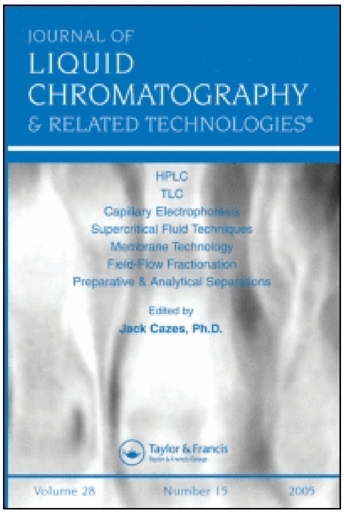


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Characterization of Surface Modification, Thermal Stability, and Metal Selectivity Properties of Silica Gel Phases-Immobilized Dithiocarbamate Derivatives

Mohamed E. Mahmoud[a]; Mohyi M. El-Essawi[b]; Eiman M. I. Fathallah[b]
[a] Medical Chemistry Department, Faculty of Medicine and Allied Sciences, King Abdullaziz University, Jeddah, Saudi Arabia [b] Chemistry Department, Faculty of Sciences, Alexandria University, Alexandria, Egypt

To cite this Article Mahmoud, Mohamed E. , El-Essawi, Mohyi M. and Fathallah, Eiman M. I.(2004) 'Characterization of Surface Modification, Thermal Stability, and Metal Selectivity Properties of Silica Gel Phases-Immobilized Dithiocarbamate Derivatives', Journal of Liquid Chromatography & Related Technologies, 27: 11, 1711 — 1727

To link to this Article: DOI: 10.1081/JLC-120037366

URL: http://dx.doi.org/10.1081/JLC-120037366

JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES®
Vol. 27, No. 11, pp. 1711–1727, 2004

Characterization of Surface Modification, Thermal Stability, and Metal Selectivity Properties of Silica Gel Phases-Immobilized Dithiocarbamate Derivatives

Mohamed E. Mahmoud,[1,*] Mohyi M. El-Essawi,[2] and Eiman M. I. Fathallah[2]

[1]Medical Chemistry Department, Faculty of Medicine and Allied Sciences, King Abdullaziz University, Jeddah, Saudi Arabia
[2]Chemistry Department, Faculty of Sciences, Alexandria University, Alexandria, Egypt

ABSTRACT

Carbon disulphide was used to modify the surface of silica gel phases containing amine moieties for the formation of four phases-immobilized dithiocarbamate derivatives (**I–IV**). Characterization of the surface modification by the organic modifier was accomplished by several means of instrumental analysis. These include infrared, secondary ion mass spectrometry (SIMS), as well as, thermal desorption analysis for determination

---

[*]Correspondence: Mohamed E. Mahmoud, Medical Chemistry Department, Faculty of Medicine and Allied Sciences, King Abdullaziz University, P.O. Box 80205, Jeddah 21589, Saudi Arabia; E-mail: memahmoud10@yahoo.com.

DOI: 10.1081/JLC-120037366
1082-6076 (Print); 1520-572X (Online)
www.dekker.com

of the surface coverage values (1.051–1.501 mmol g^{-1}). The thermal stability and structure characterization of the modified silica gel phases (**I**–**IV**), along with their mercury(II) adducts, were studied and evaluated on the basis of electron impact mass spectrometric analysis (EI-MS). The results of this study proved higher thermal stability characters incorporated into the metal adduct compared to the free silica gel phase. The selectivity properties incorporated into the modified silica gel phases for binding and interaction with a series of bi- and trivalent metal ions were studied and evaluated by determination of the distribution coefficient and separation factor. The results of these evaluation processes were found to point out the higher selectivity and preference of these four phases for binding with mercury(II), copper(II), and cadmium(II) compared to other metal ions.

Key Words: Silica gel; Surface modification; Thermal stability; Metal selectivity; Dithiocarbamate.

