually N_2) at a series of fixed pressures. By measuring the amount of gas sorbed as a function of pressure, sorption isotherms can be constructed from which, following application of theory (BET) and mathematical models, information on the specific surface area (m^2/g), specific pore volume (mL/g), average pore diameter, and pore size distribution can be extracted. The method is particularly useful for analyzing in detail medium, sized (meso-) and small (micro-) pores. Table 1 shows the typical surface area and pore size distribution data of various palladium ion-imprinted styrene–DVB polymer materials, namely, unleached and leached particles either with or without γ-irradiation (88).

Mercury Intrusion Porosimetry

Mercury intrusion porosimetry involves mercury being forced, under pressure, into a fixed mass of dry polymer. The information that can be generated from such experiments

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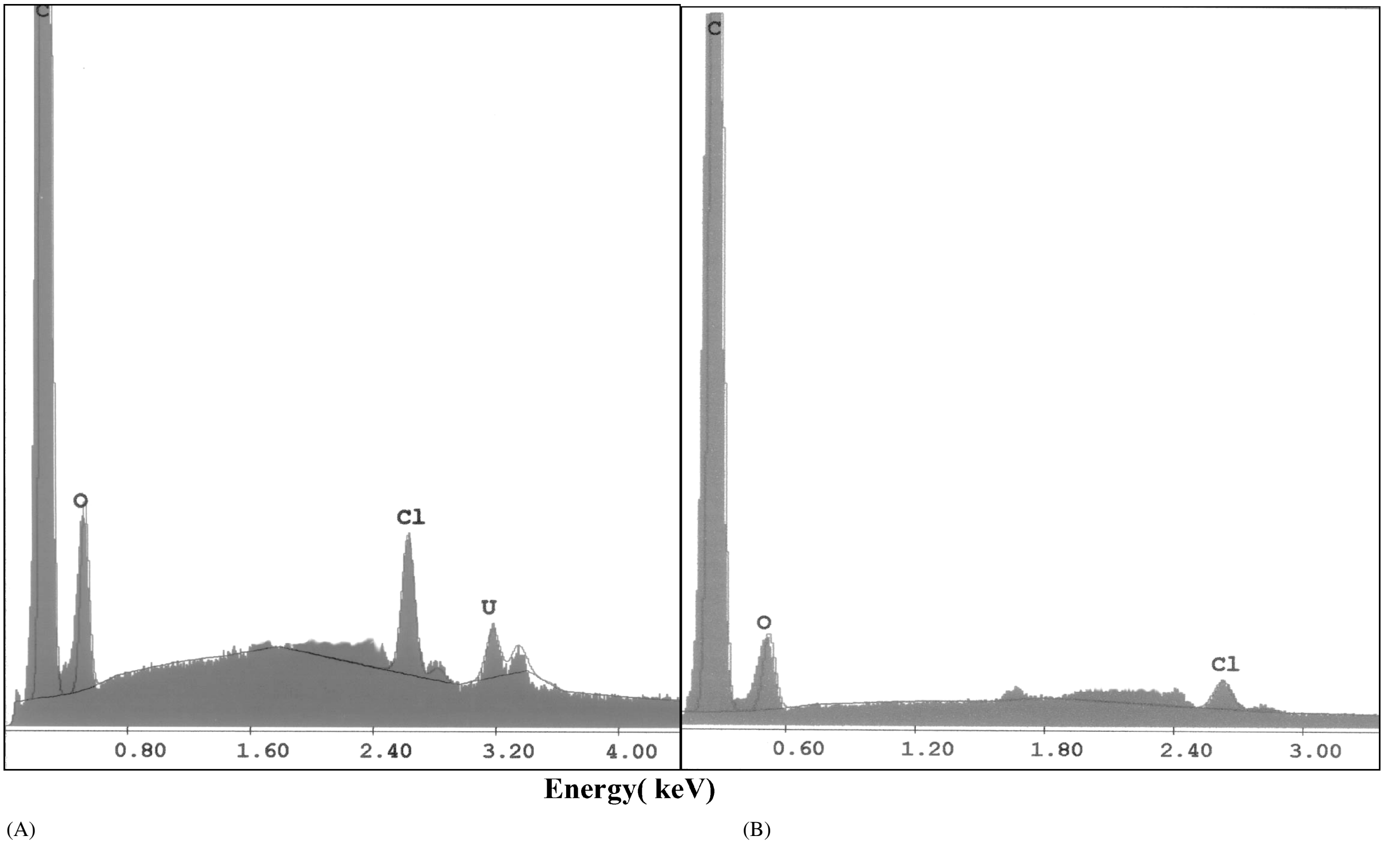

(A) (B)

FIG. 5. EDS spectra of unleached (A) and leached (B) uranyl IIP particles.

is similar to that which can be obtained from N_2 sorption porosimetry, although it is generally more sensitive at probing large (macro-) pores.

Inverse Size Exclusion Chromatography (ISEC)

In contrast to N_2 sorption porosimetry and mercury intrusion porosimetry, which analyze polymers in a dry state, ISEC enables the porous structure of the polymers to be probed in a wet state. This is perhaps significant as far as styrene–DVB copolymers in inorganic trace analysis is concerned with the wet state. In a typical ISEC experiment, the porous solid is the stationary phase in a flow-through column setup and the time taken for a series of linear soluble polymer standards of known molar mass to elute through the column at a fixed flow rate.

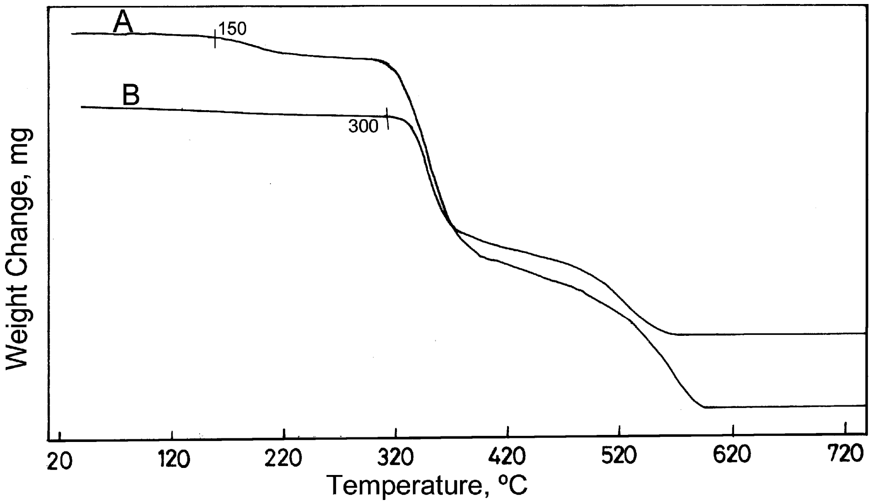

FIG. 6. TGA plots of unleached (A) and leached (B) Dy IIP materials.

