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Selective Separation and Preconcentration of Total Tin Using Quercetin as Chelating Agent

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Abstract: Three methods were developed for rapid and selective extraction of total tin as Sn(IV) using quercetin (H5Q) as chelating agent, prior to its determination by hydride generation atomic absorption spectrometry (HGAAS). H5Q was chemically or physically immobilized onto silica gel or polyurethane foam, respectively, and used for the separation of Sn(IV) by the solid phase extraction (SPE) technique. The SPE methods were compared with flotation technique using the oleic acid as surfactant from H5Q solution in amyl alcohol/kerosene solvent. Elemental analysis, thermogravimetry, spectroscopic measurements (IR, UV/vis and magic angle solid state C^{13}-NMR) were used to characterize the resulting modified extractors. The experimental conditions for efficient extraction of Sn(IV) such as: pH, time of stirring, interfering ions and eluent concentration, were optimized for the batchwise separation process. The tolerance limits of heavy metal ions in the sorption of Sn(IV) were reported. The methods were applied for the determination of total tin in water samples, zinc shots and canned beans after digestive oxidation. The suggested SPE and flotation

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techniques were found to be accurate and not subject to random error with especial preference to the SPE technique as it is cheaper and simpler.

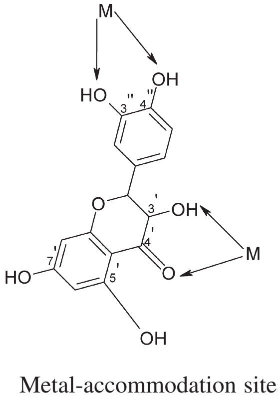
Keywords: Modified silica, polyurethane foam, quercetin, separation, preconcentration, flotation, total tin

INTRODUCTION

The determination of metal ions, tin in particular, at micro and trace level is very important in the context of high purity materials development and pollution monitoring. To avoid background interference and to lower the limit of detection, a separation and preconcentration step is prerequisite.

Recently, the differential pulse polarography (DPP) on the base of the chelating reagents modified with surfactants (1) and after preconcentration with the ion pair formed from 2-nitroso-1-naphthol-4-sulfonic acid and tetradecyldimethylbenzylammonium chloride onto microcrystalline naphthalene or by column method (2) were reported as alternative techniques for tin separation and determination. Extraction of tin(IV) with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester in toluene followed by spectrophotometric determination by morin and pyrocatechol violet was also reported (3).

Quercetin (H5Q), a flavonoid, has attracted attention as an effective multi-nuclei chelating reagent for spectrophotometric and extraction-spectrophotometric determination of many metal ions (4–11). The metal ions may bind to the 3-hydroxyl and 4-keto oxygen or to the 5-hydroxyl and 4-keto oxygen. Two adjacent hydroxyls, such as the 3′- and 4′-hydroxyls in H5Q, may also be involved in chelation as shown in Scheme 1.



Scheme 1. Metal-accommodation sites in H5Q.

Moreover, H5Q is considered to be one of the most effective chelating reagents for spectrophotometric and extraction-spectrophotometric determination of Sn(IV) (9). But these methods are time-consuming, poorly selective, vulnerable to many interferences, and/or require the use of toxic organic solvents.

The solid phase reagents using modified sorbents were reported to be simple and cost-less effective tools for analytical sampling and sensitive detection of various compounds in complicated objects (12, 13). Zaporozhets et al. (14) immobilized H5Q on silica gel by adsorption from acetone/hexane mixture (1:4) yielding a sorbent capacity as low as 0.035 mmol g^{-1}. Nevertheless, the sorbent was used to extract tin(IV) at pH 5.0 and the formed complex was eluted at pH 1.8–2.2. Quercetin was also immobilized onto the dextran type sorbent (sephadex-25) and used for the separation of tin (15). Also, recently the chemical immobilization of H5Q onto controlled-pore silica glass yielded a sorbent characterized by good stability and relatively higher metal uptake capacity (0.24–0.46 mmol g^{-1}) (16). Its use for the separation of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) from various samples was reported. In addition, Azeredo et al. (17) determined molybdenum in apple leaves after separation on H5Q-functionalized silica gel. The sorbent showed a capacity of 0.089 mmol g^{-1} towards molybdenum. Consequently, the silica species particularly silica gel proved to be the best matrices for analytical reagent immobilization because it is characterized by availability, negligible swelling, rapid sorption of metal ions, good mechanical stability, and appreciable metal uptake capacity when it is chemically functionalized.