INTRODUCTION

Chemically modified solid phases have been widely used as packing materials in column chromatographic applications.[1–3] Some of these are mainly based on the developments of modified silica gel phases with certain chelating compounds or groups for pre-concentration and separation of trace and ultra trace metal ions by either on-line or off-line mode of analysis.[4] The interaction mechanisms between metal ions and modified silica gel phases are highly dependent on the binding efficiency and properties of these analytes and the active surface chelating group, as well as, the concept and rules of coordination chemistry.[5] This has promoted researchers to explore some well designed modified solid phases for applications in selective extraction and determination of toxic and nontoxic metal ions, by using silica gel phase-loaded-chelating compounds.[6,7] A large number and variety of chelating groups were used to improve the surface reactivity of either inorganic or organic solid matrices, starting with the well known 8-hydroxyquinoline as a simple one,[8–10] to more complicated macromolecular species as crown ether and their derivatives,[11–13] as well as chelating polymeric compounds.[14,15] Understanding the selectivity incorporated into these modified phases, is considered the key point in such designing process and applications of these systems that are interpreted on the basis of several phenomena.[16] Dithiocarbamate derivatives are examples of sulfur and nitrogen containing chelating compounds, or groups similar to other classes of compounds as 2-mercaptobenzothiazol, dithizone, 2-(2-thiazolylazo)-*p*-cresol, 2-amino-1-cyclopentene-1-dithiocarboxylic acid, 2-[(2-triethoxysilyl)-ethylthio]aninline, and thiourea. These species were previously loaded on the surface of silica gel via chemical or physical approach and found to exhibit various preferences for binding with metal ions as Ag(I), Cu(II), Zn(II), Hg(II), Pd(II), and other metal ions.[17–23]

In this report, four silica gel phases-immobilized dithiocarmate derivatives were synthesized. Structural and surface modifications, thermal stability, metal binding properties, and selectivity characters toward certain metal ions were studied, characterized, and evaluated.

EXPERIMENTAL

Chemicals and Solutions

Silica gel (70–230 mesh, 60 Å pore diameter) was purchased from Riedel de Haën, Hannover, Germany. 3-Chloropropyltrimethoxysilane and 3-aminopropyltrimethoxysilane were received from Aldrich Chemical Company, USA. Ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine were purchased from Aldrich Chemical Company, USA. Carbon disulfide (CS_2) was purchased from Merck, Darmstadt, Germany. All chemicals were used as received. Organic solvents were dried according to conventional methods. Metals salts were all of analytical reagent grade and purchased from BDH Chemical Company, Poole, UK and Fluka Chemie AG, Switzerland. Metal ions solutions were prepared from doubly distilled water (DDW).

Synthesis of Modified Silica Gel Phases (I–IV)

Silica gel (50 g) was weighed and suspended in 1 L of 4.0 M hydrochloric acid. This mixture was allowed to reflux with stirring for 4 hr, then filtered and washed with distilled water till an acid free silica gel phase. Active silica gel was then dried in an oven at 150–160°C for 6 hr and left in a desiccator for future use. Silica gel phases (**I**–**IV**), with chemically bound dithiocarbamate, were synthesized by a two-step reaction. The first step is the synthesis of silica amine derivatives (i–iv). Silica monoamine was prepared by reaction of active silica gel with 3-aminopropyltrimethoxysilane. Silica-modified-di, tri, and tetramine were prepared by the direct reaction of silica-modified-propyl chloride (SiCl) with EDA, DETA, and triethylenetetramine, respectively.[7,24] The second step is the preparation of silica gel phases (**I**–**IV**) chemically bound dithiocarbamate through the reaction with carbon disulfide, according to the following procedure: 8.0 g of the monoamine phase (i) was weighed and suspended in 100 mL of dry toluene and 15 mL of carbon disulfide was added. The reaction mixture was refluxed with stirring for 8 hr, filtered, washed with toluene, ethyl alcohol, and diethyl ether, and dried in an oven at 60°C for 6 hr. The silica gel phases (**II–IV**) were also synthesized, in a similar way, by the reaction of 8.0 g of diamine silica gel phase, (ii) with 30 mL of CS_2, 8.0 g of triamine silica gel phase, (iii) with 45 mL of CS_2 and 8.0 g of tetramine silica gel phase, (iv) with 60 mL of CS_2. These reactions were refluxed with stirring, filtered, washed, and dried as previously described for the silica gel phase (**I**).

Determination of the Surface Coverage by the Thermal Desorption Method

The surface coverage of silica gel with the organic chelating compounds, was accomplished by the thermal desorption method.[2,25] In this method, 100 ± 1 mg of dry silica gel phases (**I–IV**) was weighed and ignited at 550°C in a muffle furnace. The initial temperature was 50°C and was gradually increased to 550°C in about 20 min. The ignited phase was then kept at this temperature for 1 hr and left to cool down inside the furnace till 70°C. The sample was transferred to a dessicator. The weight loss of the organic chelating compounds was determined by the difference in the sample weights before and after the process of thermal desorption. Blank samples of active silica gel were also subjected to the same thermal desorption procedure, as described, for comparison.

