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The Use of Palmitoyl Hydroxyquinoline-Functionalized Amberlite XAD-2 Copolymer Resin for the Preconcentration and Speciation Analysis of Gallium(III)

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ABSTRACT

Gallium (Ga) is a valuable element in the electronics industry for manufacturing semiconductors and lasers. The processing of bauxite ores for the recovery of Ga, as well as high-level purification of the raw Ga product as required by electronic applications, necessitate effective speciation analysis of this element. For differentiating chemically important Ga(III) species, the Amberlite XAD-2 polystyrene-divinylbenzene copolymer was chloromethylated using $AlCl_3$ as a catalyst, and later, 5-palmitoyl-8-hydroxyquinoline was covalently bound to this chloromethylated product via Friedel-Crafts reaction, resulting in the synthesis of a Ga-specific resin (Amberlite XAD-2-P·Ox).

This resin has been shown to preconcentrate Ga selectively from basic aluminate solutions. The investigation of the effect of acidity on Ga recovery revealed that Ga was quantitatively retained on the resin between pH 3 and 7. The sorbed Ga could be eluted with 1 M HCl. A 100-mL volume of 2 ppm Ga showed 100% uptake by 10 g of resin using a flow rate of 1 mL/min. Here, all simple inorganic salts of Ga (e.g., Ga(III) nitrate, chloride, perchlorate), as well as the aquated Ga^{3+} (hexaaqua-complex) species, exhibit quantitative retention.

On the other hand, oxalate-, tartrate-, citrate-, acetylacetonate, and EDTA complexes of gallium(III) were not retained by the resin under identical conditions. Thus, the synthesized chelating cation-exchanger showed selective affinity to simple inorganic Ga(III) salts, in a way acting as an ion-selective electrode for Ga^{3+} while excluding coordinatively saturated stable Ga-complexes. The developed ion-exchange

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procedure was used to separate gallium from arsenate in a commercial gallium arsenide sample, followed by Ga determination without interference.

Key Words. Gallium speciation; Gallium preconcentration; Amberlite XAD-2 copolymer resin; Hydroxyquinoline-functionalized resin; Inorganic gallium; Gallium arsenide; Semiconductors

INTRODUCTION

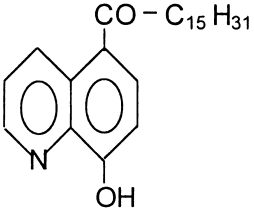
Gallium is widely used in the manufacture of semiconductor materials required by the electronics industry. During the Bayer processing of bauxite, gallium needs to be recovered from an alkaline solution containing relatively high amounts of aluminium. A commercial chelating agent known as Kelex 100, i.e., 7-dodecenyl-8-hydroxyquinoline, has been developed for the recovery of Ga by liquid–liquid extraction (1). After the development of 5-alkanoyl-8-hydroxyquinoline-type compounds as ion-flotation collectors of Ga by Koide et al. (2), Apak and Filik synthesized higher carbon chain alkanoyl oxines (3) to maintain the extracting ability of the parent oxine while decreasing its aqueous solubility in an alkaline medium. These compounds could selectively extract Ga using $CHCl_3$ as a solvent from a pH 13 aqueous solution containing twenty-fold aluminium. The problems arising from the relatively slow extraction rate and third-phase formation (4) have been solved by incorporating synergistic carbonyl compounds, e.g., 2-hexanone, and cationic surfactants such as CTAB, into the extraction medium (5).

The processing of bauxite ores for the recovery of Ga as well as high-level purification of the raw Ga product as required by electronics applications necessitate effective speciation analysis of this element. When hydroxyquinoline derivatives that show a high affinity for Ga(III) are immobilized on a nonpolar adsorbent such as Amberlite XAD-2 polystyrene-divinylbenzene copolymer, the resulting chelating ion-exchanger exhibits a high selectivity for Ga over Al in a strongly alkaline solution, enabling the separation of Ga from Al present in the Bayer aluminate liquor (6). Such a chelating resin capable of selectively preconcentrating and separating Ga from an alkaline solution was also assumed to differentiate the chemically important Ga(III) species.

Persaud and Cantwell have developed the XAD sorbent, i.e., macroporous styrene-divinylbenzene copolymer Amberlite XAD-2 onto which oxine (8-hydroxyquinoline) has been covalently attached, for free Mg^{2+} determination in aqueous solutions (7).