From the other side, among many available materials for SPE, polyurethane foam was proposed as a low cost sorbent by Bowen (18) in 1970 and since then it has been extensively used in preconcentration and separation processes. (2-(2-Benzothiazolylazo)-2-*p*-cresol (BTAC) was loaded on PUF and used to preconcentrate Pb(II) (19) and Cd(II) (20) from seafood samples which were eluted by 0.1 mol L^{-1} HCl and determined by flame atomic absorption spectrometry. Also, 9,10-phenanthaquenone monoethylthiosemicarbazone (PETSC) was used for spectrophotometric determination of Tl(III) and its separation using flotation and solid phase extraction on polyurethane foam (21).

Moreover, flotation techniques are recommended as effective and less expensive separation and preconcentration tools with most of the advancing factors (22–26). It involves the removal of surface inactive ions from aqueous solution with the aid of air bubbles using three modes: adsorptive flotation, precipitation flotation, or adsorbing-particle flotation (26).

In the current study, the use of H5Q as a selective reagent for the separation of total tin ion using SPE technique either by chemical immobilization on silica gel or physical adsorption on PUF will be described in comparison with flotation technique using oleic acid\amylalcohol\kerosene mixture system.

EXPERIMENTAL-APPARATUS, MATERIALS, AND METHODS

Materials and Reagents

All reagents used were of analytical grade A.R. from Fluka, Aldrich, or Merck and used without further purification. All solutions were prepared using double distilled water (DDW). Sn(IV) stock solutions (1000 mg L^{-1}) was prepared by dissolving tin shot (reference material number 030503) as chloride in 2 mol L^{-1} HCl and 5 mL H_2O_2. Intermediate standard solutions were prepared by appropriate dilution with 2 mol L^{-1} HCl.

For the immobilization of H5Q on silica gel, a 3 g of quercetin dehydrate was refluxed with 10 g of aminopropylsilica gel (APSG) from Fluka (capacity 1.1 mmol g^{-1}) in an ethanolic solution according to the literature (16). The capacity of QSG was found to be 0.221 mmol H5Q g^{-1} as obtained from the loss of H5Q concentration in the filtrate at 370 nm.

For the immobilization of H5Q on PUF, a 2.0 g of PUF was shaken for 30 min with 100 mL of 0.001 mol L^{-1} H5Q in amyl alcohol and the resulting yellow Q/PUF was filtered. The adsorbed amount of H5Q was found to be 0.176 mmol H5Q g^{-1} of PUF as observed from the loss of H5Q in the filtrate by measuring the absorption. The yielded Q/PUF was washed with 50% ethanol-water, squeezed between two ashless filter papers, dried at 80°C for 2 h and used for subsequent studies. Q/PUF shows negligible leaching out of the impregnated H5Q in water as observed from the capacity loss 2.1% after washing of 0.1 g of Q/PUF with 10 L of water adjusted to pH 3.8 with NaOH and HCL solutions (the remained H5Q on Q/PUF was released by DMF and determined spectrophotometrically).

A 0.001 mol L^{-1} of H5Q solution was prepared by dissolving H5Q in amyl alcohol for flotation or SPE using polyurethane foam (PUF).

Apparatus

A flame atomic absorption spectrometer Perkin Elmer 2380 supplied with a hydride generation kit was used for direct measurement of Sn according to the method described in literature (27). Unicam UV-visible Spectrometer UV2 was used for recording the absorbance of H5Q and its complexes with Sn species at 370 and 470 nm, respectively. Mattason 5000 FTIR spectrometer was used for transmittance measurements using KBr disc. Thermogravimeteric analysis (TG) of QSG and its inorganic Sn(IV) complex was carried out using a Shimadzu thermobalance using a rate of heating 10°C min^{-1}. Solid State ^{13}C-NMR measurement was performed using a BRUKER DMX 400 spectrometer operating at 100.5 MHz. The 7 mm probe was used with MAS frequencies of 4.5 kHz. The cross-polarization time was 4 ms, the repetition time 2 sec and 2700 up to 4500 scans have been acquired. High power proton decoupling was applied during data acquisition. The pH was measured by a Hanna instrument 8519 digital pH meter and adjusted within the ranges 1–8 using NaOH and HCl solutions. The poteniometric titrations were done with a Metrohm E536 potentiograph equipped with 665 DOSIMAT (Metrohm Herisau, Switzerland). All the titrations were carried out with a rate of addition 0.2 mL min^{-1} at 25°C. The flotation cell used was a cylindrical graduated glass tube of 16 mm inner diameter and 290 mm length with a stopcock at the bottom.