Determination of Metal Capacity Values of Silica Phases (I–IV) via Interaction with Hg(II)

Silica gel phase (2.0 g) (**I**) was mixed with 25 mL of 0.1 M mercuric chloride in 0.1 M sodium acetate and shaken by an automatic shaker for 1 hr. The product silica gel phase (**I**)–Hg(II) was then filtered, dried, washed with 100 mL DDW, and dried in an oven for 6 hr at 70°C.

The interaction of Hg(II) with the modified silica gel phases (**II–IV**) was performed according to the same procedure. Each silica gel (2.0 g) was mixed with 50, 75, and 100 mL of 0.1 M $HgCl_2$ in 0.1 M NaOAc for phase (**II**)–Hg(II), phase (**III**)–Hg(II), and phase (**IV**)–Hg(II), respectively. These mixtures were shaken by an automatic shaker for 1 hr, filtered, washed, and dried as above. Each of the modified silica gel phases (100 mg) (**I–IV**)–Hg(II) was added to 20 mL of concentrated nitric acid and automatically shaken for 1 hr. The desorbed Hg(II) was determined by complexometric titration and cold vapor atomic absorption analysis.

Determination of the Distribution Coefficient Values

The following metal ions were used to determine the distribution coefficient values of the various modified silica gel phases (**I–IV**). These are Mg(II), Ca(II), Mn(II), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II). The concentration of each metal ion solution is ~1.0 ppm in 0.1 M NaOAc solution except Fe(III) in buffer pH2.

In a 25-mL measuring flask, 100 ± 1 mg of the modified silica gel phase (**I–IV**) was weighed. Ten milliliters of 1.0 ppm metal ion was then added and the flask was shaken by an automatic shaker for 3 hr. This mixture was filtered and washed with 10 mL DDW. The volume of metal ion was completed to the 50 mL mark by using 5% hydrochloric acid solution. Standard and blank solutions were also prepared. The concentration of metal ions in the sample, standard and blank solutions were determined by atomic absorption analysis.

Apparatus

The flame atomic absorption spectrophotometric measurements of the tested metal ions were determined by a Perkin Elmer 2380 atomic absorption spectrophotometer. Atomic absorption analysis of Hg(II) was performed by a Varian Spect AA-10 plus atomic absorption spectrophotometer equipped with a VGA-76 vapor generation accessory at the Institute of Oceanography, Alexandria, Egypt. The thermal desorption analysis of the modified silica gel phase (**I–IV**) were performed by Vulcan A-550 muffle furnace. The electron impact mass spectra of selected silica gel phases were carried out using the CH4 and CH7 MAT-Bremen instrument at Marburg/Lahn University, Germany. The infrared spectra were performed using IFS 88 instrument from Bruker Comp-Karlsruahe at Marburg/Lahn University, Germany. The secondary ion mass spectra of selected silica gel phases were performed using a combined Secondary ion mass spectrometry (SIMS)/AES instrument (Balzers/Physical electronics) and the data was digitalized as ASCII at Münster University, Germany.

RESULTS AND DISCUSSION

Identification of Surface Modification by Infrared Analysis and Secondary Ion Mass Spectrometry

Identification of the silica gel surface modification by the organic chelating compounds can be accomplished by studying the infrared spectra of both active silica gel and modified silica gel phases.[2,22] The infrared spectrum of active silica gel was completely dominated by the presence of a strong peak centered at 1100 cm^{-1} due to the absorption of silica gel matrix, as well as a broad peak centered at 3477 cm^{-1}, which is mainly due to the presence of surface silanol group and the presence of some adsorbed water molecules.[22] Modification of the active silica gel surface with a chelating compound is pre-assumed to exhibit some functional groups in the infrared spectra of the modified silica gel phases. However, this assumption is mainly dependent on the surface coverage values of the modified silica gel phases. The infrared spectra of silica gel phases (**I**–**IV**) were found to exhibit a weak peak at 1558 cm^{-1}, which corresponds to the dithiocarbamate (ν_{ncs2}) bond.[17] Other peaks at 3100–3200 and <3000 cm^{-1}, are assigned to imine and aliphatic C–H groups, respectively. Figure 1 shows the infrared spectrum of modified silica gel phase (**IV**) as an example, and the important peaks are listed in Table 1. The structures of these modified silica gel phases (**I**–**IV**) are given in Sch. 1.