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TABLE 1
Surface Area and Pore Size Analysis Data of Control (CP) and Ion-Imprinted Pd (IIP) Particles

Parameter	CP	IIP (unleached)	IIP (leached)	IIP (unleached & irradiated)	IIP (leached & irradiated)
BET surface area (m^2/g)	217.63	261.32	372.50	144.60	180.92
Langmuir surface area (m^2/g)	383.40	876.18	956.65	393.64	479.33
BJH ads. average pore diameter (nm)	2.60	2.60	2.83	2.74	2.79
BJH ads. cumulative surface area (m^2/g)	325.84	381.19	486.11	339.89	423.56
BJH ads. cumulative pore volume (cm^3/g)	0.22	0.26	1.29	0.24	0.30

BET = Brunauer-Emmett-Teller.
BJH = Barett-Joyner-Halenda.

On application of suitable mathematical models, information on the pore structure of the polymer stationary phase can be extracted. In many respects, ISEC can be viewed as being a technique complimentary to N_2 sorption porosimetry and mercury intrusion porosimetry, with the advantage being that it can operate in the wet state.

Scanning or Transmission Electron Microscopy (SEM/TEM)

Microscopy can be used in a variety of ways to prove styrene–DVB copolymers on a variety of length scales. Thus, light microscopy can be used to verify the structural integrity of polymer beads whereas SEM/TEM can often be used to image micro/nanopores.

APPLICATIONS TO INORGANIC TRACE ANALYSIS

Lanthanides

A chelating resin prepared by sorption of 5-Br PADAP on macroporous Amberlite XAD-4 resin was used for the preconcentration of rare earth elements (REE), for example, Er, Yb, and Lu (37). The quantitation was done by X-ray fluorescence spectrometry. Masi and Olsina (32, 33, 36) loaded Amberlite XAD-4 resin with 5-Cl DMPAP and quinoline-8-ol and was used for preconcentration of Ce, La, and Pr and subsequent determination by X-ray fluorescence spectrometry. Optimum adsorption conditions were arrived at by studying adsorption isotherm and thermodynamic parameters (32). These authors claimed retention coefficients on the order of 500 which is excellent (32, 33). In a subsequent paper (36), the authors presented a method for preconcentration and elimination of the enhancement-absorption effects that occur in X-ray fluorescence analysis of REE. The conditions for preparing thin films with loaded resins were studied. Further, the critical thickness of the films were experimentally determined and compared with calculated values.

A multielement preconcentration procedure for enriching three or four lanthanides onto chelating Amberlite XAD-4 resins was developed by Dev et al. (69) and Jain et al. (71). However, none of these groups have validated their method by analyzing reference materials as applied to real samples.

Biju et al. (78) reported better selectivity coefficients for dysprosium over Y, La, Nd, and Lu using dysprosium IIP particles compared to well-known and best commercial extractants, such as, di-2-ethyl hexyl phosphoric acid and 2-ethyl hexyl-ethyl hexyl phosphoric acid. Subsequently, the same authors (79) reported two to four times higher selectivity coefficients on post γ-irradiation of Dy IIP particles. Neodymium(III) IIP particles analogously offer much better selectivity coefficients for Nd over La, Ce, Pr, Sm, and Eu compared to best liquid-liquid extractants (80).

Ion imprinting with Gd (81) resulted in higher selectivity coefficients for $\beta_{\mathrm{Gd/La}}$ and reached a maximum when approximately 50% of the cross-linker was used. Selectivity increased with the percentage of DVB and reached maximum when no styrene was used. This could be explained by the increased rigidity of the matrix and, consequently, a better definition of imprinted cavities after the removal of the gadolinium template ion.

Actinides

The sorption of uranium(VI) (46) by DBBT-impregnated Amberlite XAD-16 resin was studied spectrophotometrically using arsenazo(III) reagent. The impregnation was carried out by direct adsorption of chelating ligand onto macroporous support. The retention capacity of the resin is 0.21 mg/g of polymer which is very low. However, the precision of the method is quite good as RSD for 10 replicate determinations of 1.2 μg/ml was 2.4%.

Liquid-gel extraction of uranium from the liquors obtained by the heap leaching of local phosphatic sandstone was investigated using gels composed of styrene–DVB copolymer incorporating D2EHPA (47). The different factors that can affect the process were studied. Addition of tri-*n*-butyl phosphate into the gel was found to enhance the uranium extaction. Uranium sorbed on the gel could be efficiently eluted by a Fe(II)/H_3PO_4 solution.

Kumar et al. (49) employed tiron immobilized Amberlite XAD-2 for preconcentration of uranyl ion present in well water samples prior to fluorimetric quantitation. Thorium(IV) and uranium(VI) (58) present in monazite sand and geological materials were determined by ICP-AES and GF-AAS, respectively, after preconcentration with *o*-vanilline thiosemicarbazone immobilized Amberlite XAD-2.

Jain et al. (71) and Dev et al. (69) preconcentrated uranium(VI) and thorium(IV) along with lanthanides using *o*-vanilline semicarbazone and bicine immobilized Amberlite XAD-4 resins. The former procedure allowed the determination of the above actinides in simulated river water samples. The preconcentration of uranium(VI) onto quinoline-8-ol functionalized Amberlite XAD-4 allowed a simple technique like spectrophotometry to be used for analysis of complex real samples like soils and sediments (70).