Methodology

The given data are the average of three replicates whereas those of application were repeated five times from which the statistical evaluation is performed.

Batch Mode SPE Separation on QSG

A total of 40 mg of QSG was suspended with constant stirring for 30 min in 50 mL of 2.00 μg mL^{-1} of Sn(IV) as chloride at the desired pH value. The concentrations of the investigated ions in the filtrates were determined by HGAAS. The separation efficiency (S) is determined using the equation:

$$S = (C_i - C_f)/C_i \times 100 \tag{1}$$

where C_f is the metal concentration in the filterate and C_i is the initial metal ion concentration in the solution phase.

The effect of stirring time was studied at pH = 3.8 ± 0.1 using the same conditions applied previously then the optimum conditions (pH = 3.8 ± 0.1, time of stirring = 10 min and weight of QSG = 40 mg) were applied in all next studies unless otherwise stated.

Batch Mode SPE with H5Q Loaded on PUF

A 40 mg of Q/PUF was added to 50 mL of 2.00 μg mL of Sn(IV), adjusted to pH 3.8 using HCl and NaOH solutions, and shaken for different time intervals. After shaking, the remaining tin species was determined in the filtrate and equation (1) was used for the determination of separation efficiency.

Separation by Flotation Technique

A 2.5 mL of 1×10^{-4} mol L^{-1} of H5Q in amyl alcohol was introduced into the flotation cell containing 10 mL of 2.5 μg mL^{-1} Sn(IV). The pH was adjusted to be 3.8 by using HCl and NaOH and the solution was thoroughly mixed. The mixture was then diluted to 25 mL and 3 mL of 1×10^{-4} mol L^{-1} oleic acid in kerosene was added. The cell was vigorously shaken and kept to settle for 5 min to ensure complete flotation. The brilliant yellow precipitate of tin complexes was floated in kerosene layer, which was separated by a funnel and vaporized. After drying the residue, it was digested in aqua regia. Sn concentration was determined by HGAAS in the mother liquor or in the digested complex. The flotation efficiency was calculated from the relation

$$\text{Flotation efficiency} = (C_s/C_i) \times 100 \qquad (2)$$

where C_i and C_s are the initial and the scum content of tin, respectively.

Preparation of Solid Complex

The solid complex of tin–H5Q was prepared by mixing equimolar amounts of H5Q in ethyl/amyl (70/30) alcohols and Sn(IV) in aqueous-ethanolic solution. The resulting yellow precipitate was filtered off, washed well with water and dried in vacuum desiccator.

From the SPE technique, a 0.5 g QSG or Q/PUF was shaken at optimum pH 3.8, in presence of 250 mL 3.0 mmol L^{-1} Sn(IV). The Sn-sorbent complexes were filtered off, washed well with water and dried in desiccator.

From the flotation technique, the complex isolated from scum was obtained by mixing equimolar amounts of 2×10^{-3} mol L^{-1} of H5Q in amyl alcohol, oleic acid in kerosene, and Sn(IV) in aqueous-ethanolic solution. The bright yellow scum solid complex gathered by filtration in sintered glass gosh (G4), washed with plenty of water, ethanol, and finally with diethyl ether and kept in a vacuum desiccator.

Application to Natural Sample

Surface water samples were collected from diverse oigins on 1 July, 2006. Then the samples were acidified with concentrated HNO_3 acid to pH $\cong 2$ and preserved in polyethylene vessels. The samples were subjcted to digestive oxidation prior to the separation process to eliminate organic content and to turn all tin species to Sn(IV); a 0.5 g of $K_2S_2O_8$ and 5 mL of 98% (wt/vol) H_2SO_4 were added to 1 L of the water sample and refluxed for 30 min at 95°C then left to cool to room temperature.

A 100 mg of QSG or Q/PUF was added to a 500 mL of the sample, the pH value was adjusted to 3.8 ± 0.1 and stirred for 30 min then filtered. To the filtrate another 50 mg of QSG or Q/PUF was added and the pH value was again controlled and the sample was stirred again for 10 min and filtered. The two residues (150 mg) were gathered and the collected metal and metalloid ions were released by 5 mL 2 mol L^{-1} HCl, to give a concentration factor of 100 fold and determined by HGAAS.

