Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Separation of Uranium using Alizarin Red S (ARS)-Modified Anion-Exchange Resin or by Flotation of U-ARS Chelate

Magdi E. Khalifa

To cite this Article Khalifa, Magdi E.(1998) 'Selective Separation of Uranium using Alizarin Red S (ARS)-Modified Anion-Exchange Resin or by Flotation of U-ARS Chelate', Separation Science and Technology, 33: 14, 2123 — 2141
To link to this Article: DOI: 10.1080/01496399808545719
URL: http://dx.doi.org/10.1080/01496399808545719

SEPARATION SCIENCE AND TECHNOLOGY, 33(14), pp. 2123–2141, 1998

Selective Separation of Uranium Using Alizarin Red S (ARS)-Modified Anion-Exchange Resin or by Flotation of U–ARS Chelate

MAGDI E. KHALIFA
DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MANSOURA
MANSOURA, EGYPT

ABSTRACT

An alizarin red S (ARS)-modified anion-exchange resin was prepared by a simple reaction of ARS with the anion exchanger Doulite A101 and used for the efficient sorption of uranium from aqueous media. The effect of various parameters on the sorption of U(VI) (pH effect, sorption kinetics, resin capacity and breakthrough curves) was investigated. The modified resin sorbs U(VI) over a wide range of pH (2.8–5) with a maximum sorption capacity of 0.68 mmol·g^{-1} at pH 3.2 to 4.0. Iron (III), Zr(IV), Ti(IV), Cu(II), and Th(IV) ions are also sorbed to different extents, but Be(II), Bi(III), Ca(II), Mg(II), Pb(II), Hg(II), Zn(II), Cd(II), Al(III), Mn(II), Co(II) and Ni(II) are not sorbed; thus, conditions for separating U(VI) from these metal ions have been identified. For eluting U(VI) from the resin, 0.2 mol·L^{-1} HCl was used and the recovery recorded was as high as 99.9%. The use of ARS is extended to float uranium quantitatively and selectively from aqueous media at pH ≈ 4 by using oleic acid as a surfactant. The different parameters affecting the flotation process have also been investigated. Uranium(VI) has been effectively separated from natural water samples and certified uranium ores using both procedures.

Key Words. Uranium(VI) separation; Alizarin red S modified resin; Flotation

INTRODUCTION

Various methods for the separation and/or preconcentration of metal ions prior to their determination are available (1–3). These methods include vola-

tilization, liquid–liquid extraction, selective dissolution, sorption, ion exchange, liquid chromatography, flotation, freezing, and zone melting. The use of uranium in reactors places stringent demand on the level of impurities, particularly those of nuclear interest. Further, the presence of uranium in seawater at concentrations of ~3 ppb associated with other heavy metal ions makes its separation of special interest (4). Several approaches for separation of U(VI) from its matrix constituents using different tools have been reported (5–7). Solvent extraction procedures are mostly used for separation of uranium (8). However, such treatment is relatively expensive, particularly when prepurification of the ore is needed (9). Though the use of ion-exchange resins might minimize the cost of uranium recovery, these methods suffer from the presence of a high concentration of electrolytes. Sodium chloride is used to elute uranyl citrate sorbed on an anionic exchanger resin (10). Relatively few chelating ion exchangers (11, 12) have been used for the separation and preconcentration of U(VI), among which resins containing amidoxime group are worthy of mention (13–15). These resins show a selective absorption ability for uranium in seawater. Resins containing the quinalidinic acid amide group (16) and *N*-phenyl- and *N*-methyl-substituted hydroxamic acid (17) have also been applied for the selective separation of uranium. Recently Lee et al. (18) studied the sorption behavior of uranium on a chelating resin containing 4-(2-thiazolylazo) resorcinol as the functional group. Also, a new chelating resin in which *p-tert*-butylcalix[8]arene is incorporated into a polymeric matrix has been synthesized and used for the selective separation of uranium and thorium from other metal ions (19). The use of the flotation technique for separation of uranium has the particular merit of providing quick, quantitative, and selective separation under proper conditions. The conditions suitable for the flotation of U(VI) from aqueous solutions, wastes, and natural waters (20–25) have been reported.

In this work a strongly basic anion-exchange resin, Doulite A101, has been modified with alizarin red S (ARS) and its sorption behavior toward U(VI) has been investigated in batch and column modes. Alternatively, the use of ARS for the flotation and separation of U(VI) from aqueous solutions is investigated. The two procedures were successfully applied to separation of U(VI) from natural water and certified U ores. A literature survey indicated that little information is available about the use of ARS for the preconcentration of transition metal ions (26). Neither information concerning the use of ARS for the flotation of U(VI) or the presence of a resin containing the ARS moiety seems to have been reported.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out on a Unicam UV2-100, UV-Visible spectrometer in the 350–650 nm range using 1 cm matched

quartz cells. The concentration of the metal ions used was determined with a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. The infrared spectra were obtained using a Mattson 5000 FT-IR spectrometer as KBr discs. The pH measurements were carried out with a Hanna Instrument 8519 pH-meter with a combined glass electrode. In column operation, a funnel-tipped glass column with a length of 10 cm and an i.d. of 8 mm was packed with 3.0 g of dry resin. The resin was initially swollen with 0.05 mol·L^{-1} HCl and then washed with deionized water, followed by acetate buffer (pH 3.5). The flow rate was adjusted to 0.5–1.0 mL·min^{-1}. The flotation cell was a tube of 16 mm i.d. and 29 cm length, with a stopcock at the bottom.

Reagents

Unless otherwise specified, all reagents used were of analytical reagent grade. Working solutions were prepared by appropriate dilution with doubly distilled water.

A uranium(VI) stock solution of 4.2×10^{-3} mol·L^{-1}, equivalent to 1000 ppm, was prepared from uranyl acetate (B.D.H.) by weighing 0.4455 g of $UO_2(CH_3COO)_2 \cdot 2H_2O$ and dissolving it in 250 mL water in a calibrated flask. Solutions of other foreign metal ions were prepared by dilution from standard 1000 ppm solutions (B.D.H.).

An ARS stock solution of 5×10^{-3} mol·L^{-1} was prepared by dissolving 0.4503 g of alizarin red S (Riedel de Haen, AG) in 250 mL water in a calibrated flask.