The method of synthesis of the Amberlite XAD-oxine was that of Warshawsky et al. (8, 9), based on the methylene linkage of oxine to the copolymer backbone, which was superior to the azo linkage method (10, 11) that leaves residual amine groups on the polymer. The fixing of oxine by an azo group gives limited stability to acidic and oxidizing media as well as a second chelating group with the $-N=N-$ functionality (12).

Although the Amberlite XAD-oxine sorbent prepared according to Persaud and Cantwell's procedure (7) exhibits a relatively high capacity for Mg(II) at neutral pH, its synthesis requires the presence of a 5-chloromethylated oxine intermediate, which may pose problems when 5-alkanoyl oxines (see structural formula below) are substituted for the parent oxine, i.e., the 5-alkanoyl substituent hinders the occupation of the 5-position by a $-CH_2Cl$ group. Thus, the chloromethylation of the macroporous copolymer in the first stage, followed by Friedel-Crafts alkylation of the oxine derivative with this chloromethylated intermediate as follows for pure oxine by Seubert et al. (12), is a more reasonable alternative.



5-Palmitoyl oxine (P.Ox)

EXPERIMENTAL SECTION

Reagents and Solution

Oxine (8-hydroxyquinoline), palmitic acid, anhydrous aluminium chloride, and sodium sulfate, NaOH, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, $NaClO_4$ concentrated solutions of HCl, HNO_3, $HClO_4$, H_2SO_4 (analytical reagent grade), Na_2-EDTA, trisodium citrate, oxalic acid dihydrate, tartaric acid, acetic acid, sodium acetate, ammonium acetate, $Na_2HAsO_4 \cdot 7H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, stannous chloride (crystallized), metallic Ga (LAB), ether, ethanol, acetone, $CHCl_3$, methylene chloride, nitrobenzene, octanol, glycerol, and thionyl chloride (for synthesis) were purchased from E. Merck, acetylacetone from Riedel de Haen, and Amberlite XAD-2, a copolymer of styrene and divinylbenzene (40–60 mesh) from Rohm and Haas. The gallium arsenide semiconductor sample was received from TUBITAK (Turkish Scientific Research Council) Marmara Research Centre Laboratories. As described previously, 5-palmitoyl-8-hydroxyquinoline (P·Ox) was synthesized by a modified route based on the Fries rearrangement (4).

The gallium(III) stock solution was prepared by dissolving Ga metal in dilute nitric acid with some HCl, evaporating to expel nitrogen oxide fumes, and diluting to volume with 1% HCl. Working solutions of Ga were prepared from the stock solution.

Other solutions used for Ga speciation analysis were $NaClO_4$ (2.0 M), 8-hydroxyquinoline (0.5% w/v), pH 7 buffer (1.0 M CH_3COONH_4), pH 5 buffer (prepared by dilution from a mixture of 0.2 M CH_3COOH and 0.2 M CH_3COONa), disodium EDTA (2.87×10^{-3} M), sodium citrate (2.87×10^{-3} M), oxalic acid (5.74×10^{-3} M), tartaric acid (5.74×10^{-3} M), $Na_2HAsO_4 \cdot 7H_2O$ (1.0×10^{-3} M), ammonium heptamolybdate (first prepared in 56 wt% H_2SO_4, then diluted with water to yield 0.02 M solution), and $NaNO_3$ (8.61×10^{-3} M) were all prepared in distilled water. Stannous chloride solution (2.5 g $SnCl_2 \cdot 2\,H_2O$ per 100 mL) was prepared in glycerol.

Instrumentation

A Cary 1E UV-Vis spectrophotometer equipped with quartz cuvettes was used for spectrophotometric Ga measurements in the column eluates. The oxinized copolymer was characterized by a ATI Unicam (Mattson 1000) FT-IR spectrometer in KBr disks. The metal determinations were confirmed by N_2O-acetylene flame AAS using a Varian 220 AAFS atomic absorption spectrometer. The pH values of the solutions were measured with a Metrohm E-512 pH-meter. Batch equilibration of the solution with the resin was performed by using a NÜVE ST 402 thermostatic water bath-shaker. The column experiments were performed using a ø 1-cm pyrex glass column partly filled with 5–10 g of resin, as appropriate.