For the flotation technique, a 1 mL of 1×10^{-4} mol L^{-1} of H5Q in amyl alcohol was introduced into a 1 L separation funnel containing 500 mL of the water sample. The pH was adjusted to be 3.8 by using HCl and NaOH and a

3 mL of 1×10^{-4} mol L^{-1} oleic acid in kerosene was added. The cell was vigorously shaken and kept to settle for 5 min to ensure complete flotation. The scum was floated in a kerosene layer, which was separated and vaporized. After drying the residue, it was digested in aqua regia, evaporated till near dryness, and the volume was made up 5 mL by 2 mol L^{-1} HCl.

A 100 g of canned beans, purchased from a local food company, was digested with ultra pure nitric acid till near dryness, then diluted to 500 mL with DDW, and treated as in natural water.

A 1 g zinc shot (reference material number 835023) was dissolved in 10 mL 2 mol L^{-1} HCl, diluted to 500 mL with DDW and treated as in natural water.

RESULTS AND DISCUSSION

Characterisation of QSG

The TG curve of QSG (Fig. 1) shows two main stages. The water loss amounts 6.57% in the first stage whereas the second one is the organic degradation which ends at 538°C and it amounts a loss of 8.37% in weight. Elemental analysis of QSG (C = 5.37 and N = 0.51%) is in agreement with the weight loss of TGA but the nitrogen content is slightly more than the predicted 1:1 product of QSG. This may indicate that during reflux of APSG with H5Q, the aminopropyltrihydroxysilane substrate is partially hydrolyzed and ca. one-third of the remained substrate is bonded with H5Q. The low reaction yield was previously attributed to the steric hindrance of

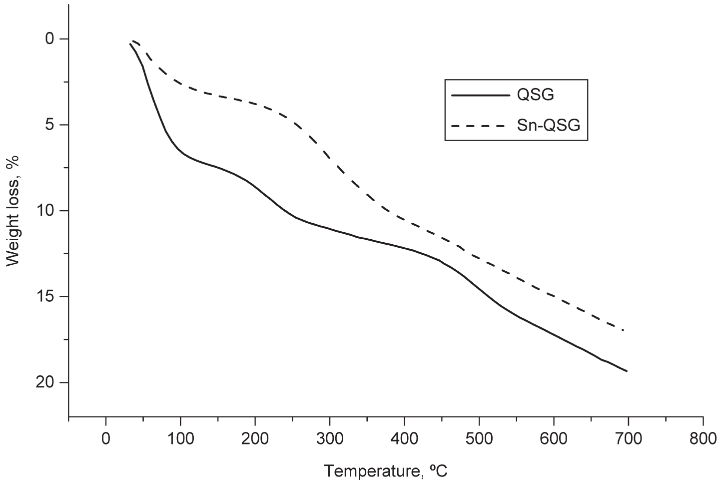


Figure 1. Thermogravimetric analysis of QSG and its complex with Sn(IV).

the bulky H5Q molecule (16). Consequently, the weight loss due to H5Q is calculated to be 7.71% yielding a theoretical capacity of 0.23 mmol g^{-1} of QSG. IR absorption spectrum of QSG showed the disappearance of bands at 3064 and 3189 cm^{-1} (assigned previously to (ν_s) and (ν_{as}) of NH_2 in the IR absorption spectrum of APSG due to the particular involvement of this group in the reaction in addition to hydrolysis(16, 29, 30). Solid State ^{13}C-NMR spectrum was found to be typical to that of H5Q immobilized on controlled-pore silica glass (16).

Calibration and Detection Limit

The HGAAS absorption signals were found to be a linear function of the concentration range (0–100 ng mL^{-1}). The instrumental detection limits $(DL)_i$ of Sn(IV), based on three times the standard deviation of the blank (5 mL 2.0 mol L^{-1} HCl passed through 150 mg of QSG, Q/PUF or digested scum after preconcentration of 500 mL DDW subjected to oxidative digestion of organic content and adjusted to pH 3.8 ± 0.1 by NaOH and HCl) above its mean value, were 3.47, 2.24, or 9.19 ng mL^{-1}, respectively.

The analytical detection limits $(DL)_a$ were calculated by dividing the instrumental detection limits by the preconcentration factor 100. The analytical detection limit was estimated to be 34.7, 22.4, and 91.9 pg mL^{-1} respectively.