Thenoyl trifluoroacetylene functionalized Merrifield chloromethylated resin (75) was used for selective separation of uranium(VI) and thorium(IV) from several transition metal ions and neutral electrolytes. The developed preconcentration procedure in conjunction with spectrofluorimetric determination allows the analysis of well and seawaters for uranium(VI). The resin column can be used repeatedly for 30 cycles. Furthermore, the retention capacities for uranium(VI) and thorium(IV) are very good, namely, 32.98 and 27.19 mg/g of resin, respectively.

Uranyl ion-imprinted polymer resins were used to preconcentrate trace amounts of uranyl ions present in spiked tap water samples prior to determination by spectrophotometry or ICP-MS (86). Furthermore, the developed procedure was validated by analyzing a NIST 610 glass sample. However, this procedure offers very low enrichment factors ∼10. Subsequently, Gladis et al. (82, 83) obtained enrichment factors of around 100 during preconcentration of trace and ultratrace amounts of uranyl ions present in synthetic seawater, soil, and sediment samples. Further, the developed preconcentration procedure was validated by analyzing marine sediment Certified Reference Material (MESS-3) supplied by the National Research Council, Canada. Subsequently the same authors (84) reported better selectivity coefficients for uranium over thorium and retention capacities for uranium with medium polar porogens compared to low- and high-polar porogens. Metilda et al. (85) reported enrichment of uranyl ions from dilute aqueous solutions using IIP particles prepared with uranyl-DCQ or uranyl-VP or nascent IIP particles. The detection limits of the arsenazo III spectrophotometric procedure in conjunction with the above preconcentration were 5 μg/L. The retention capacity was also quite high, namely, 34.05 mg uranyl ion per g of polymer.

Noble Metals

Trace levels of gold (12) in geological materials and anodic slimes were determined by direct enrichment onto an Amberlite XAD-16 column, followed by flame atomic absorption spectrometry (FAAS) determination after elution. The degree of preconcentration ranged from 10 to 75 for different sample volumes which were not that good. The detection limit was also poor (46 ng/mL). Tunceli and Turker (13) determined palladium in alloy samples by using FAAS after preconcentration of its iodo complex onto Amberlite XAD-16. The retention capacity was found to be 35.6 mg per g polymer which is quite impressive compared to other sorbents. The detection limit was also good (5.1 ng/mL). Some authors (14) preconcentrated silver from thiocyanate solutions onto an Amberlite XAD-16 resin column and quantitation was done by flame AAS. The developed procedure applied to standard alloys, though, had very low retention capacity (4.66 mg per g of polymer).

Sobhi et al. (88) employed palladium ion-imprinted polymer particles for preconcentration of 2.5–100 μg of palladium present in 1.0 L of solutions and eluted completely by stirring with 2 × 10 mL of 50% (v/v) HCl. The Pd IIP gave a 100 times higher distribution ratio than control or ion recognition polymers. The selectivities of palladium over platinum, copper, zinc, and nickel increased by severalfold on imprinting. The retention capacity and detection limits were also quite good, namely, 21.5 mg of Pd per g of polymer and 2.5 μg of Pd per L, respectively.

Transition and Heavy Elements

Amberlite XAD-1180 resins are used for preconcentrative determination of trace metals such as Bi, Cd, and Pb as their iodo complexes in column mode in high-purity aluminum, zinc, and commercial steels by FAAS or graphite furnace atomic absorption spectrometry (GF-AAS) (8). The detection limits for FAAS and GF-AAS were in the ranges of 0.002 to 0.11 μg/mL and 0.003 to 0.004 μg/mL which are quite impressive. The same resin has been used for preconcentration of trace amounts of tungsten as its thiocyanate complex and determined spectrophotometrically via the SCN^-–$SnCl_2$ method (9). The recovery, relative standard deviation (RSD), and detection limits were 95%, 6%, and 12 μg/L which are rather poor. Tokalioglu et al. (10) determined Cu, Cd, Pb, Bi, Ni, Fe, Mn, and Co from sulfuric, nitric, and hydrochloric acid solutions containing iodide thiocyanate or their mixtures onto a short column filled with Amberlite XAD-1180 resin. The proposed procedure was applied to the determination of Cu, Cd, Pb, and Bi in pure zinc metals by FAAS or GF-AAS. Even though the authors claimed good results, the recovery and RSD values were not impressive, namely, 95%, <6%.

Soylak and Elci (11) determined Ni, Cd, Pb, Cu, and Co in drinking water from wells, direct sources, and storage tanks in 18 sites in Kayseri (Turkey) by GF-AAS after enrichment on an Amberlite XAD-4 resin to reduce the incidence of contamination. The Ni, Pb, Cd, Cu, and Co levels in drinking water supplies of Kayseri City were below the maximum tolerable limits set by the World Health Organization (WHO) and water pollution control regulation of the Turkish authorities.

Ion exchange of Sr (16) and Co (17) onto cationic Amberlite IR-120 resin was used for their enrichment (online analysis in case of latter). The precision and reproducibility were quite good. Automatic chromium(III) or (VI) preconcentration was accomplished by ion exchange and speciation by flow injection FAAS (18). Cr(III) was separated and preconcentrated on a

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cation exchange resin Amberlite IR-120 and Cr(VI) on Amberlite IRA-400. Good detection limits of 14.3 and 1.4 ng/mL were obtained for Cr(III) and Cr(VI), respectively. An ion exchange resin Amberlite IRA-410 (19) was used as column material during flow injection preconcentration and determination by hydride generation electrothermal AAS. Arsenate, iron(III), and Hg(II), were found to depress the selenium signal at concentrations greater than 20, 10, and 3 mg/mL during the determination of 0.5 μg/mL of selenium. However, Cu, Co, Pb, Mg, and Ni were found to be tolerated up to 50–70 μg/mL. Quite significantly 500–900 μg/mL of Cl^-, Br^-, I^-, ClO_4^- and SO_4^{2-} do not have any deleterious effect.