Secondary ion mass spectrometry in the static mode (SSIMS) was proven to be a versatile and direct method for determination of the composition, structure identification, and surface analysis of thermally stable compounds as polymeric ones or chemically modified surfaces. However, the advantages of SIMS in surface analysis applications were previously reported.[26] The positive SIMS of silica gel phase (**IV**) exhibited several fragment ion peaks at m/z 76, 116, and 238, and these were identified and correlated to the assigned structure of the modified silica gel phase (**IV**), as presented in Sch. 2.

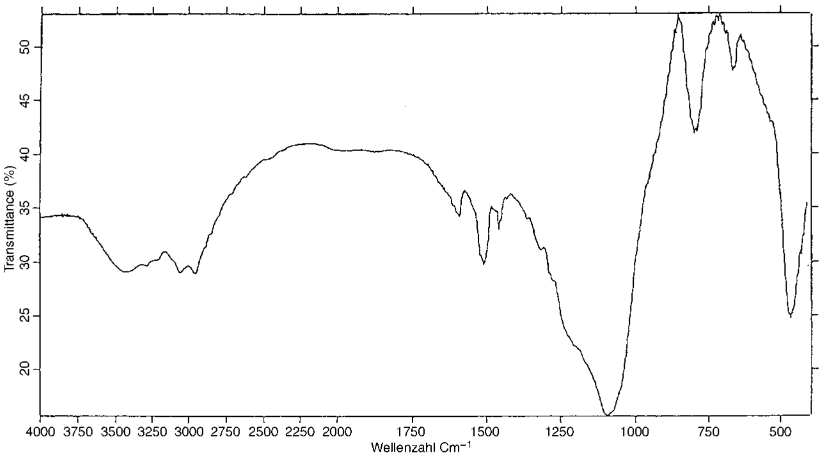


Figure 1. Infrared spectrum of silica gel phase (**IV**).

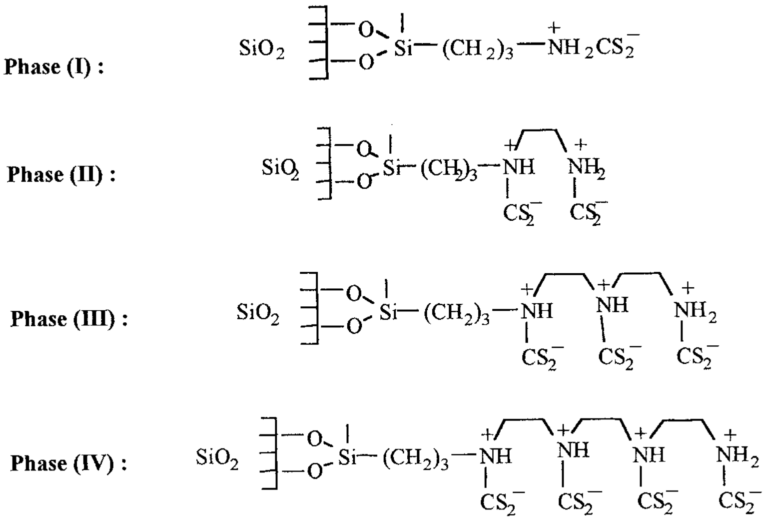
Table 1. Metal capacity values in mmol g^{-1} for the interaction of Hg(II) with modified silica gel phases (**I–IV**).

Silica gel phase	Surface coverage (mmol g^{-1})[a]	Metal ion	Metal capacity (mmol g^{-1})	Important infrared peaks (cm^{-1})
(**I**)	1.501	Hg(II)	0.330	1,100, 1,558, <3,000
(**II**)	1.266	Hg(II)	0.610	3,100–3,200, 3,477
(**III**)	1.051	Hg(II)	0.950	
(**IV**)	1.052	Hg(II)	1.000	

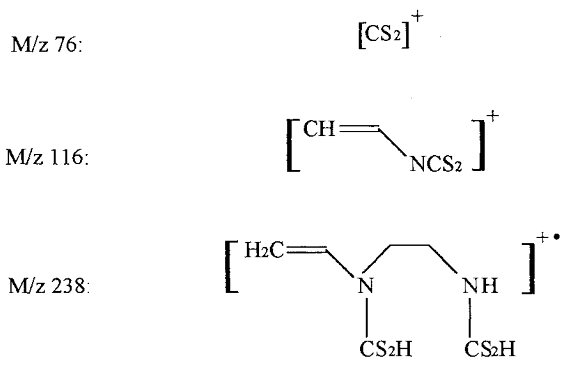
[a] Values are based on thermal desorption method.