Uptake Behavior of QSG and Q/PUF

Figure 2 shows the effect of pH on the uptake behavior of Sn(IV) on QSG or Q/PUF. The separation efficiencies (R, %) are generally low at high acidity whereas they rapidly increase with increasing pH values and reach maximum values (97.91–98.99 and 97.14–98.49% respectively) at pH range 3.8–7.5. So pH 3.8 was chosen as it is a recommended working range of pH for silica to avoid its hydrolysis (31) and to enhance the selectivity avoiding competition from many metal ions which can be co-sorbed at higher pH values (16).

Effect of Time of Stirring

Although silica gel is being vulnerable to hydrolysis even at pH 5 (31), the stability of QSG against silica hydrolysis up to pH 8 was shown (16). So it may be concluded that QSG is adequately stable during the stirring time (wt loss = 0.45% after 60 min stirring). Figure 3 represents the effect of time of stirring on the recovery of Sn(IV) at pH 3.8 using QSG or Q/PUF. Both QSG and Q/PUF show fast kinetics of equilibration so that 10 min of stirring was enough to reach maximum values of recovery.

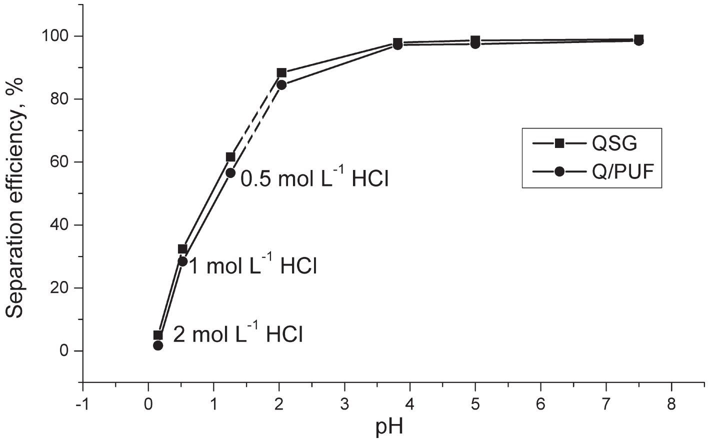


Figure 2. Effect of pH on the separation efficiency of Sn(IV) on QSG or Q/PUF.

Effect of Concentration of Eluent Acid

Although, many eluting agents are available such as HCl, thiourea or EDTA, but HCl is mostly preferred for the HGAAS determination, hence it was used in the present study (32). Figure 4 shows the effect of concentration of the eluting acid HCl on the recovery after separation at pH = 3.8 and weight = 40 mg. An acid concentration of 2 mol L^{-1} was sufficient to obtain maximum recovery. Comparing these results with those obtained for CMPS-PAN resin (33), it can be noticed that the recovery of Sn(IV) from QSG or Q/PUF is remarkably better indicating its reversible behavior.

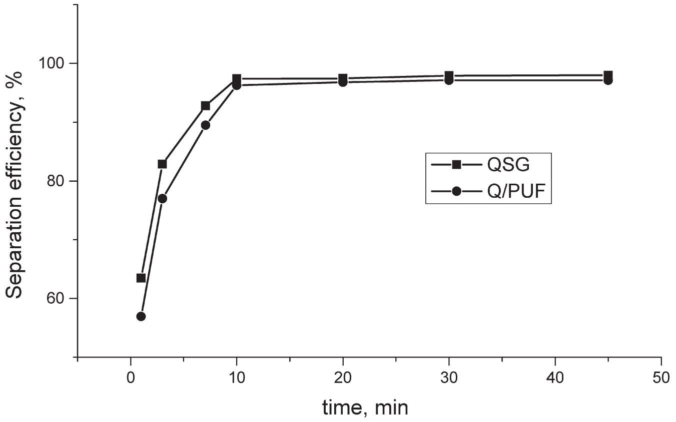


Figure 3. Effect of time of stirring on the recovery of Sn(IV) separated on 40 mg QSG or Q/PUF at pH = 3.8 ± 0.1.

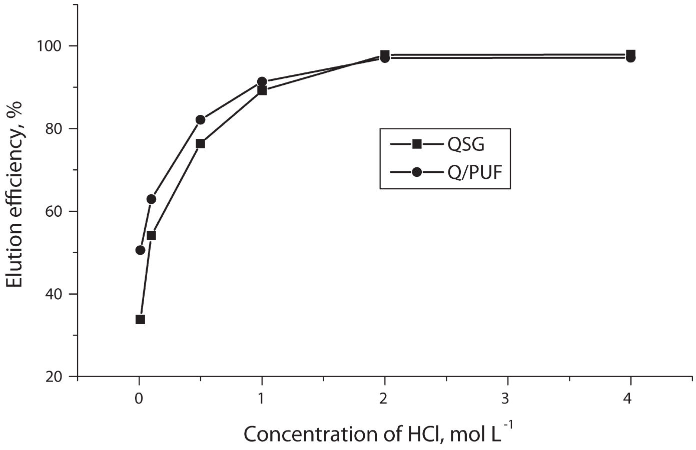


Figure 4. Effect of HCl concentration on the recovery of Sn(IV) separated on 40 mg QSG or Q/PUF at pH = 3.8 ± 0.1 and time of stirring = 10 min.