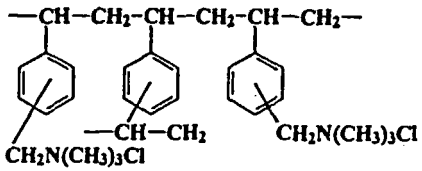
The anion-exchange resin Duolite A101, particle size 0.044–0.074 mm, was purchased from Rohm and Haas. An oleic acid (HOL) stock solution (6.36×10^{-2} mol·L^{-1}) was prepared by dispersing 20 mL of oleic acid, food grade ($d = 0.895$), in 1 L of kerosene.

The pH values of the solutions were maintained by using one of the following buffers: hydrochloric acid (HCl)–glycine (pH 1–2.5), acetic acid–sodium acetate (pH 3–4.2), hexamine–nitric acid (pH 4.3–8), and sodium borate–hydrochloric acid (pH 8–9). The ionic strength of these buffer solutions was kept constant at 0.2 mol·L^{-1} by using 0.5 mol·L^{-1} KNO_3 solution. The pH of solutions in flotation experiments was adjusted with hydrochloric acid and ammonia to avoid the effect of buffer constituents on the flotability of the U–ARS chelate.

Preparation of ARS–Duolite A101 Modified Resin

Duolite A101 is a strongly basic anion-exchange resin, gel type, commercial grade, which corresponds to Diaion SA 10 A, Amberlite IR A-400, and Dowex SBR, and has the constitutional formula shown by Structure I (27).

To attain its complete reactivity before interaction with ARS, the resin was washed with 0.05 mol·L^{-1} hydrochloric acid, distilled water, 0.05 mol·L^{-1}



STRUCTURE I

NaOH solution, plenty of doubly distilled water, and then dried at 60°C for 12 hours This resin (15 g) was added portion by portion to 250 mL of a hot (90°C) aqueous solution of 3% ARS; the solution was maintained hot on a magnetic stirrer for 3 hours. The fading of the red color of the ARS solution and the coloration of the resin to intense red were taken as indications of the progress of the reaction. After cooling, the mixture was filtered off and the resin was thoroughly washed with doubly distilled water. The color of the modified resin is affected by the variation of the pH of the solution in a manner similar to that of the ARS monomer: yellow at pH $\leq$ 4, orange to intense red in the 4–8 pH region, and violet at pH $>$ 9.

Optimum pH for Uranium Uptake

The optimum pH for uranium uptake was determined using the batch equilibrium technique. Excess metal ion (50 mL of 4.2×10^{-4} mol·L^{-1}) was shaken with 0.2 g of resin for 30 minutes in the presence of different buffer solutions over the 2.5–6 pH range. After equilibrium, the resin was filtered through a sintered glass Gooch (G_4), and the sorbed uranium ion was eluted with 5 mL of 0.2 mol·L^{-1} hydrochloric acid. The concentration of U(VI) was determined spectrophotometrically using the Arsenazo III method (28).

Determination of Resin Capacity

The capacity of the resin was determined by shaking excess uranium ion, 50 mL of 4.2×10^{-4} mol·L^{-1}, with 0.2 g of resin for 4 hours at the optimum sorption pH. The resin was filtered off, and the sorbed uranium was eluted and determined as described above.

Kinetics of Uranium Sorption

To determine the time required for complete separation of uranium, five similar samples, having 50 mL of 2.1×10^{-4} mol·L^{-1} U(VI) for each at

the optimum pH, were shaken with 0.2 g of the resin at different time intervals (5, 10, 20, 30, 40, and 60 minutes). Then the concentration of sorbed uranium was determined.

Effect of Diverse Metal Ions

The effect of diverse ions which usually accompany uranium in its ores (alkali and alkaline earth elements, Al^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Th^{4+}, Ti^{4+}, and Zr^{4+}) on the recovery of uranium from aqueous solutions has been investigated. For this, 50 mL solutions containing 100 $\mu g \cdot mL^{-1}$ U(VI) and other metal ions in various amounts (100–200 $\mu \cdot mL^{-1}$ for each) were buffered and equilibrated with the resin at pH 3.5. Uranium(VI) retained on the resin was eluted and analyzed. The concentration of foreign ions was determined in the mother liquor by AAS. Diethylenetriaminepentaacetic acid trisodium salt (Na_3DTPA) was used to suppress the chelation of Cu^{2+}, Th^{4+}, Fe^{3+}, Zr^{4+}, and Ti^{4+} with the resin (29).

Preconcentration and Separation of U(VI)

The batch equilibrium technique was used to concentrate trace amounts of uranium. A sample solution (300–600 mL) containing 2.1×10^{-4} $mmol \cdot L^{-1}$ U(VI) was buffered at the optimum pH for sorption and then shaken with 0.2 g of the resin for 15 minutes. After filtration, the sorbed U(VI) was eluted with 5 mL of 0.2 $mol \cdot L^{-1}$ HCl and then the concentration of U(VI) ions was determined in the concentrate.

Recommended Procedure for Flotation of U(VI)–ARS Chelate

In a 50-mL beaker, 1 mL of 10^{-4} $mol \cdot L^{-1}$ U(VI) was mixed with 1 mL of 5×10^{-4} $mol \cdot L^{-1}$ ARS, 2 mL of 1 $mol \cdot L^{-1}$ Na_2SO_4, and 2 mL of 1×10^{-2} $mol \cdot L^{-1}$ DTPA (to overcome any possible interference). The pH of this solution was adjusted using a few drops of 1.0 $mol \cdot L^{-1}$ HCl. The solution was conditioned for 2 minutes to ensure complete reaction between U(VI) and ARS. Then it was transferred quantitatively to the flotation cell and completed up to 10 mL with doubly distilled water. Three millititers of HOL solution (1.27×10^{-3} $mol \cdot L^{-1}$) were added to this 10-mL solution. The flotation cell was then inverted 20 times by hand while opening the stopcock after each inversion to allow for the entry of air (30). Vigorous shaking of the flotation cell in the presence of the surfactant HOL led to the creation of bubbles in the solution, which enhanced the flotability of the U(VI)–ARS chelate. The amount of U(VI) in the mother liquor or in the scum (after

stripping with 5 mL of 0.2 mol·L^{-1} HCl) was determined spectrophotometrically.