Calmagite-loaded Amberlite XAD-2 (27, 28) was employed in an online continuous flow system for preconcentration of traces of copper and subsequent determination by FAAS. However, an enrichment factor of 32 was achieved with 3 min preconcentration time which is rather poor as enrichment factors of 50–100 are achieved for inorganics using C_{18}-bonded silica gel with 1 min preconcentration time. Nagmush et al. (21) developed a similar procedure for copper in which PV, PAR, and Eriochrome blue black R loaded Amberlite XAD-2 were used instead of calmagite. For determination of copper in natural waters the authors recommended the use of 20 min of preconcentration time, thus restricting the number of samples that can be analyzed.

TAN-loaded Amberlite XAD-2 (24) was used for preconcentration of copper and zinc in natural waters in conjunction with inductively coupled plasma atomic emission spectrometry. This procedure offered a reasonably good enrichment factor of ~80. Trace amounts of Cd, Co, Cu, Fe, Ni, and Pb were determined after solid-phase extraction onto DDTC or APDC loaded Amberlite XAD-2 resin and slurry sampling ICP-AES (22). The developed procedure was successfully tested for the recovery of above elements in synthetic hemodialysis solutions. Total organotin present in marine water samples was determined by ETAAS after preconcentrating on tropolone sorbed Amberlite XAD-2 (23). A good detection limit of 13 pg/ml was reported with an RSD of $<10\%$ and recoveries ~100%. PAN loaded Amberlite XAD-2 (25) was used for preconcentrative separation of nickel present in saline matrices and subsequent determination by ICP-AES. The precision of the method was reasonably good (3.9%) for 0.2 μg/mL of nickel. Taher et al. (29) developed a solid-phase extraction procedure for bismuth using 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol loaded Amberlite XAD-2 in conjunction with anodic stripping voltammetric (ASV). The calibration curve was linear in the range of 0.05 to 160 μg/mL with an RSD of $+1.2\%$. Further, as low as 0.15 μg of bismuth could be concentrated in the column from 1100 mL of aqueous sample. The developed procedure was successfully applied to wide variety of biological (hair and tea leaves), metallurgical (alloys), and environmental samples (waters).

The 5-Br PDDAP chelate adsorbed on sulfonated Amberlite XAD-4 resin was used as column material during high-performance liquid chromatography (HPLC) determination of cobalt (35). Even though this procedure offers only 25-fold enrichment, it allows the determination of as low as 65 ng/mL of cobalt(II) and is free from interference due to Cu(II) and Zn(II). Trace amounts of Ga and In present in geological samples were preconcentrated with 5-phenylazo-8-quinolinol loaded Amberlite XAD-4 macroporous resin (38). The detection limits for these procedures in conjunction with XRD quantitation were 98 and 81 ng/mL for Ga and In, respectively.

Cu, Cd, Mn, Co, Pb, Ni, and Fe were determined by FAAS in dialysis solutions (31), river waters (30), and chemical grade potassium salts (39) by using APDC, APDC oxine, and 1-nitroso-2-naphthol–loaded Amberlite XAD-4 resins, respectively. The RSD values were in the range of 1% to 7% which are rather high. The same group (40) determined Cu, Fe, Pb, Ni, Cd, and Bi at trace levels in wastewaters after preconcentrative separation using sodium diethyl dithiocarbamate loaded Amberlite XAD-4 resin. The limits of detection are impressive as they were in the range of 4 to 23 ng/mL but RSD's were quite high as in earlier procedures. Yang et al. (34) developed an online sample pretreatment method to preconcentrate Cu, Cd, Co, Ni, and Pb in waters as their butane-2,3-dione bis(N-pyridino acetyl hydrazone) complexes onto Amberlite XAD-4 resin packed column. The metal complexes were removed from the column by an acidic eluent and detected by ICP-mass spectrometry (ICP-MS). The detection limits were in the range of pg/mL. The accuracy of the method was tested by analyzing riverine Certified Reference Material SLRS-2.

Cobalt(II) present in natural water samples was preconcentrated by adsorption of Co(II)–TAR complex on Amberlite XAD-16 and subsequently determined by FAAS (44). The same group (43) developed similar procedures for Cu, Ni, and Fe with poor recoveries. However, the precision is good as RSDs were in the range of 3% to 5%. Turker and Tunceli (41) obtained quantitative recoveries of Cu, Ni, and Zn only after complexing them with PAN during enrichment by Amberlite XAD-16 macroporous resin. The method was applied to tap water only. Soylak and Dogan (42) preconcentratively separated Zn, Cu, Fe, Cd, Co, and Ni after complexing with NaDDTC onto Amberlite XAD-16 resin column. The use of GF-AAS for quantification enabled the determination of above elements in urine samples. A similar preconcentration procedure was adopted by Soylak and Elci (45) for sorption of trace metal ions, namely, Fe, Ni, Cu, Zn, Cd, and Co present in seawater prior to determination by FAAS.

Chemically immobilized Amberlite XAD-2 resins were used for preconcentration of transition elements, namely, Cu, Zn, Cd, Pb, Fe, Co, and Ni prior to determination by FAAS by the Singh (48–56), Jain (57, 58), Dogutan (59), and Trozanowicz (61) groups. Of these, a few procedures were used for analysis of waters (48–57) and vitamin tablets (49, 51, 53, 56) for transition elements and gallium in semiconductors (59).

Salicylic acid grafted Amberlite XAD-4 syntehsized by Boudenne et al. (66) was found to complex aluminum selectively. Hirata et al. (64) determined iron(II) and iron (total) in environmental samples after preconcentration in flow injection mode onto N-hydroxy ethyl ethylene diamine immobilized Amberlite XAD-4 resin. The quantitation was done by chemiluminescence detection using brilliant sulfoflavine and hydrogen peroxide reagent solutions. Chromium(VI) and (III) (67) were preconcentrated into maleic acid functionalized Amberlite XAD-4 resin. The developed method was validated with a blended coal sample CRC-1632. Dev and Rao (68) and Cekic et al. (63) developed multielement preconcentration procedures for various transition elements by using bicine and *o*-aminobenzoic acid functionalized Amberlite XAD-4 resins. The latter authors successfully applied the developed preconcentration method for the analysis of synthetic metal mixture solution, coal sample Certified Reference Materials, and brackish lake water.