Obviously, too strong a chelation between the sorbent and the metalloid ion is not favored due to irreversible binding (34).

Effect of some Interfering Specie

No effect on the efficiency of separation of the investigated metal and metalloid ions was found from most common ions such as sulfate, phosphate, chloride, tartarate, Na(I), K(I), Mg(II), and Ca(II) ions. Trace metal ions B(III), Cr(III), Al(III), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), and Bi(III), with concentration of 50 fold that of the investigated metal ions do not affect the separation process. Mo(VI), Zr(IV), and Fe(III) in equal concentration, were observed to compete with Sn(IV) extraction on QSG but not on Q/PUF. This indicates that replacing the nitrogen atom of propylamine moiety with the pyran oxygen enhances the H5Q chelating activity towards these metal ions. However, using of excess sorbent eliminates this interference. Thiourea, thionalide, and EDTA in similar concentration, causes strong interference on the metal ions separation. This indicates that in case of application, the organic content should be digested prior to separation. The tolerance limits are shown in Table 1.

Flotation Separation

Effect of Oleic Acid Concentration

The flotability of 25 mL 1.0 μg mL^{-1} Sn(IV) using different concentrations of oleic acid in the absence and in the presence of 4×10^{-6} mol of H5Q L^{-1} at

Table 1. Effect of interfering ions on the separation of Sn(IV) [1 μg mL^{-1}] from 50 mL with SPE-QSG, SPE-Q/PUF and flotation techniques

Interfering ion	Tolerance limit
Na(I), K(I), Cl^-, acetate	40,0000 fold
Mg(II), Ca(II), CO_3^-, NO_2^-, SO_4^-	10,0000 fold
Sr(II), Ba(II), F^-, Br^-, PO_4^-	1000 fold
B(III), Cr(III), Al(III), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Bi(III)	50 fold
NO_3^-	5 fold
Fe(III), Mo(VI), Zr(IV)	1 fold (in case of QSG) and 50 fold in case of Q/PUF or flotation
Thiourea, Thionalide, EDTA	0.5 fold

pH 3.8 has been thoroughly investigated at room temperature. The data obtained showed that the maximum flotation (ca. 100%) is obtained in a wide range of concentration of oleic acid (5×10^{-5} to 6×10^{-4} mol L^{-1} in kerosene) in the presence of 4×10^{-6} mol of H5Q L^{-1} whereas in its absence only 7.9% flotation could be achieved. Consequently, the role of PET in the separation process is quite essential. For subsequent measurements, 3 mL of 1×10^{-4} mol L^{-1} oleic acid was used.

Effect of H5Q and Sn(IV) Concentration

The effect of H5Q concentration in the range ($0.1-4 \times 10^{-6}$ mol L^{-1}) on the flotability 25 mL 1 μg mL Sn(IV) using 3 mL of 1×10^{-4} mol L^{-1} of oleic acid at pH 3.8 ± 0.1 was investigated. Data obtained indicated that complete flotation of Sn(IV) is attained only if H5Q $\geq$ [Sn(IV)], so during the flotation process excess amounts of H5Q were added. Such excess in reagent concentration facilitates the application of the procedure to real samples. Furthermore, another series of experiments was conducted to float 25 mL of different concentrations (0.01–1.0 μg mL) of Sn(IV) in presence of 4×10^{-6} mol L^{-1} PET and 3 mL of 1×10^{-4} mol L^{-1} of oleic acid at pH 3.8 ± 0.1. The data obtained confirmed those found in the preceding experiments, i.e., maximum separation (ca. 100%) was obtained by flotation when the H5Q:Sn(IV) ratio is $\geq 1/2$.

Effect of Foreign Ion

Similar effect of foreign ions was found as discussed above in the SPE separation study. Only Mo(VI), Zr(IV), and Fe(III) interfere with the flotation process if their concentration was comparable to that of Sn(IV). Use of concentration of H5Q exceeding their molar concentration eliminates this interference.