Flotability (%F) was calculated from

$$\%F = \frac{a_0 - a_1}{a_0} \times 100\ (\%)$$

where a_0 and a_1 denote the concentrations of uranium in the solution before and after flotation, respectively.

Separation and Determination of Uranium in Certified Ores

A weighed amount of the certified ore (150–250 mg) was digested with 10 mL of aqua regia and heated to near dryness. Then the sample was heated with 5 mL of concentrated sulfuric acid for 30 minutes. The solution was then diluted and neutralized with NaOH, evaporated, and the remaining solid was ignited at 800–850°C for a short time (5–10 minutes). Sulfates were converted to the corresponding oxides under these conditions. These oxides were boiled with concentrated nitric acid to near dryness, cooled, and diluted with doubly distilled water in a 100-mL calibrated flask. After adjusting the pH of the ore solution, U(VI) was separated either by using the modified resin or by flotation of the U-ARS chelate.

Preparation of U(VI)–ARS Solid Complex

The $UO_2(ARS)OH{\cdot}H_2O$ complex was prepared by refluxing equimolar amounts of ARS and uranyl acetate (1 mmol of each) in absolute ethanol for 30 minutes. The solid formed was filtered off, washed several times with ethanol, and dried in a vacuum desiccator over anhydrous $CaCl_2$. The isolated solid complex is violet and easily soluble in water. The molar conductance of its 0.001 mol·L^{-1} aqueous solution is similar to that of 0.001 mol·L^{-1} ARS (260 ohm^{-1}·cm^2·mol^{-1}), thereby indicating the sameness of the electrolytic natures (1:2 electrolyte) of ARS and its uranium complex (31). The complex is thermally stable (m.p. > 300).

RESULTS AND DISCUSSION

Characterization of the Modified Resin

In order to verify the presence of the active functional groups of ARS in the modified resin, the IR spectra of Duolite A101, ARS, modified duolite–ARS resin, and the modified resin loaded with U(VI) were obtained with

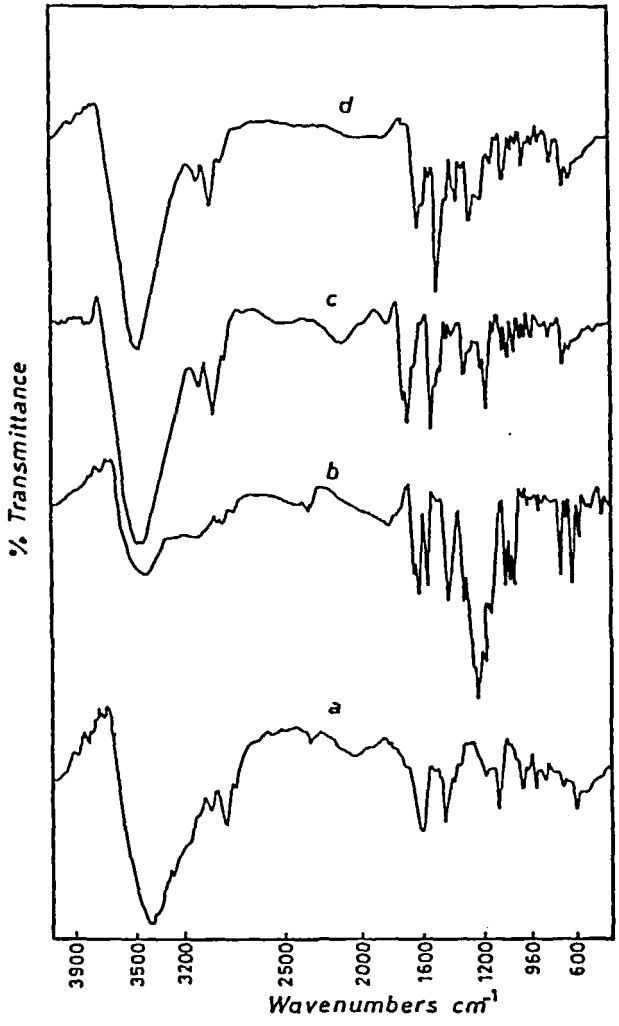


FIG. 1 Infrared spectra of (a) Duolite A101 resin, (b) ARS, (c), ARS-modified resin, and (d) modified resin loaded with U(VI), (KBr discs).

KBr discs (Fig. 1). The IR spectrum of Duolite A101 resin exhibited less intense bands at 3295, 3227, and 3150 cm^{-1}, which may be attributed to the quaternary ammonium N^+R_4 group (32). The bands at 2922 and 1633 cm^{-1} are assigned to the aliphatic —CH_2—CH_2 chains and the phenyl rings, respectively. Upon modification with ARS, the quaternary ammonium bands are

weakened and slightly shifted to lower wavenumbers; this indicates sharing of this group in reaction with ARS. Moreover the bands assigned to SO_3^{2-} stretching (33) at 1202, 1230, and 1285 cm^{-1} and the ν_{C-S} band at 600 cm^{-1} in the spectrum of ARS are shifted to 1192, 1215, 1304, and 590 cm^{-1} in the spectrum of the modified resin, indicating the following reaction mode for supporting ARS on Duolite:

$$\text{—Ph—}CH_2\text{—N—}(CH_3)_3Cl + NaSO_3\text{—Aliz} \rightleftharpoons \text{—Ph—R—N—}SO_3\text{—Aliz} + NaCl$$

It is worth mentioning that other IR frequencies for ARS–Duolite resin are in good agreement with those assigned for ARS monomer and Duolite A-101. The IR spectrum of the modified resin loaded with U(VI) (Fig. 1,d) is characterized by the shift of the $\nu_{C=O}$ band at 1640 cm^{-1} to 1630 cm^{-1} and the presence of new bands at 913, 850, and 485 cm^{-1} which are assigned to the ν_3, ν_1, and ν_4 bands of dioxouranium ion (34). The disappearance of the 1333 cm^{-1} band (assigned to ΔOH in the ARS and modified resin spectra) indicates the participation of this group in chelation after deprotonation. Inspection of these results indicates that sorption of uranium takes place through complexation with ARS loaded on the resin and that Duolite is applied only as an immobilization substrate for ARS reagent.