Thermal Stability of Modified Silica Gel Phases (I–IV) by Electron Impact Mass Spectrometry

The mass spectrometry technique is one of the powerful analytical methods of analysis for qualitative and quantitative determination of organic and inorganic compounds.[27] It can be used for the identification of products formation, as well as, study of the reaction follow-up. The most commonly used mode of ionization is the electron impact. Several techniques are usually used to apply the sample for introduction into the mass spectrometer and the



Scheme 1. Silica gel phases (**I–IV**).



Scheme 2. Characteristic fragment ions produced from SIMS of phase (**IV**).

ionization chamber. The most commonly used sample application methods are the direct insertion probe (DIP). In this, the sample is loaded and heated on a probe tip. This allows the sample evaporation and insertion into the ion source. The probe temperature of 200–300°C is usually applied and is sufficient for evaporation of volatile species of the sample molecules and detection by the mass spectrometric detector. Thus, the mass spectrometric technique can be used to study the thermal stability via desorption of the organic compounds. Moreover, silica gel phases-chemically or physically loaded-organic compounds can be tested for thermal stability via their analysis by the mass spectrometric technique, under electron impact ionization with a heating temperature of 300°C.

The mass spectrum of phase (**I**) is characterized by the presence of the base peak at m/z 28, due to the presence of nitrogen gas inside the ion source. A few other fragment ions at m/z 32 and 44 were also characterized by the presence of O_2 and CO_2 inside the ion source. Two other fragment ions were also characterized at m/z 76 and 91 with relative intensity of 5.0 and 1.0%, respectively. These two fragment ions may be due to the formation of $[CS_2]^+$ and $[NHCS_2]^+$ ions, respectively, from the modified silica gel phase (**I**), as shown in Fig. 2. However, these two fragment ions clearly confirm the immobilization of the modified silica gel phase with the dithiocarbamate moiety. In addition, the identification of these two fragment ions can be taken into account for the thermal decomposition of the dithiocarbamate moiety, upon heating by the DIP. This procedure can be considered as an alternative method for TGA. The electron impact mass spectrometric analysis (EI-MS) of the modified silica gel phase (**I**)–Hg(II) given in Fig. 2, indicates the absence of the two peaks at m/z 76 and 91 due to the possible binding of these functional groups with the loaded Hg(II), and confirming their thermal