Synthesis of the Amberlite XAD P·Ox Sorbent

The preferred route of synthesis of the oxinized copolymer was a modified procedure of that of Seubert et al. (12). To 2 g of Amberlite XAD-2 resin (40–60 mesh) were added 10 mL octanol and 20 mL methylene chloride previously dried over anhydrous Na_2SO_4; 5 g of anhydrous $AlCl_3$ were added in small increments to the mixture while cooling, and the final mix was heated for 24 h under a reflux condenser. The product was isolated by filtration, washed once with acetone and twice with 1 : 1 aqueous HCl, finally washed with water until neutral, then with acetone, and dried in a vacuum.

The dried intermediary product, i.e., chloromethylated copolymer, was transfered to a flask, 30 mL nitrobenzene was added, and finally 3 g palmitoyl oxine hydrochloride with continuous stirring. The reaction was continued at 70°C for 72 h. At the end of this period, the solvent nitrobenzene was removed by filtration, and the product was washed twice with 1 : 1 aqueous HCl, then with $CHCl_3$, alcohol, and ether. The final product was heated in ethanol for 2 h, filtered and dried in a vacuum to yield the amberlite XAD-P·Ox sorbent. The resin was left to expand in 1 : 1 alcohol–water before usage. The covalent binding of the P·Ox on the resin was tested by IR-spectrometry.

Procedures

The column-retained Ga was eluted with 1–2 M HCl using a flow rate of 2 $mL \cdot min^{-1}$. Gallium determinations in eluate portions were carried out by extraction of gallium oxinate from a pH 7 solution with $CHCl_3$ using the spectrophotometric method of Moeller and Cohen (13), where the molar absorptivity for Ga was $\varepsilon_{392\,nm} = 6.5 \times 10^3\ L \cdot mol^{-1} \cdot cm^{-1}$. For this purpose, 2 mL of the acidic (1 M HCl) eluate was buffered with 2 mL pH 7 buffer (1 M CH_3COONH_4 solution), and to this mixture 1 mL of the oxine solution was added. Extraction was made with 5 mL $CHCl_3$ for 5 min. The organic phase was separated, dehydrated with anhydrous Na_2SO_4, and filtered through a blue-band Whatman filter paper. The absorbance of this solution was measured at 392 nm against a reagent blank extracted in the same manner.

For optimal pH determination in column preconcentration and speciation analysis, 2 mL of the 100 ppm Ga^{3+} solution was partly diluted with water. Then 10 mL of dilute HCl or suitable buffer were added to give a final pH from 1 to 8, and the final mixture was passed through the resin column at a rate of 12 $mL \cdot min^{-1}$, and the eluate was analyzed for Ga.

Distribution coefficients ($D = C_{Ga(org)} / C_{Ga(aqueous)}$) and selectivities ($S = D_{Ga(NO_3)_3} / D_{GaL}$) for the ligands (L): oxalate, tartrate, citrate, and EDTA, were also investigated as a function of pH. For this purpose, 2 mL of the 100 ppm Ga solution were mixed with the corresponding ligand (L) solution such that the mole ratio of Ga-to-L was 1 : 1 for L : EDTA or citrate, 1 : 2 for L : $C_2O_4^{2-}$ or $C_4H_4O_6^{2-}$, and 1 : 3 for L : NO_3^-. The mixtures were brought to the desired pH from 2 to 7, and contacted batchwise with the resin for 4 h in 250-mL volumetric flasks using a liquid-to-solid ratio of 100 : 1. After equilibration, the resin was filtered off, and the filtrate was analyzed for Ga. The problem encountered with Ga-EDTA solutions in analyzing the filtrates by Moeller and Cohen's method (13) was overcome by evaporating a suitable aliquot of the filtrate to dryness, destructing the organic matter by $H_2SO_4 + HClO_4$ evaporation, and extracting the neutralized residue (obtained by wet ashing) with oxine/$CHCl_3$.

Distribution coefficients and selectivities for Ga-L solutions were also studied as a function of time at a constant pH of 5.0. Ga-to-L mole ratios were chosen as described previously for pH dependence. The chosen pH of 5.0 was maintained by an acetate buffer. The batch contact periods were varied from 10 to 60 min. The adsorption isotherm of Ga on the resin was established at the selected pH and contact time.

The ionic strength (μ) dependency of Ga(III) uptake from a 2.87×10^{-5} M gallium solution at pH 5 was studied between $0.001 \leq \mu \leq 0.01$ ($NaClO_4$).