The modified resin is stable in 2 $mol \cdot L^{-1}$ HCl, HNO_3, or H_2SO_4 acids or 5.0 $mol \cdot L^{-1}$ NaOH solution, because no appreciable changes in the sorption capacity is noticed after its treatment with the above-mentioned reagents for 24 hours.

Metal Sorption Capacity and Separation

The sorption behavior of some metal ions on the ARS-modified resin has been examined at different pH values using the batch method; the results are shown in Fig. 2. Among the metal ions used in this study, Ca^{2+}, Mg^{2+}, Bi^{3+}, Al^{3+}, Mn^{2+}, Be^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} did not show appreciable sorption at pH $\leq$ 6, whereas Fe^{3+}, Cu^{2+}, Th^{4+}, Zr^{4+}, and Ti^{4+} showed different sorption patterns in the 3–5 pH range. The presence of EDTA, DTPA, or thiourea suppressed the chelation of these metal ions to the modified resin. We chose to use DTPA because it does not affect the sorption of uranium and because of its superiority in acidic solutions due to its ability to form more stable complexes (35); complexes of EDTA with Cu^{2+} and thiourea with Th^{4+} are less stable at pH $\approx$ 3. Generally, the addition of 2 mL of 0.01 $mol \cdot L^{-1}$ DTPA solution makes the separation of 10^{-4} $mol \cdot L^{-1}$ of U(VI) from 10^{-3} $mol \cdot L^{-1}$ solution of Th^{4+}, Cu^{2+}, Fe^{3+}, Ti^{4+}, or Zr^{4+} in the 3–4.5 pH range possible with a recovery $\geq$ 99.8%.

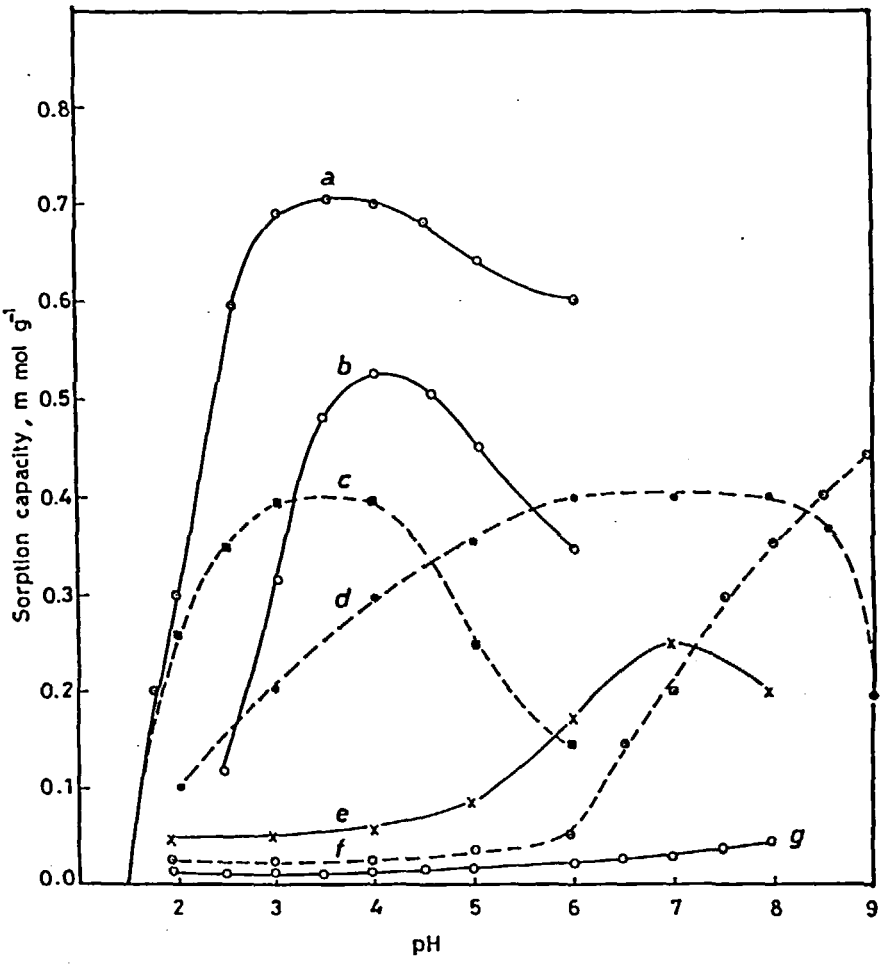


FIG. 2 Sorption capacity of the ARS-modified resin for different metal ions as a function of pH: (a) U(VI), (b) Th(IV), (c) Fe(III), (d) Cu(II), (e) Al(III), (f) Ca(II), and (g) Th(IV), Fe(III), and Cu(II) in the presence of 2 mL of 0.01 mol·L^{-1} DTPA solution.

The sorption capacity of the resin has been determined at pH 3.5. The capacity for U(VI) is found to be 0.68 mmol·g^{-1} of resin. The selectivity of the proposed procedure as well as the sorption capacity of U(VI) are considerably higher or comparable to other chelating resins (16, 19). The sorption capacity of the resin proved to be reproducible after at least 10 sorption–regeneration

cycles. After elution, the resin was thoroughly rinsed with water to remove excess acid, then reused.

The study of the time needed for quantitative sorption of uranium on the modified resin is very important for establishing the possibility of applying column operation. Fast equilibrium reactions make the resin suitable for packing and using in a column. Alternatively, batch methods are preferable for slow sorption systems. Kinetic experiments carried out at the optimum conditions of sorption indicate that at least 85–90% of U(VI) was sorbed within 8–10 minutes of the interaction with the resin depending on the concentration of uranium. Thus, the sorption rate was considered rapid enough for separation in a column.

Preconcentration of U(VI) on the resin was carried out. The sorbed uranium from 500 mL of 2.1×10^{-4} mmol·L^{-1} solution on 0.5 g of the resin was easily desorbed with 5 mL of 0.2 mol·L^{-1} HCl. After filtration, the resin was washed with about 3 mL of water, and the volume of the filtrate was completed to 10 mL in a calibrated flask. The concentration of uranium in this solution was found to be 1.04×10^{-2} mmol·L^{-1}, which indicates that U(VI) can be enriched up to 50 times with the ARS-modified resin.