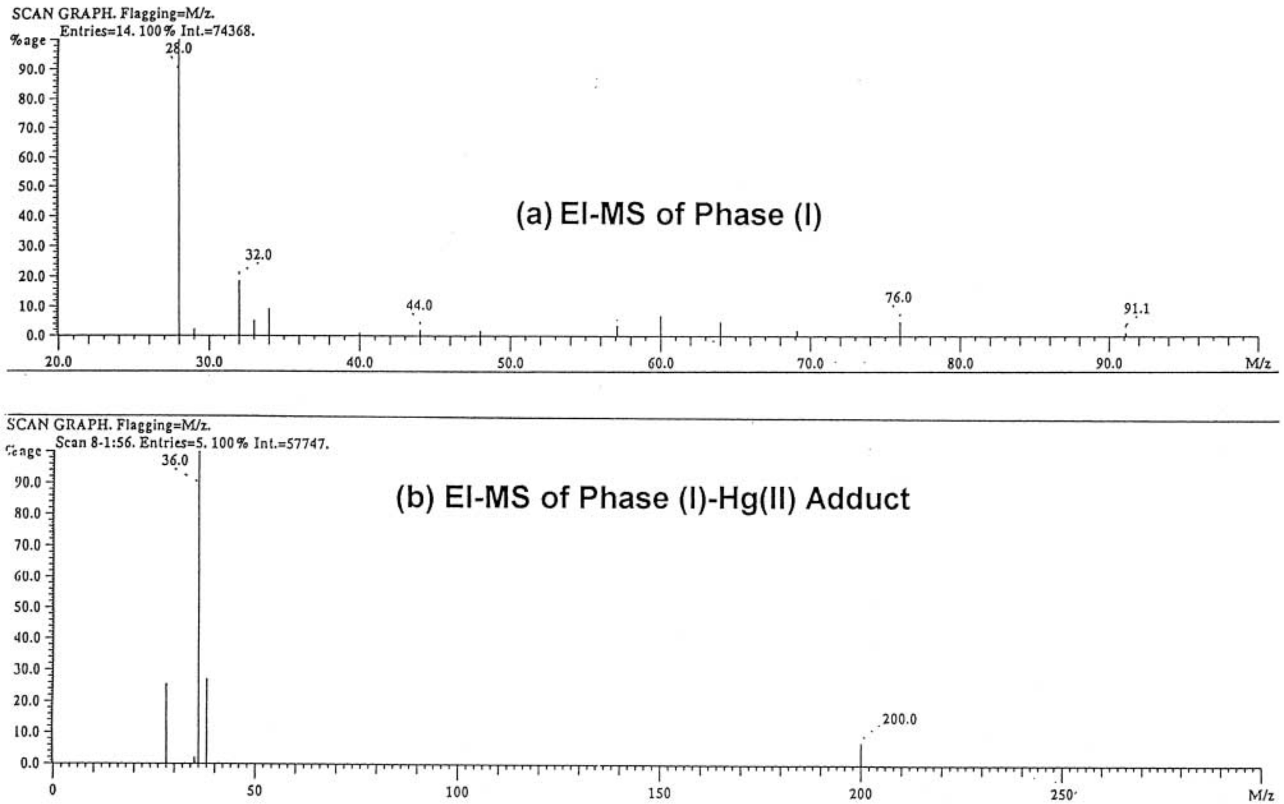


Figure 2. EI-MS of (a) silica phase (**I**) and (b) silica phase (**I**)–Hg(II).

stability in the presence of metal ion. In addition, the EI-MS is characterized by the presence of a fragment ion peak at m/z 200, which is mainly due to the presence of loaded mercury on the surface of silica gel phase (**I**). Formation of this ion at m/z 200 is mainly due to the possible volatilization of mercury from the surface.

The EI-MS of silica gel phases-chemically bonded-dithiocarbamate (**II–IV**), along with their mercury(II) products, were also found to be similar for that described in modified silica gel phase (**I**). Few fragment ions are produced from the dithiocarbamate moiety at m/z 76 and 91 from the modified silica gel phases (**II–IV**), as well as the formation of the fragment ion at m/z 200, due to the loss of mercury ion from these modified silica gel phases. The conclusion attained from this study is the higher thermal stability of modified silica gel phases–Hg(II) as compared to the modified ones.

Determination of the Surface Coverage Values (mmol g^{-1}) by Thermal Desorption

The surface of active silica gel either in a crystalline or amorphous type is characterized by the presence of silanol groups, silanediol groups, or silanetriol groups. These groups are arranged into several possible arrangements depending on the interaction between them.[28] The general procedure for chemical immobilization of organic chelating compounds on the surface of silica gel matrix is accomplished by using a silylating agent as an intermediate between these two species. Thus, the first step is the reaction of free surface silanol groups with 3-chloropropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, and 3-thiolpropyltrimethoxysilane.[16,24] The newly modified silica gel surface is directly bound to chloro, amino, and thiol groups that can be used in further modification and loading of a large number of chelating compounds.

Identification of the silica gel surface modification can be accomplished by the determination of the surface coverage values, expressed in mmol or μmol of the organic modifier per one gram of the silica gel phase (mmol g^{-1} or μmol g^{-1}). This evaluation can be accomplished by several known methods, the most efficient one is known as thermal desorption method[2] in which the modified silica gel phases are heated at high temperatures ~500–600°C for a certain period of time, approximately 1 hr. These heating times and temperatures are sufficient to desorb the organic matter loaded on the surface of silica gel into volatile species that are easily removed from the surface of silica gel phases. The residue obtained from this procedure corresponds to the stable and dry SiO_2 matrix that can be used for the determination of the mmol g^{-1} values.

The identified surface coverage values ($\mathrm{mmol\,g^{-1}}$) clearly indicate that all the modified silica gel phases (**I–IV**) based on the method of chemical immobilization, are highly loaded and bound with the organic modifiers. The highest surface coverage value ($1.501\,\mathrm{mmol\,g^{-1}}$) was found to belong to silica gel phase (**I**). The other surface coverage values were found to be 1.266, 1.051, and $1.052\,\mathrm{mmol\,g^{-1}}$ for (**II**), (**III**), and (**IV**), respectively.