The feasibility of analyzing $Ga(NO_3)_3$ in the presence of GaL by using the developed resin column was studied by mixing $Ga(NO_3)_3$ and GaL solutions in the mole ratio of 0.1 : 1.0. When GaL solutions at a fixed concentration of 2.87×10^{-4} M were mixed with $Ga(NO_3)_3$ solutions of variable concentrations from 2.87×10^{-5} to 2.87×10^{-4} M, the expected selective preconcentration and separation of $Ga(NO_3)_3$ by the column were not achieved. When these analytical concentrations were decreased roughly by an order of magnitude, e.g., GaL was kept constant at 4.08×10^{-6} M, while $Ga(NO_3)_3$ was varied from 4.08×10^{-7} to 4.08×10^{-6} M, the goal of retaining $Ga(NO_3)_3$ quantitatively while excluding GaL was achieved.

In all these experiments, the prior equilibration of gallium with the chosen ligand (L) was ascertained by heating at 70–90°C (with the exception of oxalic acid, the most heat-sensitive organic acid tested, where care was taken not to exceed 55–60°C to avoid thermal decomposition) for $\frac{1}{2}$ h when necessary. Thus, the formation of GaL complexes was complete before competition with $Ga(NO_3)_3$ in the column.

The capacity of the sorbent for Ga at pH 5.0 was found by passing 10-mL portions of 1.43×10^{-4} M gallium solution through 5 g resin, followed by the mathematical integration of the breakthrough curve up to the throughput volume where saturation was attained with 200 mL of solution.

The developed ion-exchange technique for the preconcentration of Ga was applied to a real sample, i.e., GaAs semiconductor material containing 48.2% Ga and 51.8% As. For this purpose, a 0.0100 g GaAs sample was dissolved in aqua regia (3 HCl + 1 HNO_3, v/v), brought twice to dryness, and the residue was taken up with 0.5 M HCl and diluted to 100 mL with the same solution yielding a final Ga concentration of 6.91×10^{-4} M. A 1.16-mL aliquot was taken, 5 mL of 0.2 M acetate buffer (pH 5) was added, and diluted to 50 mL with water. This solution was passed through the column, and the effluent was tested for arsenate by the molybdenum blue spectrophotometric method, i.e., 2 mL molybdate followed by 0.25 mL stannous chloride solution were added, with 10–12 min allowed for color development. The column-retained Ga was eluted with 20 mL of 1 M HCl, and Ga was spectrophotometrically determined in the eluate by the oxine method (13).

RESULTS AND DISCUSSION

Seubert et al.'s procedure (12), in preference to that of Persaud and Cantwell (7), proved efficient for the covalent linkage of palmitoyl oxine to the Amberlite XAD-2 copolymer by comparison of the IR spectra of the oxinized resin to that of the copolymer backbone. When the parent oxine compound, i.e., 8-hydroxyquinoline itself, was covalently attached to the copolymer by the latter method, the product resin did not show stability in a strong alkaline solution, necessitating the usage of a long C-chain oxine derivative such as P·Ox for limiting alkaline aqueous solubility.

It was previously shown that 2 mg Ga retained at pH 5 in the resin could be quantitatively eluted with 25 mL of 2 M HCl solution on the condition that the flow rate did not exceed 2 mL·min^{-1} (6). A 100-mL volume of 2 ppm Ga solution from pH 3 to 7 showed 100% uptake by 10 g resin. Here, all simple inorganic salts of Ga (nitrate, sulfate, chloride, acetate, etc.), as well as aqua complexes, exhibit quantitative retention.

Figure 1 shows that Ga^{3+} (as gallium nitrate) is quantitatively retained by the column from pH 3 to 7. Thus a pH within this interval should be selected for preconcentration and speciation analysis.