Due to the association of U(VI) with many metal ions, it is crucial to separate uranium from these metal ions. The proposed ARS-modified resin was found to be effective for such a selective separation. At pH 3.5 the resin selectively takes up U(VI) from an aqueous solution containing a group of metal ions which usually accompany it in its ores when the column procedure is used. The interfering Cu^{2+}, Fe^{3+}, Th^{4+}, Zr^{4+}, and Ti^{4+} ions are not retained on the resin in the presence of DTPA. The concentration of these metal ions was determined in the effluent. Table 1 shows the results of the separation of U(VI) from other metal ions.

Breakthrough Curves

In the utilization of a column, the breakthrough capacity is an important parameter which depends mainly on the U(VI) concentration. In order to obtain the breakthrough curve, a column of 4 mm i.d. and 6 cm length was packed with 450 mg of the resin, and a 2.1×10^{-2} mmol·L^{-1} uranium solution buffered at pH 3.5 was passed at a flow rate of 1 mL·min^{-1}. The effluent received after an elapsed time of 10 minutes was fractionized into 5-mL portions and U(VI) was determined. The breakthrough curve, presented in Fig. 3, indicates that the column is exhausted with 0.30 mmol of U(VI).

Elution of Sorbed Uranium

The uranium sorbed on the resin during column operation was subjected to elution with 0.2 mol·L^{-1} HCl. The results, presanted in Fig. 4, show that

TABLE 1
Separation of 20 μg·mL^{-1} of U(VI) from Other Metal Ions at pH 3.5 When the Concentration of Foreign Ion Added Is 50 μg·mL^{-1} (column method)

Metal ion	Uranium found (μg·mL^{-1})	Metal ion found (μg·mL^{-1})	% Recovery U(VI)
Cu(II)[a]	19.6	48.9	98.0
Zn(II)	19.7	49.0	98.5
Al(III)	19.8	49.9	99.0
Fe(III)[a]	19.5	48.6	97.5
Pb(II)	19.8	49.3	98.5
Th(IV)[a]	19.5	48.3	97.5
Zr(IV)[a]	19.4	47.8	97.0
Ti(IV)[a]	19.1	48.1	95.5
Co(II)	19.8	49.6	99.0
Ni(II)	19.8	49.8	99.0
Mg(II)	20.0	50.0	100
Ca(II)	19.7	49.8	98.5

[a] In the presence of 2 mL of 0.01 mol·L^{-1} DTPA.

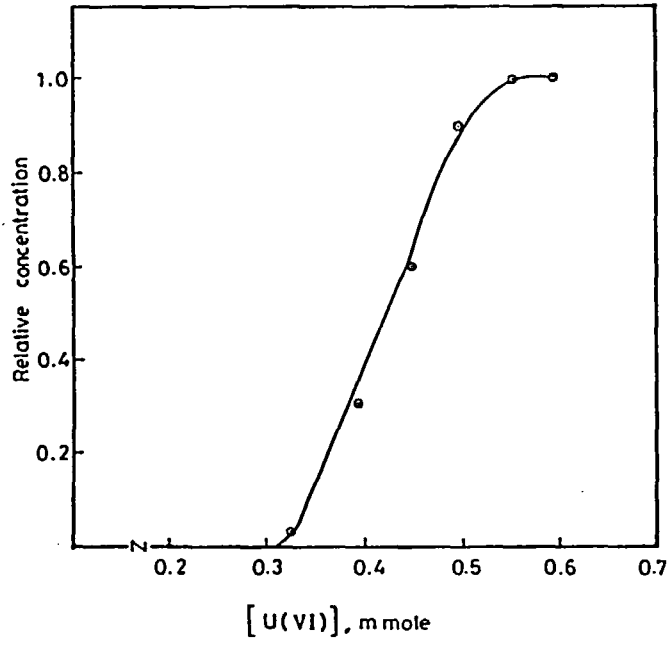


FIG. 3 Breakthrough curve for 50 μg·mL^{-1} U(VI), flow rate 1 mL·min^{-1}, whose relative concentration is the fraction of uranium detected in the effluent to the total amount loaded.

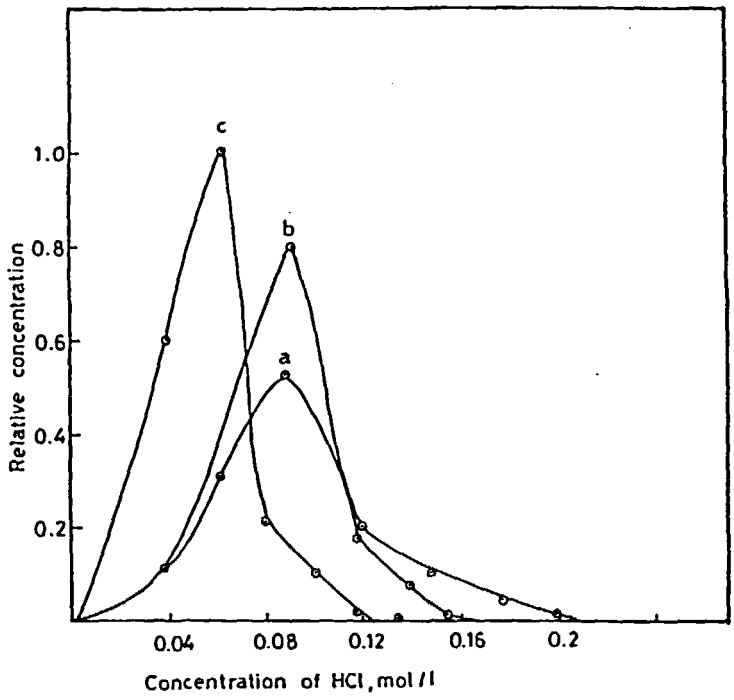


FIG. 4 Elution curves for U(VI) as a function of the flow rate. U(VI) eluted with HCl at flow rates of (a) 1 mL·min^{-1}, (b) 0.5 mL·min^{-1}, and (c) 0.1 mL·min^{-1}, whose relative concentration is the fraction of U(VI) detected from the total amount loaded.

5 mL of the eluent is sufficient to recover all the uranium sorbed with a flow rate of 0.1 mL·min^{-1}. After elution, the excess acid was rinsed with distilled water until the effluent became free from the acid; the yellow color of the resin changed to red, and then the column could be reused.