Flotation Mechanism

Firstly, it must be taken into consideration that oleic acid begins to dissociate at pH ≥ 5.2 (35). Since the recommended pH for this investigation was 3.8 ± 0.1, oleic acid molecules share in flotation in the undissociated form. Accordingly, the flotation mechanism is proposed to proceed through hydrogen bonding between oleic acid and Sn(IV)-H5Q system. This observation stems from the following experimental data and observations:

1. The floated species (Sn(IV)-H5Q-oleic acid) has the same λ_{max} as those obtained in the solid phase of Sn(IV)-H5Q.
2. Comparison of the infrared spectrum of the Sn(IV)-H5Q complex isolated from ethyl/amyl (70/30) alcohols with that of the complex formed in oleic acid layer shows that all the bands are similar except those appearing at ca. 1820, 2050, and 2400 cm^{-1} in the spectrum of the latter. These bands are due to ν(O-H … O) vibrations of the intermolecular hydrogen bonding. Therefore, the oleic acid is headed with its carboxylic group directed towards the Sn(IV)-H5Q complex whereas its tail directed to the solution and Sn(IV)-H5Q-oleic acid system became hydrophobic and floated with air bubbles to the surface of the solution.

Nature of Bonding Between H5Q and Tin(IV) in Different Techniques

To establish the formation of the tin complex with quercetin in different phases, the UV-visible studies were carried out. The spectra of QSG and Sn(IV)-QSG were recorded in nujol mull. In case of Q/PUF, DMF was used to leach out H5Q and its Sn(IV)-complex. DMF was also used to dissolve H5Q-scum and the corresponding tin complex.

From the data tabulated in Table 2, it is clear that there is a change in color of the H5Q in case of QSG (brown) whereas in case of immobilization on PUF or scum, there was no color change. This is attributed to that in case of QSG; H5Q is immobilized via chemical bonding whereas in case of Q/PUF and scum, H5Q is physically adsorbed as confirmed by its easily leaching out in DMF.

The pH-metric titration with 0.013 mol L^{-1} NaOH was carried out in order to characterise the bonding between QSG and Sn(IV). A typical titration curve for the sorbent is shown in Fig. 5, which is in agreement with that reported earlier (16). When the same titration was performed in the presence of the studied metal ion, the titration curve was shifted to the right side (more consumption of NaOH). This may indicate that the organic substrate is bonded to Sn metal ions via the displacement of the protons of the phenolic groups.

Table 2. UV-vis data of H5Q species and their complex with Sn(IV) nujol mull

Phase	Colour	Absorption band (nm)
QSG	Brown	535
Tin complex	Golden brown	535
Q/PUF	Yellow	370
Tin complex	Brilliant yellow	470
H5Q-Scum	Yellow	370
Tin complex	Brilliant yellow	470

Comparing the thermogravimetric analysis of QSG and its complex with Sn(IV) (Fig. 1), it is clear that the weight loss stages of QSG described above, are strongly shifted to higher temperatures. This is attributed to the complexation of QSG with Sn(IV) which increases the stability of the organic substrate.

The capacity of QSG and Q/PUF towards Sn(IV) at that pH was found to be 0.526 and 0.331 mmol g^{-1}, respectively, indicating a 2:1 Sn/H5Q ratio.

Application of the SPE and Flotation Techniques to the Separation of Sn(IV) from Natural Samples

The proposed procedure was applied for the separation and preconcentration of Sn(IV) from Nile river water, canned beans, and high purity zinc shot

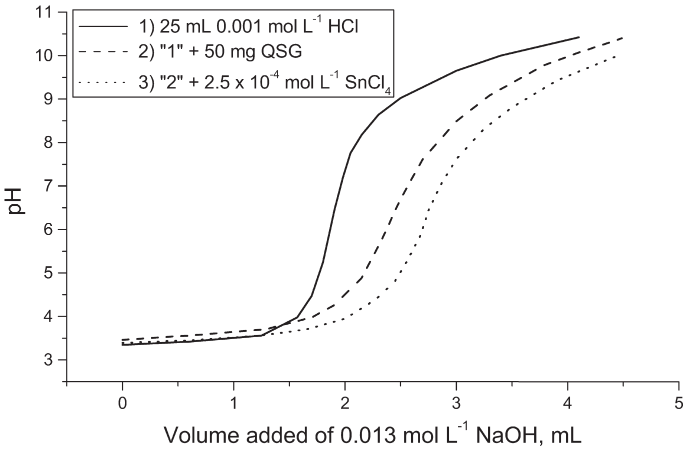


Figure 5. pH-Metric titration of QSG and its complex with Sn(IV). Solid line 1) 25 mL 0.001 mol L^{-1} HCl, dashed line 2) "1" + 50 mg QSG and dotted line "2" + 2.5 × 10^{-4} mol L^{-1} $SnCl_4$.