Figures 2(a) and 2(b) show the variation of distribution coefficients and selectivities, respectively, as a function of pH in batch equilibration. Although the highest selectivity was not attained at pH 5, this pH was chosen for further speciation analyses because higher pH would give rise to hydrolytic interference when other heavy metals are present. Especially in a column where the recommended preconcentration and speciation analysis would be performed, any hydrolytic precipitates would cause clogging of the resin material. The

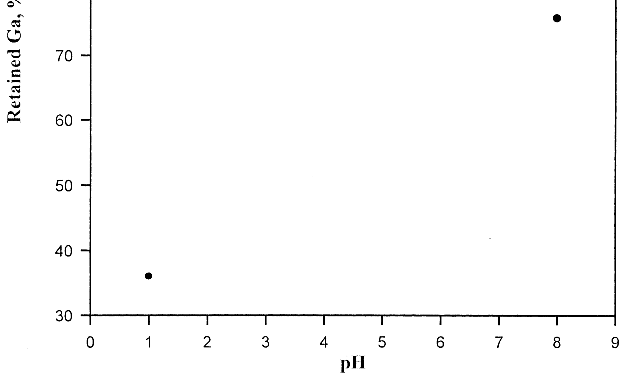


FIG. 1 Column retention percentage of Ga (as gallium nitrate) as a function of pH.

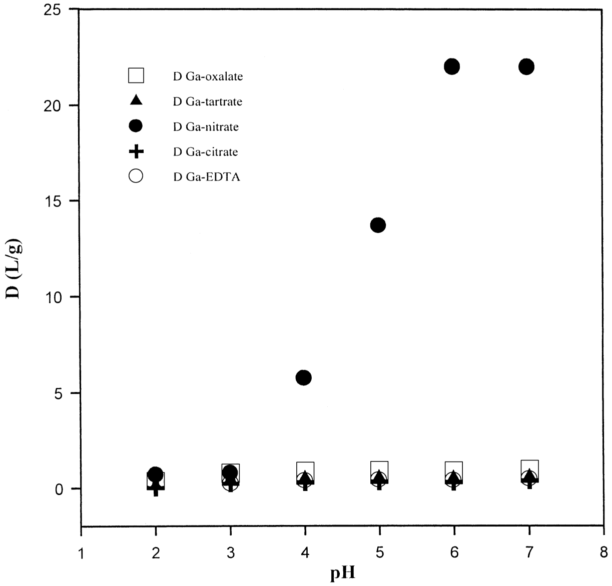


FIG. 2(a) D vs. pH [distribution coefficient of $Ga(NO_3)_3$ and GaL complexes as a function of pH].

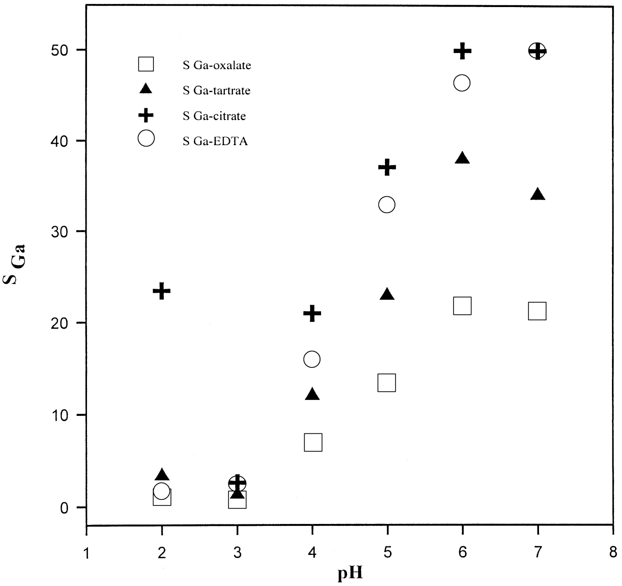


FIG. 2(b) S vs. pH [selectivities of $Ga(NO_3)_3$ over various GaL complexes as a function of pH]; equilibration time = 4 h.

problem encountered in analyzing the filtrates from Ga-EDTA equilibration by Moller's method was due to the high stability of GaY^- comparable to that of gallium oxinate, the latter of which was responsible for color development as the basis of spectrophotometric Ga determination. Therefore destruction of organic matter by wet ashing was necessary in this case prior to analysis.

Figures 3(a) and 3(b) show the variation of distribution coefficients and selectivities, respectively, as a function of batch contact time at a constant pH of 5.0 adjusted by employing a final concentration of 0.02 M as total acetate species. A contact period of 40 min would give optimal separation in batch experiments.