Spectrophotometric Characterization of U(VI)–ARS Complex

The reaction of ARS with U(VI) was followed spectrophotometrically in the 3.0–5.0 pH region. The visible absorption spectrum of ARS is characterized by an absorption band at 420 nm. This band is shifted to 570 nm on adding U(VI) solution (Fig. 5). Job's method of continuous variation (36) was applied to establish the stoichiometric ratio of the formed complex. In a series of solutions, the molar fractions of U(VI) and ARS were varied continuously while keeping their combined concentration constant at 1 ×

10^{-4} mol·L^{-1} and measuring the absorbance at 570 nm against a reagent blank. The results obtained indicated the formation of a 1:1 U(VI):ARS complex at λ_{max} 570 nm. The stability constant of this complex, according to the Harvey and Manning method (37), is 1×10^9, log $K = 9.00$ at 25°C. Beer's law is obeyed over the 2×10^{-6} to 8×10^{-5} mol·L^{-1} U(VI) range, $\epsilon = 1.1 \times 10^4$ L·mol^{-1}·cm^{-1}. Eight identical determinations of samples with a final concentration of 2.7×10^{-5} mol·L^{-1} gives a mean absorbance of 0.3. Further, characterization of the solid complex indicates that the chelation of U(IV) with ARS takes place through 10-CO and 1-OH groups of ARS (Structure II). This mode of chelation is suggested based on the shift of the $\nu_{C=O}$ band and the disappearance of the 1333 cm^{-1} band beside the appearance of new bands which were assigned to dioxouranium [discussed earlier in the IR spectrum of the resin loaded with U(VI)]. The electronic spectrum of the solid complex dissolved in water is identical with that of equimolar mixture of ARS and U(VI) aqueous solutions, and its maximum absorption is at 570 nm.

The blue-violet color of the solid complex dissolved in water abruptly changed to yellow at pH $\leq$ 2.7. All these observations indicate that only one type of complex is formed in solution at pH $\geq$ 2.7 or in the solid state. The blue-violet color of the resin loaded with U(IV), besides the similarity of its IR spectrum with that of the isolated solid complex, indicates the formation

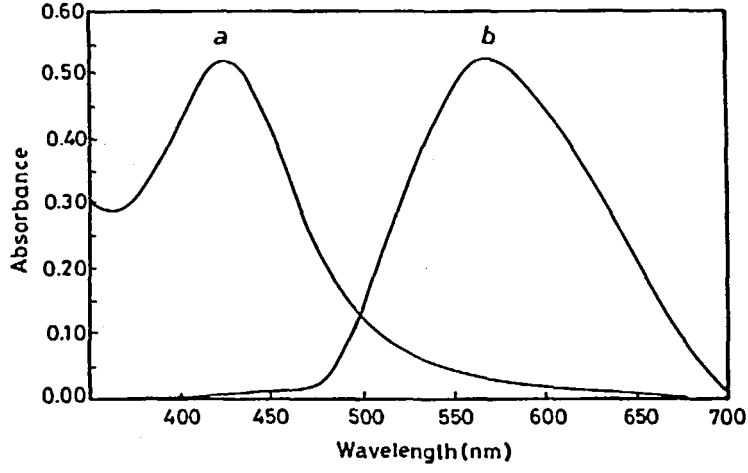
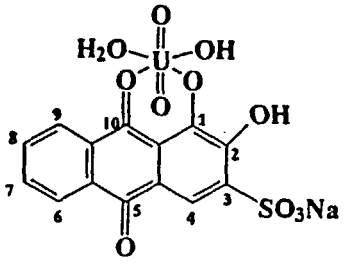


FIG. 5 Absorption spectra of (a) 1×10^{-5} M ARS and of (b) 1 mL of 5×10^{-4} mol·L^{-1} U(VI) + 2 mL of 1×10^{-3} mol·L^{-1} ARS + 2 mL acetate buffer of pH 3.5 completed to 10 mL with water. The absorbance is recorded against a reagent blank.



STRUCTURE II

of the same type of complex in the sorption of U(VI) from aqueous solution with the modified resin.

Use of U–ARS Chelate for Flotation of U(VI)

The use of the U(VI)–ARS chelate for the flotation of U(IV) from aqueous solutions was also studied as was the effect of pH on the flotability of the U–ARS chelate. It was noticed that U–ARS chelate formation started at pH > 2.7, and maximum flotability was reached in the 3.5–5.0 pH range (Fig. 6), hence the optimum pH recommended is 4.0. The maximum flotation efficiency was obtained by using 4–5 $\times$ 10^{-5} mol·L^{-1} ARS for the quantitative flotation of 1 $\times$ 10^{-5} mol·L^{-1} U(VI). Excess ARS favors the formation of the U–ARS complex and hence enhances its flotation efficiency. Quantitative flotation was achieved after shaking the U–ARS mixture with HOL solution for about 5 minutes. Figure 7 shows the effect of the concentration of oleic acid on the flotability of different concentrations of U(VI). The data of this figure imply that the maximum flotation of 1 $\times$ 10^{-5} mol·L^{-1} U(VI) can be attained by the use of 3 $\times$ 10^{-3} mol·L^{-1} HOL or more.

Effect of Ionic Strength on the Efficiency of Flotation

Table 2 lists the effects of ionic strength on the flotability of 1 mL of 1 $\times$ 10^{-5} mol·L^{-1} U(VI) using 1 mL of 5 $\times$ 10^{-5} mol·L^{-1} ARS and 3 mL of 1.27 $\times$ 10^{-3} mol·L^{-1} HOL at pH 4.0. The salts NaCl, K_2SO_4, and Na_2SO_4 were added to prepare an aqueous media with a composition similar to seawater. All the salts used enhance the flotation efficiency, which reached its maximum when 0.2 mol·L^{-1} or more was used. This may be attributed to the adsorption of SO_4^{2-} or Cl^- ions to the surface of the UO_2–ARS chelate, which allows for more U(VI) to coagulate within the particles during flotation. When the recommended procedure for the flotation of U(VI) from seawater

is applied, there is no need to add these salts. Thus, the use of 0.2 mol·L^{-1} Na_2SO_4 as an activator is recommended in the proposed procedure.