(reference material no. 835023) samples spiked with tin shot (reference material no. 030503) followed by HGAAS determination. The samples were first subjected to an oxidative digestion to digest the organic matter present and to guarantee the conversion of all tin species, i.e., Sn(II) and organotin(IV), to Sn(IV). The results, shown in Table 3, indicate that there is no significant difference between the spiked amount and those recovered by SPE using QSG or Q/PUF or floatation techniques in case of Nile river water and zinc shot samples. In case of Elmanzalah lake and seawater samples, there was a Sn(IV) background as seen from the non-spiked samples. The reliability of the flotation and SPE techniques was statistically examined for the Nile river water and zinc shot using the null hypothesis of $|t|_1$ for $P = 0.05$ and $n = 10$. It was found that $|t|_1 = 0.22-0.81$ which is lesser than the tabulated value ($|t|_1 = 2.31$) (36). This indicates that the three methods of separation and preconcentration of Sn(IV) using H5Q

Table 3. Analysis of natural samples using ICP-MS for determination of Sn(IV) in $\mu g\,L^{-1}$* (values given as average of five replicates), after preconcentration with solid phase extraction (SPE) using QSG or Q/PUF in comparison with those obtained by the flotation technique. (volume of water samples = 500 mL, pH = 3.8 ± 0.1, weight of QSG or Q/PUF = 150 mg, stirring time = 10 min at 25°C, and values between brackets are relative standard deviation (RSD, %)

Sample	Spike* $\mu g\,L^{-1}$	SPE-QSG ($\mu g\,L^{-1}$*)		SPE-Q/PUF ($\mu g\,L^{-1}$*)		Floatation-H5Q-oleic acid ($\mu g\,L^{-1}$)*	
		$\bar{X}$ (RSD)	$\lvert t\rvert_1$	$\bar{X}$ (RSD)	$\lvert t\rvert_1$	$\bar{X}$ (RSD)	$\lvert t\rvert_1$
Mansoura (nile river)	0	BDL	—	BDL	—	BDL	—
	0.5	0.497 (1.87)	0.72	0.501 (1.99)	0.22	0.501 (1.72)	0.26
	1	1.002 (1.29)	0.35	0.998 (1.59)	0.28	1.002 (1.11)	0.40
Elmanzalah lake (brackish)	0	0.419 (1.55)	—	0.421 (1.29)	—	0.417 (1.91)	—
	0.5	0.916 (1.29)	—	0.917 (0.87)	—	0.918 (1.89)	—
	1	1.422 (1.04)	—	1.42 (0.91)	—	1.415 (1.02)	—
Port Said (seawater)	0	0.478 (1.35)	—	0.476 (1.88)	—	0.472 (1.95)	—
	0.5	0.979 (0.98)	—	0.976 (0.65)	—	0.975 (1.56)	—
	1	1.48 (1.23)	—	1.481 (1.99)	—	1.471 (1.19)	—
100 g canned beans*	1	1.799 (1.00)	—	1.799 (1.22)	—	1.792 (1.59)	—
1 g zinc shot spiked with 1 μg tin(IV)*	1	1.002 (0.72)	0.62	0.997 (0.83)	0.81	0.998 (1.39)	0.32

BDL means below analytical detection limit and * values given in $\mu g\,g^{-1}$ in case of zinc shot and $\mu g\,100\,g^{-1}$ in case of canned beans. $|t|_1$ values were calculated only for samples containing known amount of tin (i.e., free from tin background).

chemically-immobilized on silica (QSG), physically-adsorbed on PUF (Q/PUF), or floated in oleic acid/kerosene are not subject to random errors (i.e., precise).

CONCLUSION

H5Q chemically-immobilized on silica, physically-adsorbed on PUF or floated in oleic acid/kerosene forms stable complex with Sn(IV) at pH 3.8. The three sorbents were successfully used for the separation and preconcentration of total tin with high selectivity and accuracy using SPE and flotation techniques. The solid phase extraction using QSG was recommended due to relative long-term durability, low-cost, and simplicity, and there is no contamination risk coming from flotation reagents.

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