The isotherm for Ga(III) adsorption on the resin (equilibrated by batch contact at a liquid-to-solid ratio of 100 : 1) exhibited an S-type curve conforming to a BET isotherm of multilayered adsorption (see Fig. 4). On the other hand, the breakthrough curve enabling the calculation of the resin capacity for Ga(III) (see Fig. 5) was established under dynamic column conditions. The upper part of C/C_0 vs. effluent–volume curve was integrated to yield a column capacity of 3.15 μmol Ga per g-resin.

$Ga(NO_3)_3$ solutions from 4.08×10^{-7} to 4.08×10^{-6} M could be retained by the resin whereas 4.08×10^{-6} M GaL solutions (L : EDTA, oxalate, tartrate, citrate, and acetyl acetone) were not retained from Ga-nitrate + GaL

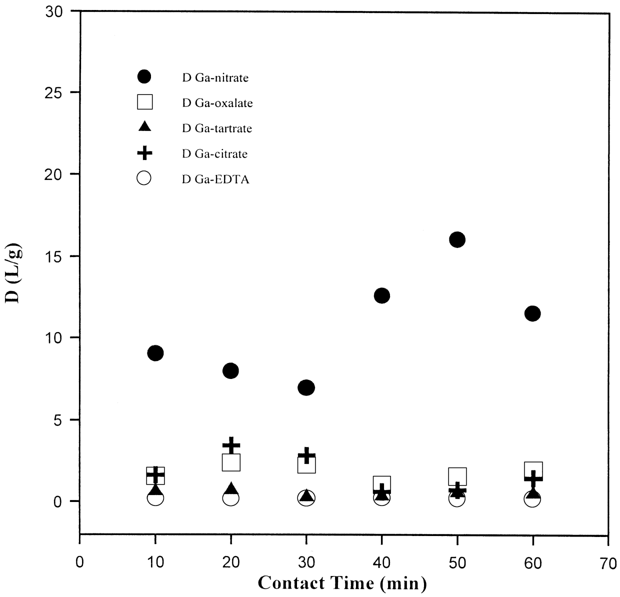


FIG. 3(a) Distribution coefficients as a function of batch contact time.

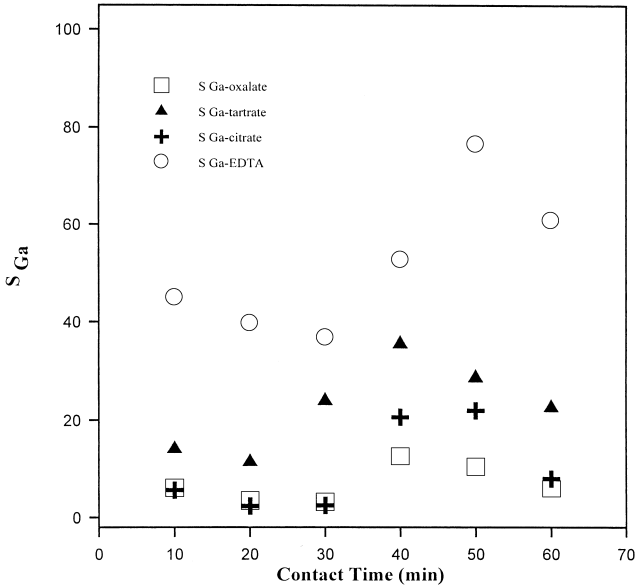


FIG. 3(b) Selectivities of $Ga(NO_3)_3$ over various GaL complexes as a function of batch contact time; (pH = 5.0 constant).

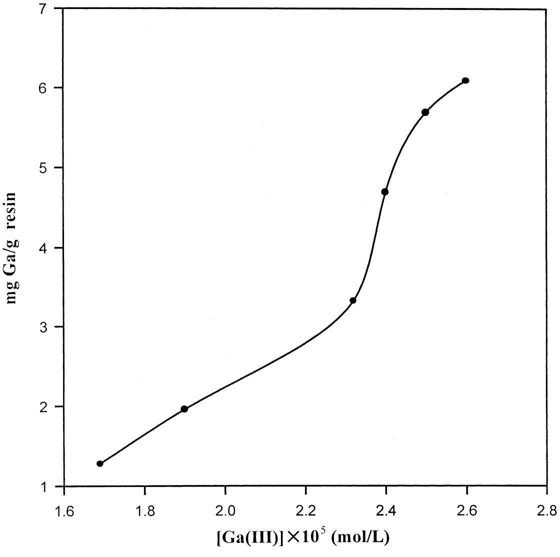


FIG. 4 Adsorption isotherm of Ga(III) on the resin; (100 mL of Ga solution was equilibrated with 1 g of resin for 4 h).