Effect of Foreign Ions

To assess the possible application of this study to the separation of U(VI), the effects of diverse ions which had been tested in the resin experiments were examined. The results obtained showed a behavior similar to that noticed in the resin experiments. The interference effects of the foreign ions were completely eliminated by adding 2 mL of 0.01 mol·L^{-1} DTPA to the flotation medium. This amount of DTPA is recommended for use in the proposed flotation procedure.

Application

To evaluate the feasibility of the separation procedures under investigation, the separation of U(VI) from three certified ore samples was carried out. The

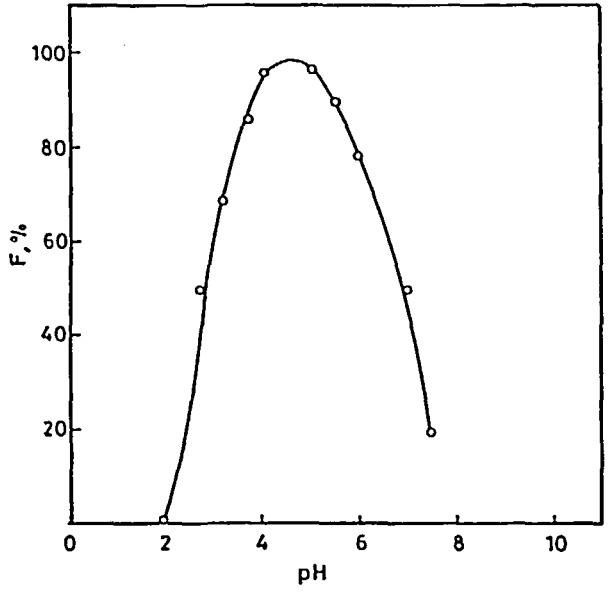


FIG. 6 Flotability of 1 × 10^{-5} mol·L^{-1} U(VI) as a function of pH. The sample was prepared by mixing 1 mL of U(VI), 2 mL of 5 × 10^{-5} mol·L^{-1} ARS, and 2 mL of 1 mol·L^{-1} Na_2SO_4, adjusting the pH and completing the volume to 10 mL. Then the mixture is shaken with 3 mL of 1.27 × 10^{-3} mol·L^{-1} HOL.

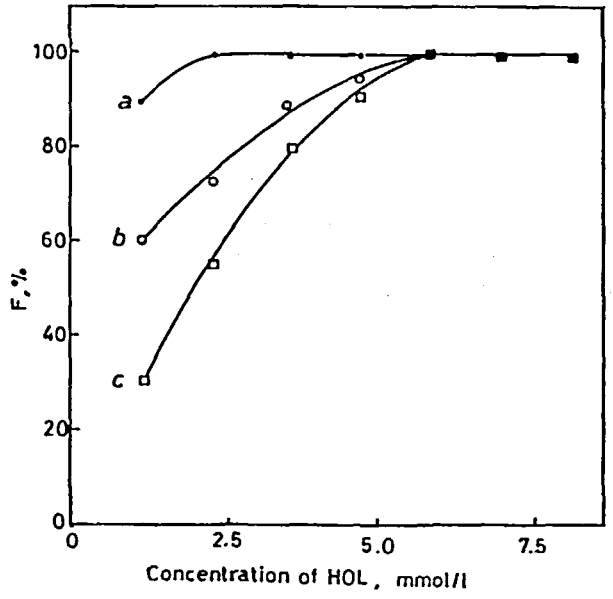


FIG. 7 Flotability of different concentrations of U(VI) with different concentrations of HOL under the optimum conditions: (a) 1×10^{-5} mol·L^{-1} U(VI), (b) 5×10^{-5} mol·L^{-1} U(VI), and (c) 1×10^{-4} mol·L^{-1} U(VI).

results are given in Table 3. For the determination of U(VI) in seawater media, 24 μg of U(VI) was added to 10 mL of prefiltered seawater and recovered by the two procedures under the optimum conditions for each. The results are presented in Table 4. The results obtained are better than or comparable to those obtained using the famous amidoxime surfactants (28).

TABLE 2
Effect of Ionic Strength on the Flotability (%) of 1×10^{-5} mol·L^{-1} U(VI) Using 5×10^{-5} mol·L^{-1} ARS and 1.27×10^{-3} mol·L^{-1} HOL at pH 4.0

	F, % in the presence of [salt][a]							
Salt	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
NaCl	75	83	90	98.1	97.7	99.7	96	90
Na_2SO_4	76	84	91	98.6	98.8	99.2	95	89
K_2SO_4	75	82.9	90.1	98.2	99.4	98.8	96	89.5

[a] Concentration of salt in mol·L^{-1}.

TABLE 3
Recovery of U(VI) from Certified Ores[a] Using ARS-Modified Resin (a) or Flotation Process (b) under the Optimum Conditions

Ore number	Certificate composition (%)	U(VI) (%) Certified	Mean U (%), $\bar{x}$ (a)	s_1 (%), $n = 5$	Mean U (%), $\bar{x}$ (b)	s_2 (%), $n = 5$
1-BL_{2a}	SiO_2 (59.12), Al (6.6), Fe (4.75), Ca (4.06), Na (3.42), Mg (1.5), S (0.36), K (0.33), Pb (0.09)	0.430	0.418	0.02	0.410	0.04
2-DH_{1a}	SiO_2 (79.75), Fe (5.17), S (4.82), Al (3.44), K (1.43), Mg (0.07), C (0.05), Ca (0.04), Na (0.04)	0.263	0.260	0.02	0.256	0.03
3-Bl_{-5}	Si (22.0), Al (6.0), Fe (5.9), Ca (4.0), Na (3.6), C (1.9), Pb (1.5), Mg (1.5), K (0.4), Ti (0.4), S (0.3), P (0.07), Mn (0.5), Zr (0.04), Sr (0.03), Cr (0.01), Th (0.004)	7.09	7.0	0.08	6.95	0.10

[a] Purchased from the Canadian Certified Reference Material Project (CRMP) and kindly supplied by the Atomic Energy Authority, Cairo, Egypt.