Chromotrope 2R immobilized Amberlite IRA-400 chelating resin was used for quantitative separation of copper from cobalt, nickel, zinc, calcium, magnesium, and cadmium present in tapwater and seawater (72). A similar chelating resin was used for the determination of traces of aluminum in waters and dialysis fluids (73). An N-benzoyl phenyl hydroxyl amine derivative of styrene–DVB copolymer derivative sorbs Zr(IV) and H(IV) in the pH range of 1 to 2 (77). The sorbed Zr was recovered by using a mixture of HF and HCl. The retention capacity of the resin for Zr(IV) was fairly good, that is, 59.29 mg/g.

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Miscellaneous

Traces of Pb, Bi, Au, Pd, and Cd present as impurities in Raney Ni and nickel oxide were determined by FAAS after their preconcentrative separation onto an Amberlite XAD-16 resin column from a solution containing 1 M HCl and 0.3 M NaI (15). The limit of detection was between 10 and 270 mg/g which are reasonable values. Mentasti et al. (20) have determined various metals at trace levels present in the Antarctic (Ross Bay) using ICP-AES after preconcentration of oxine or 1-(2-thiazolylazo)-2-naphthol complexes onto Amberlite XAD-2 resin. Use of closed-loop online treatment samples ensures very limited alteration of the sample.

CONCLUDING REMARKS

Nascent styrene–DVB resins are used for preconcentration of metal-inorganic ligand solutions. But, the recoveries are usually nonquantitative. Even though cationic styrene–DVB resins such as Amberlite IR-120, IRA-400, and IRA-410 are employed, they are not very popular due to lack of selectivity. On the other hand, several research groups are working on (1) the adsorption of metal-chelate complexes onto macroporous styrene–DVB resins and (2) enrichment of metal ions through surface-adsorbed chelate loaded styrene–DVB resins. The above three classes of styrene–DVB polymers have good adsorption capacities but do not have the desired stability. Several research groups during the past decade have worked on the synthesis of chelate incorporated styrene–DVB copolymers by grafting. This trend will continue by chemically immobilizing various chelating ligands onto macroporous styrene–DVB resins. A recent trend is the grafting by in situ polymerization to produce nanoporous materials with high surface area and increased stability so that they can offer selectivity in addition to high retention capacity.

REFERENCES

1. V. Canel, Solid phase extraction of trace elements, *Spectrochim. Acta* B 53 (2003):1177–1233.
2. C. F. Poole, New trends in solid-phase extraction, *Trends in Anal. Chem.* 22 (2003):362–372.
3. I. Ferrer and D. Barcelo, Validation of new solid-phase extraction materials for the selective enrichment of organic contaminants from environmental samples. *Trends in Anal. Chem.* 18 (1999):180–192.
4. N. Masque, R. M. Marce, and F. Borrull, New polymeric and other types of sorbents for solid-phase extraction of polar organic micropollutants from environmental water. *Trends in Anal. Chem.* 17 (1998):384–394.
5. I. Liska, Fifty years of solid-phase extraction in water analysis—historical development and overview. *J. Chromatogr.* A 665 (1993):163–168.
6. T. Hayashita, M. Goto, Y. C. Lee, J. S. Khim, J. Kuzykawski, and R. A. Bartsch, Selective sorption of alkali-metal. Cations by carboxylic acid resins containing acyclic or cyclic polyether units. *Anal. Chem.* 62 (1990):2283–2287.
7. M. E. Leon-Gonzalez and L. V. Perez-Arrivas, Chemically modified polymeric sorbents for sample preconcentration. *J. Chromatogr.* A 902 (2000):3–16.
8. S. Tokaliglu, S. Kartal, and L. Elci, Determination of some trace elements in high purity aluminium, zinc and commercial steel by AAS after preconcentration on Amberlite XAD-1180 resin. *Microchim. Acta* 127 (1997):281–286.
9. M. Soylak, L. Elci, and M. Dogan, Spectrophotometric determination of trace amounts of tungsten in geological samples after preconcentration on Amberlite XAD-1180. *Talanta* 42 (1995):1513–1517.
10. S. Tokalioglu, S. Kartal, and L. Elci, Determination of copper, cadmium, lead and bismuth in high purity zinc metal samples by atomic absorption spectrometry after preconcentration using Amberlite XAD-1180 resin. *Anal. Sci.* 10 (1994):779–782.
11. M. Soylak and L. Elci, Solid phase extraction of trace metal ions in drinking water samples from Kayseri-Turkey. *J. of Trace and Microprobe Techniques* 18 (2000):397–403.
12. A. Tunceli and A. R. Turker, Determination of gold in geological samples and anode slimes by atomic absorption spectrometry after preconcentration with Amberlite XAD-16 resin. *Analyst* 122 (1997):239–242.
13. A. Tunceli and A. R. Turker, Determination of palladium in alloy by flame atomic absorption spectrometry after its preconcentration if its iodocomplex on Amberlite XAD-16. *Anal. Sci.* 16 (2000):81–85.
14. A. Tunceli and A. R. Turker, Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution. *Talanta* 51 (2000):889–894.