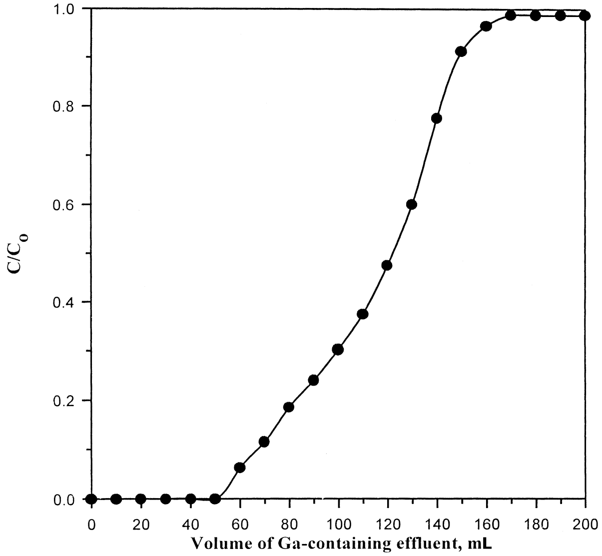


FIG. 5 The breakthrough curve enabling the calculation of column capacity of the resin for Ga ($C : C_0$ is the ratio of Ga concentration of the column effluent to that of the feed solution; C_0: 1.43×10^{-4} M Ga(III), pH: 5.0).

mixtures in 0.1 : 1.0 mole ratio. These ligands were selected on the basis of their importance in industrial and commercial usage of Ga, e.g., Ga-67 citrate has diagnostic use in tumor detection, and Ga-EDTA is used for labeling proteins and antibodies (14–16).

The relative concentration (abundance) of the coordinatively saturated complex GaL_k (L : organic acid chelating agent) in a medium containing Ga-L, Ga-L′ (L′: inorganic ligands) and Ga-OH complexes is denoted with α_{GaL_k} where

$$\alpha_{GaL_k} = \beta_k[L]^k/(1 + \sum_{i=1}^{n} \beta_i[L]^i + \sum_{j=1}^{n} \beta_j[L']^j + \sum_{l=1}^{n} \beta_l[OH]^l) \qquad (1)$$

Now, although ligands like citrate (Log $K_1 = 20.0$), acetylacetonate (Log $K_1 = 9.5$, Log $\beta_2 = 17.9$, Log $\beta_3 = 23.6$), and EDTA (Log $K_1 = 20.3$) form relatively stable complexes with Ga(III) rendering these species as the predominant ones in aqueous solution, the less stable complexing ligands like oxalate (Log $K_1 = 7.5$, Log $\beta_2 = 13.6$, Log $\beta_3 = 18.5$) and tartarate (Log $\beta_2 = 9.8$) (see Fig. 2(b) for lower selectivities of inorganic Ga salts over complexes formed with these latter ligands at pH 5) may not effectively compete with hydroxide (Log $K_1 = 11.0$, Log $\beta_2 = 21.7$) in terms of thermodynamic stability of corresponding complexes at neutral-to-weakly-acidic pH. However, ligand exchange with OH^- or binding to the oxine-functionalized resin may be kinetically so slow that the inert Ga-L complexes are not practically held by the resin under the optimized working conditions (concentration, pH etc.) during flow. No common inorganic anions studied (NO_3^-, SO_4^{2-}, Cl^-, etc.) formed a Ga complex of significant stability compared to those of the chelating organic acids, and acetate, the buffering substance, formed a weak (Log K < 2.5) and noncompetitive complex that does not obstruct the retention of inorganic Ga species. Even hydroxide, the strongest complex-forming inorganic anion, does not prevent the selective uptake of inorganic Ga complexes by the palmitoyl oxine-functionalized resin (Log β_3 of analogous Ga-oxinate $= 40.8$) as demonstrated in previous work regarding the preconcentration of Ga from strongly alkaline solution (6) with this resin (stability constants of various complexes mentioned were collected from various sources such as Lange's "Handbook of Chemistry" and Meites' "Handbook of Analytical Chemistry").