TABLE 4
Recovery of U(VI) from Seawater Using ARS-Modified Resin or by Flotation of U-ARS Chelate under the Optimum Conditions

Concentration of U(VI) added ($\mu g \cdot mL^{-1}$)	Recovery (%) By flotation[a]	By resin[b]
0.005	95.1	99.4
0.3	97.9	100
0.5	98.8	101
0.7	99.0	101

[a] Using 1.27×10^{-3} mol·L^{-1} HOL and 1 mL of 0.02 mol·L^{-1} DTPA at pH ~ 4.0.
[b] Using batch experiment.

CONCLUSION

The most important feature of the proposed procedures is that a satisfactory separation of U(VI) is achieved either by its sorption through complex formation with the active functional groups of ARS bonded to the resin or by flotation of the U–ARS chelate formed in aqueous solution with oleic acid dispersed in kerosene. Most metal ions were tolerated in high proportions. The methods were extended to the separation of U(VI) from certified ores. The separation processes are simple, rapid, selective, and reproducible. In all instances the recovery of U(VI) is 100 ± 1% using the ARS modified resin and 100 ± 2.5% using the flotation procedure.

Although the flotation process is less time-consuming and more economic than use of the ARS-modified resin, the latter has the capability to preconcentrate minor amounts of U(VI) (≤0.005 ppm) which could not be separated quantitatively by the flotation procedure. A real benefit is expected when the ARS-modified resin is used as a complementary method to flotation or the well-known solvent extraction procedures, i.e., flotation can be economically used to separate most U(VI) (>98%) when it is present in relatively high concentrations, while the use of modified resin for the preconcentration and separation of the remaining uranium traces is recommended.

REFERENCES

1. Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, 2nd ed., Ellis Horwood, England, 1986.
2. C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta, 37*, 461 (1990).
3. N. Arik and H. R. Turker, *Fresenius Z. Anal. Chem., 339*, 874 (1991).
4. K. H. Lieser, P. Burba, W. Calmano, W. Dyck, E. Heuss, and S. Sondermeyer, *Mikrochim. Acta, II*, 445 (1980).
5. Y. Meguro, S. Iso, H. Takeishi, and Z. Yoshida, *Radiochim. Acta, 75*(4), 185 (1996).
6. N. Raje, S. Kayasth, T. P. S. Asari, and S. Gangadharan, *Anal. Chim. Acta, 290*, 371 (1994).
7. V. D. Pillai and V. M. Shinde, *Indian J. Chem., 35A*, 906 (1996).
8. S. E. Lauritzen, J. Hurum, and J. Astald, *Chem. Geol., 137*(3-4), 265 (1997).
9. N. M. T. El Hazek and E. M. Hussien, *Proc. Egypt. Acad. Sci., 45*, 159 (1995).
10. N. M. T. El-Hazek, E. M. Hussien, M. M. Aly, and A. A. Mohamed, *Arab J. Nucl. Sci. Appl., 27*(3), 129 (1994).
11. F. Vernon and T. W. Kyffin, *Anal. Chim. Acta, 94*, 317 (1977).
12. J. P. Ghosh and H. R. Das, *Talanta, 28*, 274 (1981).
13. N. Kabay and H. Egawa, *Sep. Sci. Technol., 28*, 1985 (1993).
14. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ind. Eng. Chem. Res., 32*(3), 540 (1993).
15. H. Egawa, N. Kaby, S. Saigo, T. Nonaka, and T. Shuto, *Nippon Kaisu Gakkai-Shi, 45*(6), 324 (1991).
16. N. Das and J. Das, *Indian J. Chem., 28*(A), 150 (1989).

17. R. J. Philips and J. S. Fritz., *Anal. Chim. Acta*, *139*, 237 (1982).
18. C. H. Lee, J. S. Kim, M. Y. Suh, and W. Lee, *Ibid.*, *339*(3), 303 (1997).
19. R. Pathak and G. N. Rao, *Ibid.*, *335*(3), 283 (1996).
20. X. Feng and D. E. Ryan, *Ibid.*, *182*, 47 (1984).
21. L. D. Skrylev and V. V. Menchuk, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, No. 5, 100 (1985); *Chem. Abstr.*, *104*, 54056g (1986).
22. Y. Koide, H. Takamoto, K. Matsukawa, and Y. Yamada, *Bull. Chem. Soc. Jpn.*, *56*, 3364 (1983).
23. M. Takahashi, M. Hayashi, N. Yoshioka, T. Tanimoto, and H. Takeuchi, *Nippon Kagaku Kaishi*, *9*, 812 (1996).
24. K. Shakir, K. Benyamin, and M. Aziz, *Can. J. Chem.*, *62*, 51 (1984).
25. A. Mizuike and M. Hiraide, *Pure Appl. Chem.*, *54*(8), 1555 (1982).
26. T. Naghiro, G. F. Wang, and M. Satake, *Microchem. J.*, *53*(3), 247 (1995).
27. DIAION, *Manual of Ion Exchange Resins (I)*, Revised Edition, Mitsubishi Chemical Industrial Ltd., Japan, 1961, p. 106.
28. Y. Koide, H. Takamoto, K. Matsukawa, and Y. Yamada, *Bull. Chem. Soc. Jpn.*, *56*, 3364 (1983).
29. F. W. Strelow and T. N. Van der Walt, *Talanta*, *26*, 537 (1979).
30. T. Kidokoro, K. Matsui, S. Ishiwata, T. Sasaki, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, *61*, 1505 (1988).
31. D. B. Hibbert and A. M. James, *Dictionary of Electrochemistry*, 2nd ed., Macmillan, London, 1984, pp. 58, 59.
32. K. Nakanish and P. H. Solomon, *Infrared Absorption Spectroscopy*, 2nd ed., Holden-Day, Oakland, CA, 1977, p. 34.
33. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, NY, 1970.
34. A. A. El-Asmy, T. Y. Al-Ansi., M. Mounir, and S. A. Ashour, *Synth. React. Inorg. Met.-Org. Chem.*, *19*(4), 309 (1989).
35. K. Ueno, T. Imamura, and K. L. Cheng, *Handbook of Organic Analytical Reagents*, 2nd ed., CRC Press, 1992, p. 261.
36. P. Job, *Ann. Chim. (Rome)*, *10*, 113 (1928).
37. A. M. Abdallah, M. E. Khalifa, and M. A. Akl, *Anal. Chim. Acta*, *251*, 207 (1991).

Received by editor November 10, 1997
Revision received February 1998