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15. L. Elci, M. Soylak, A. Uzym, E. Buyukpatir, and M. Dogan, Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin. *Fresenius J. Anal. Chem.* 368 (2000):358–361.
16. M. C. Yebrabiurrum, A. Bermejovarrera, and P. Bermejobarrera, Preconcentration and determination of traces of strontium in natural waters by ion exchange and flame atomic absorption spectrometry. *Bulletin Des Societies Chimiques Belges* 101 (1992):473–478.
17. M. S. Jimenez and J. R. Castillo, Tandem preconcentration of cobalt by online ion exchange and gas phase chelates generated by merging zones flow injection analysis with electrothermal atomic absorption spectrometric determination. *J. of Analytical Atomic Spectrom.* 12 (1997):1397–1462.
18. M. S. Jimenez, L. Martin, J. M. Mir, and J. R. Castillo, Automatic chromium(III)/(VI) preconcentration and speciation by flow injection-flame AAS. *Atomic Spectroscopy* 17 (1996):201–207.
19. P. E. Carrero and J. F. Tyson, Flow injection determination of selenium by successive retention of Se(IV) and tetraphenylborate(III) on an anion exchange resin and hydride generation electrothermal atomic absorption spectrometry with inatomizer trapping—Part I: Method development and investigation of interferences. *Spectrochim. Acta, Part* B 53 (1998):1931–1943.
20. E. Mentasti, V. Porta, O. Abollino, and C. Sarzanini, Metal trace determinations in sea water samples from Antarctica. *Annali Di Chimica* 81 (1991):343–355.
21. A. M. Nagmush, M. Trojanowicz, and E. Olbrychleszynska, Flow injection flame atomic absorption spectrometric determination of copper with preconcentration ligand loaded Amberlite XAD-2. *J. of Anal. At. Spectrom.* 7 (1992):323–328.
22. O. Abollino, M. Aceto, M. C. Bruzzoniti, E. Mentasti, and C. Sarzamini, Determination of metals in highly saline matrices by solid phase extraction and slurry-sampling inductively coupled plasma atomic emission spectrometry. *Anal. Chim. Acta* 375 (1998):293–298.
23. P. Bermejo-Barrera, G. Gonzalez-Campos, M. Ferron-Novais, and A. Bermejo-Barrera, Column preconcentration of organotin with tropolone-immobilized and their determination by electrothermal atomization absorption spectrometry. *Talanta* 46 (1998):1479–1484.
24. S. L. C. Ferreira, H. C. Dossantos, J. R. Ferriera, N. M. L. Dearaujo, A. C. S. Costa, and D. S. Dejesus, Preconcentration and determination of copper and zinc in natural water samples by ICP-AES after complexation and sorption on Amberlite XAD-2. *J. of Brazilian Chem. Soc.* 9 (1998):525–530.
25. S. L. C. Ferreira, C. F. Debrito, A. F. Dantas, N. M. Lopode Araujo, and A. C. S. Costa, Nickel determination in saline matrices by ICP-AES after sorption on Amberlite XAD-2 loaded with PAN. *Talanta* 48 (1999):1173–1177.
26. S. L. C. Ferreira and C. F. Debrito, Separation and preconcentration of cobalt after sorption onto Amberlite XAD-2 loaded with 2-(2-thiazolylazo)-p-cresol. *Anal. Sci.* 15 (1999):189–191.
27. S. L. C. Ferreira, J. R. Ferreira, A. F. Dantas, V. A. Lemos, N. M. L. Araujo, and A. C. S. Costa, Copper determination in natural water samples using fAAS after preconcentration onto Amberlite XAD-2 loaded with calmagite. *Talanta* 50 (2000):1253–1259.
28. S. L. C. Ferreira, V. A. Lemos, B. C. Moveira, A. C. S. Costa, and R. E. Santelli, An on-line continuous flow system for copper enrichment and determination by flame atomic absorption spectrometry. *Anal. Chim. Acta* 403 (2000):259–264.
29. M. A. Taher, E. Razeipour, and D. Afzali, Anodic stripping voltammetric determination of bismuth after solid phase extraction using Amberlite XAD-2 modified with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. *Anal. Chim. Acta* (forthcoming).
30. L. Elci, M. Soylak, and M. Dogan, Preconcentration of trace metals in river waters by the application of chelate adsorption on Amberlite XAD-4. *Fresenius J. Anal. Chem.* 342 (1992):175–178.
31. M. Soylak, L. Elci, and M. Dogan, Determination of some trace metals in dialysis solutions by atomic absorption spectrometry after preconcentration. *Anal. Lett.* 26 (1993):1997–2007.
32. A. N. Masi and R. A. Olsima, Amberlite XAD copolymers loaded with 8- hydroxyquinoline and 2-(2-5-chloropyridylazo)-5-dimethylaminophenol as chelating agents for Rare earth preconcentration. *Annales De Quimica* 89 (1993):341–345.
33. A. N. Masi and R. A. Olsima, Preconcentration and determination of Ce, La and Pr by X-ray fluorescence analysis using Amberlite XAD resins loaded with 8-quinolinol and 2-(2-5-chloropyridylazo)-5-dimethylamino)-phenol. *Talanta* 40 (1993):931–934.
34. H. Yang, K. Huang, S. Jiang, C. Wu, and C. Chou, Determination of trace metal ions in water samples by on-line preconcentration and inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 282 (1993):437–443.
35. N. Uehra, A. Katamine, and Y. Shijo, High-performance liquid chromatographid determination of cobalt(II) as the 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol chelate after preconcentration with a cation-exchange resin. *Analyst* 119 (1994):1333–1335.
36. A. N. Masi and R. A. Olsima, Preparation and characterization of chelating resins loaded with 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol for preconcentration of rare earth elements. *Fresenius J. Anal. Chem.* 357 (1997):65–68.
37. A. N. Masi and R. A. Olsima, Preparation of thin films with loaded resins for the preconcentration and determination of rare elements by X-ray fluorescence spectroscopy. *X-ray Spectrom.* 25 (1996):221–224.
38. A. N. Masi and R. A. Olsima, Determination by XRF of trace amounts of Ga and in geological samples preconcentrated with macroporous resins loaded with 5-phenylazo-8-quinolinol (5-phaq). *J. of Trace and Microprobe Techniques* 17 (1999):315–325.
39. M. Soylak, L. Elci, and M. Dogan, Flame atomic absorption spectrometric determination of cadmium, cobalt, copper, lead and nickel in chemical grade potassium salts after an enrichment and separation procedure. *J. of Trace and Microprobe Techniques* 17 (1999):149–156.
40. A. Uzun, M. Soylak, and L. Elci, Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd and Bi at trace levels in waste water samples by flame atomic absorption spectrometry. *Talanta* 54 (2001):197–202.
41. A. R. Turker and A. Tunceli, Preconcentration of copper, nickel and zinc with Amberlite XAD-16 resin. *Fresenius J. Anal. Chem.* 345 (1993):755–758.
42. M. Soylak and M. Dogan, Separation and enrichment of zinc, copper, iron, cadmium, cobalt and nickel from urine with Amberlite XAD-16 resin. *Trace Elements and Electrolytes* 13 (1996):130–132.
43. M. Soylak, V. Divrikli, and M. Dogan, Column separation and enrichment of trace amounts of Cu, Ni and Fe on XAD-16 resin

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in industrial fertilizers after complexation with 4-(2-thiazolylazo) resorcinol. *J. of Trace and Microprobe Techniques* 15 (1997):197–204.