At the low concentration levels studied, the prepared resin could act as a selective speciation-preconcentration agent for inorganic Ga species as if it were an ion-selective electrode. Because coordinatively saturated GaL complexes are excluded by the resin under the selected optimal conditions, many important ligands used in the processing and purification of valuable Ga compounds could be distinguished from inorganic Ga species by using this resin in column form. On the other hand, this separation would not work at higher concentrations as Persaud and Cantwell suggested for Mg determination (7), because some GaL would accompany $Ga(NO_3)_3$ held by the resin phase. When the inorganic Ga(III) in solution is not totally sorbed, the chelating resin titration (CRT) technique might increase sorption, CRT was used for nonquantitative Cu(II) or Cd(II) sorption on an iminodiacetic chelating resin (17) based on the determination of the concentration of metal ion sorbed on the resin at different liquid-to-solid ratios. In that case, a good correlation was reported between the total concentration of the metal ion in solution and that found by CTR.

The reported preconcentration/determination ion-exchange technique for Ga is believed to have potential usage in the indirect determination of the formation constants of some stable complexes for which excess alkali hydroxide addition and HCl back-titration are carried out according to the reaction

$$Ga(OH)_4^- + L^{n-} + 4H^+ \rightleftharpoons GaL^{(n-3)-} + 4\,H_2O \qquad (2)$$

In this manner, the stability constants of over 20 Ga(III) complexes—which were fully formed at low pH (~2)—have been measured and reported (18). If $Ga(OH)_4^-$ in such a medium is in excess of L^{n-}, i.e., the strong complexing ligand, both inorganic Ga(III)—as hydroxo complexes—and strongly complexed Ga(III)—as $GaL^{(n-3)-}$ species—may be determined simultaneously by the proposed method because the synthesized ion-exchanger resin efficiently concentrated Ga in a strongly basic medium, as reported elsewhere (6).

There was some difficulty in stripping the retained Ga from the resin column in the presence of $NaClO_4$ (between 10^{-3} and 10^{-2} M concentrations) where the strength of the HCl solution used in stripping was increased to 6 M to force effective removal. This cannot be interpreted on the basis of pure ion exchange because ion-exchange-held Ga should be normally eluted with dilute HCl as described in the conventional procedure. Previous investigations (5) had shown that the solvent-extracted Ga-alkanoyl oxinate (L) had a stoichiometry of $[GaL_2]^+$, leaving a positively charged chelate. Likewise, the resin-held gallium as a cationic species may form an ion-association complex with the relatively large anion ClO_4^-, thus possibly explaining strong adsorption on the resin.

Analysis of gallium arsenide semiconductor material yielded the claimed weight percentages of 48.2% Ga and 51.8% As with ±2% error (in the analysis of three aliquots of the column effluent and HCl eluate containing the arsenate and gallium, respectively). The final solution obtained from the dissolution of GaAs contained equimolar (1.6×10^{-5} M) concentrations of Ga^{3+} and AsO_4^{3-}, and the retention of Ga(III) by the palmitoyl oxine-functionalized resin was not interfered by arsenate(V), which was rejected by the column. This showed that AsO_4^{3-}, like the other common inorganic anions studied in speciation analysis, did not prevent the uptake of uncomplexed Ga(III) by the resin because arsenate(V) neither forms a complex with Ga(III) nor binds to the oxine-based resin. According to the HSAB (Hard and Soft Acids and Bases) theory put forward by Pearson (19), the functional group of the resin is 8-hydroxyquinoline (oxine), which is a hard base showing an affinity for the hard Lewis acid Ga(III), and not for the soft arsenate. However, the concentrations used in the analysis of GaAs material were 1 to 2 orders of magnitude higher than those used in speciation analysis, because a delicate separation of species having somewhat close distribution coefficients was not required in this case.

CONCLUSION

When 5-palmitoyl-8-hydroxyquinoline was covalently bound to chloromethylated Amberlite XAD-2 polystyrene-divinylbenzene copolymer, the resulting resin, which was shown to preconcentrate Ga from alkaline aluminate solution, proved to be efficient in preconcentration/speciation analysis of inorganic Ga-species in the presence of coordinatively saturated complexes of Ga with EDTA, citrate, oxalate, tartrate, and acetylacetonate. Thus the preparation and purity of commercially important Ga-chelates could be followed and controlled by simultaneously measuring the accompanying simple inorganic salts of Ga(III) remaining in solution. The developed procedure was applied to Ga analysis in a commercial semiconductor sample of gallium arsenide.

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