44. M. Soylak, L. Elci, and M. Dogan, Determination of trace amounts of cobalt in natural water samples as 4-(4-thiazolylazo) resorcinol complex after adsorptive preconcentration. *Anal. Lett.* 30 (1997):623–631.
45. I. M. Soylak and L. Elci, Preconcentration and separation of trace metal ions from sea water samples by sorption on Amberlite XAD-16 after complexation with sodium diethyl dithiocarbamate. *Int. J. of Environ. Anal. Chem.* 66 (1997):51–59.
46. M. Merdivan, M. Z. Ouz, and C. Hamamci, Sorption behaviour of uranium(VI) with N,N-dibutyl-N'-benzoylthiourea impregnated in Amberlite XAD-16. *Talanta* 55 (2001):639–645.
47. K. Shakir, M. Aziz, and S. G. Beheir, Studies on uranium bearing phosphatic sandstone by a combined Heap leaching liquid gel extraction process 2-Liquid gel extraction. *Hydrometallurgy* 31 (1992):41–54.
48. R. Saxena, A. K. Singh, and S. S. Sambi, Synthesis of a chelating polymer matrix by immobilizing Alizarin Red-S on Amberlite XAD-2 and its application to preconcentration of lead(II), cadmium(II), zinc(II) and nickel(II). *Anal. Chim. Acta* 295 (1994):199–204.
49. M. Kumar, D. P. S. Kathore, and A. K. Singh, Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: analytical applications. *Analyst* 125 (2000):1221–1226.
50. P. K. Tewari and A. K. Singh, Synthesis, characterization and application of pyrocatechol amberlite XAD-2 resin for preconcentration and determination of metal ions in water samples by flame atomic absorption spectrometry (FAAS). *Talanta* 53 (2001):823–833.
51. P. K. Tewari and A. K. Singh, Thiosalicylic acid-immobilized Amberlite XAD-2: Metal sorption behaviour and applications in estimation of metalions by flame atomic absorption spectrometry. *Analyst* 125 (2000):2350–2355.
52. M. Kumar, D. P. S. Rathore, and A. K. Singh, Amberlite XAD-2 functionalized with o-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II). *Talanta* 51 (2000):1187–1196.
53. P. K. Tewari and A. K. Singh, Amberlite XAD-2 functionalized with chromatropic acid: Synthesis of a new polymer matrix and its applications in metal ion enrichment for their determination by flame atomic absorption spectrometry. *Analyst* 124 (1999):1847–1851.
54. R. Saxena and A. K. Singh, Pyrocatechol violet immobilized Amberlite XAD-2: Synthesis and metal-ion uptake properties suitable for analytical applications. *Anal. Chim. Acta* 340 (1997):285–290.
55. R. Saxena, A. K. Singh, and D. P. S. Rathore, Salicylic acid functionalized polystyrene sorbent Amberlite XAD-2. Synthesis and applications as a preconcentrator in the determination of zinc(II) and lead(II) by using atomic absorption spectrometry. *Analyst* 120 (1995):403–405.
56. M. Kumar, D. P. S. Rathore, A. K. Singh, Pyrogallol immobilized Amberlite XAD-2: A newly designed collector for enrichment of metal ions prior to their determination by flame atomic absorption spectrometry. *Mikro Chim. Acta* 137 (2001):127–134.
57. V. K. Jain, S. S. Sait, P. S. Shrivastav, and Y. K. Agrawal, Application of chelate forming resin Amberlite XAD-2-o-vanillin-thiosenicarhazone to the separation and preconcentration of copper(II), zinc(II) and lead(II). *Talanta* 45 (1997):397–404.
58. V. K. Jain, S. S. Sait, P. Shrivastav, and Y. K. Agrawal, Sequential separation and trace enrichment of thorium(IV) and uranium(VI) on chelating resin Amberlite XAD-2-orthovanillin thiosemicarbazone (O-Vtsc). *Sep. Sci. and Technol.* 33 (1998):1803–1818.
59. M. Dogutan, H. Filik, S. Demirci, and R. Apak, The use of palmitoyl hydroxyquinoline functionalized Amberlite XAD-2 copolymer resin for the preconcentration and speciation analysis of gallium(III). *Sep. Sci. and Technol*. 35 (2000):2083–2096.
60. A. Suebert, G. Petzold, and J. W. McLaren, Synthesis and application of an inert type of 8-hydroxyquinoline-based chelating ion exchanger for sea water analysis using on-line inductively coupled plasma mass spectrometry detection. *J. Anal. Atomic Spectrometry* 10 (1995):371–380.
61. E. Obrychsleszynska, K. Brazter, W. Matu-Zewski, M. Trojanowicz, and W. Frenzel, Modification of nonionic adsorbent with eriochrome blue black R for selective nickel(II) preconcentration in conventional and flow injection atomic absorption spectrometry. *Talanta* 39 (1992):779–787.
62. D. Yuan and I. L. Shuttler, Flow injection column preconcentration directly coupled with electrothermal atomization atomic absorption spectrometry for the determination of aluminium. Comparison of column packing materials. *Anal. Chim. Acta* 316 (1995):313–322.
63. S. D. Cekic, H. Filik, and R. Apak, Use of o-aminobenzoic acid-functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal(II) ions. *Anal. Chim. Acta* 505 (2003):15–25.
64. S. Hirata, H. Yoshihara, and M. Aihara, Determination of iron(II) and total iron in environmental water samples by flow injection analysis with column preconcentration of chelating resin functionalized with N-hydroxyethylene diamine ligands and chemiluminescence detection. *Talanta* 49 (1997):1059–1067.
65. K. Dev and G. N. Rao, Synthesis, characterization and metal sorption studies of a chelating resin functionalized with N-hydroxyethylenediamine ligands. *Analyst* 120 (1995):2509–2512.
66. J. Boudenne, S. Boussetta, C. Brach-Papa, C. Branger, A. Margaillan, and F. Theraulaz, Margaillan and F. Theraulaz, Modification of poly(styrene-co-divinylbenzene) resin by grafting on an aluminium selective ligand. *Poly. Int.* 51 (2002):1050–1057.
67. S. Yalcin and R. Apak, Chromium(III, VI) speciation analysis with preconcentration on a maleic acid—functionalized XAD sorbent. *Anal. Chim. Acta* 505 (2003):25–39.
68. K. Dev and G. N. Rao, Preparation and analytical properties of a chelating resin containing bicine groups. *Talanta* 42 (1995):591–596.
69. K. Dev, R. Pathak, and G. N. Rao, Sorption behaviour of lanthanum(III), neodymium(III), terbium(III), thorium(IV) and uranium(VI) on Amberlite XAD-4 resin functionalized with bicine ligands. *Talanta* 48 (1999):579–584.
70. J. M. Gladis and T. Prasada Rao, Quinoline-8-ol immobilized Amberlite XAD-4: synthesis, characterization and uranyl ion uptake properties suitable for analytical applications. *Anal. Bioanal. Chem*. 373 (2002):867–872.
71. V. K. Jain, A. Handa, S. S. Sait, P. Shrivastav, and Y. K. Agrawal, Preconcentration, separation and trace determination of lanthanum(III), cerium(III), thorium(IV) and uranium(VI) on

polymer supported o-vanillin semicarbazone. *Anal. Chim. Acta* 429 (2001):237–246.

72. O. Hermandeztores and J. J. Ariasleon, Preconcentration of copper in tap and sea water by use of chromotrope 2R immobilized on an anionic resin. *Int. J. Environ. Anal. Chem.* 54 (1993):15–26.
73. O. H. Torres, F. J. Moreno, A. J. Abiz, and J. J. A. Leon, Use of an azo derivative immobilized on an anionic resin for the determination of aluminium in water and dialysis fluids. *Clin.-Chim. Acta* 209 (1992):35–46.
74. P. Burba, Anion exchangers functionalized by chelating reagents (Anchel) for preconcentration of trace elements—capabilities and limitations. *Fresenius J. Anal. Chem.* 341 (1991):709–715.
75. D. Prabhakaran and M. S. Subramanian, Chemically modified chloromethylated resin as an effective metal chelator in the extraction of U(VI) and Th(IV). *Anal. Lett.* 36 (2003):2277–2289.
76. H. Egawa, T. Namaka, and H. Nonaka, Preparation and properties of macroreticular chelating resins containing armidoxime groups from styrene-(divinyl type compound) copolymer beads. *Nipponkagadu Kaishi* 6 (1993):752–760.
77. M. Pobi and J. Das, Synthesis of N-benzoyl phenyl hydroxylamine derivative of styrene divinylbenzene copolymer and its application in separation of zirconium and hafmium. *Anal. Lett.* 25 (1992):779–789.
78. V. M. Biju, J. M. Gladis, and T. Prasada Rao, Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications. *Anal. Chim. Acta* 478 (2003):43–51.
79. V. M. Biju, J. M. Gladis, and T. Prasada Rao, Effect of γ-irradiation of ion imprinted polymer (IIP) particles for the preconcentrative separation of dysprosium from other selected lanthanides. *Talanta* 60 (2003):747–754.
80. P. Gopikrishna, J. M. Gladis, T. Prasada Rao, and G. R. K. Naidu, Selective recognition of neodymium(III) using ion imprinted polymer particles. *J. Mol. Recognition* (in Press).
81. R. Garcia, C. Pinel, C. Madic, and M. Lemaire, Ionic imprinting effect in gadolinium/lanthanum separation. *Tetrahedron Lett.* 39 (1998):8651–8654.
82. J. M. Gladis and T. Prasada Rao, *Synthesis of Solid Phase Extractant Materials by Polymer Imprinting Suitable for Uptake of Uranyl Ions and a Process Thereof*, IPA/516 DEL, dt. 28.3.2003. (2003).
83. J. M. Gladis and T. Prasada Rao, Synthesis and analytical applications of uranyl ion imprinted polymer particles. *Anal. Lett.* 36 (2003):2107–2121.
84. J. M. Gladis and T. Prasada Rao, Effect of porogen type on the synthesis of uranium ion imprinted polymer materials for the preconcentration/separation of traces of uranium. *Mikrochim. Acta* 146 (2004):251–258.
85. P. Metilda, J. M. Gladis, and T. Prasada Rao, Influence of binary/ternary complex of imprint ion on the preconcentration of uranium(VI) using ion imprinted polymer materials. *Anal. Chim. Acta* 512 (2004):63–73.
86. S. Y. Bae, G. L. Southard, and G. M. Murray, Molecularly imprinted ion-exchange resin for purification, preconcentration and determination of UO_2^{2+} by spectrophotometry and plasma spectrometry. *Anal. Chim. Acta* 397 (1999):173–181.
87. A. Kimaro, L. A. Kelly, and G. M. Murray, Molecularly imprinted ionically permeable membrane for uranyl ion. *Chem. Commun.* (2001):1282–1283.
88. D. Sobhi, J. M. Gladis, and T. Prasada Rao, Synthesis of ion imprinted polymer material with palladium ion nanopores and its analytical application. *Anal. Chim. Acta* 488 (2003):173–182.
89. B. Sellergren, *Molecular Imprinted Polymers: Man-Made Mimics Antibodies and Their Application in Analytical Chemistry* (Amsterdam: Elsevier Science, 2001), Chapter 47.
90. P. A. G. Cormack and A. Z. Elorza, Molecularly imprinted polymers: synthesis and characterization. *J. Chromatogr*. B, 804 (2004):173–182.
91. G. Wulff, W. Vesper, R. Grove-Einster, and A. Sarhan, Grove-Einster and A. Sarhan, Enzyme-Analogue built polymers, 4) on the synthesis of polymers containing chiral cavities and their use for the resolution of racemates. *Makromol. Chem. and Physics* 178 (1977):2799–2816.
92. L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (London: Chapman and Hall, 1980).
93. J. M. G. Cowie, *Polymers: Chemistry and Physics of Modern Materials* (London: Blackey and Sons Ltd., 1991).

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