Metal Capacity Values of Silica Gel-Chemically Immobilized Dithiocarbamate Phases (I–IV)

Mercury(II), palladium(II), platinum(II) and (IV), and silver (I) are commonly classified as soft acids. Sulfur containing compounds and phases are also classified as soft bases on the basis of hard–soft acids–bases. Thus, strong binding and interaction between these two species are expected. This phenomenon has been exploited and applied in a series of published papers.[18–23] Silica gel-immobilized dithiocarbamate derivatives have been recently used as selective solid phase extractors for mercury(II).[17] The metal capacity values listed in Table 1 are determined and calculated from the actual adsorbed Hg(II) on the surface of modified silica gel phases, while those of other reports[19–22] are based on the unbound metal ion from the total amount added for the interaction with the modified silica gel phases, as described by the batch equilibrium technique.

The reactivity of the modified silica gel phases (**III**) and (**IV**) were found to be optimum, judging from the close values of the surface coverage and the mercury(II) capacity values by these two modified silica gel phases. Moreover, loading and complexation of the surface donor atoms is near completion, with an estimated stoichiometric ratio of 1 : 1 for these two silica gel phases-chemically immobilized dithiocarbamate (**III** and **IV**) vs. mercury(II). On the other hand, the modified silica gel phase (**VI**) was found to interact with mercury(II) to a lesser extent than those reported for silica gel phases (**III**) and (**IV**). This means, that the reactivity of silica gel phase (**II**) is considered to be less than those experienced with silica gel phases (**III**) and (**IV**) for binding and extraction of Hg(II). A stoichiometric ratio of 1 : 2 can be estimated from the metal capacity value and the surface coverage value of silica gel phase (**II**) vs. mercury(II). This also can indicate about 50% reactivity of the donor atoms loaded on the surface of silica gel phase (**II**). The reactivity of silica gel (**I**) towards Hg(II) can be considered as the lowest one amongst the other modified silica gel phases-loaded dithiocarbamate derivatives (**II–IV**).

The stability of the modified silica gel phases in different acidic solution was determined in buffer solutions with pH 1–6. These phases were found to be more resistant to leaching processes in buffer solutions pH > 3. Therefore, the application of strong acid solutions ($\geq 0.1\,\text{M}$) as a recycling reagent will cause strong leaching of the organic modifier from the surface of silica gel phase. Alternatively, ethylenediaminetetraacetic acid (EDTA) solution was tested and found to exhibit reasonable results as a recycling reagent.

Distribution Coefficient and Separation Factor of Silica Gel Phases with Various Metal Ions

The immobilization of organic chelating compounds on the surface of solid supports such as silica gel phase, is mainly aimed to change the chemical properties of silica gel. The surface modification either by the chemical immobilization approach or physical adsorption approach can lead to incorporation of certain selectivity characters into the modified silica gel phase, due to the presence of certain donor atoms. The major application fields of the modified silica gel phases with organic chelating compounds is their use as solid phase extractors and pre-concentrators of metal ions from various matrices.[3,4] The evaluation of the modified silica gel phases as solid phases for extraction of metal ions, is based on determination of the distribution coefficient value (K_d).[2,21] This evaluation process is considered to be more convenient when the metal capacity values of the tested metal ions are very close, or when the concentrations of the tested metal ions are very low, especially in the range of part per million (ppm) or part per billion (ppb). In addition, the distribution coefficient values can lead to a more detailed list, which can assist in further evaluation of the metal-uptake properties, as well as the selectivity properties incorporated into the modified silica gel phases. The metal ions concentration selected to conduct this study is 1.0 ppm of each metal ion and the K_d-values of 12 tested metal ions, viz., Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II) were determined by the modified silica gel phases (**I–IV**).

The separation factor (α) is another important value and expression for the conclusion of the possible separation efficiency and selectivity characters incorporated into chemically and physically adsorbed silica gel phases with organic chelating compounds towards various metal ions.[7] In order, for the silica gel-modified-chelating compound, to accomplish any separation of two ions, it is necessary that one of these cations is extracted by the silica gel phase in a distinct preference to the other. The separation factor of any two cations can be calculated from the following equation:

$$\alpha_{\mathrm{A/B}} = \frac{K_{\mathrm{d}}(\mathrm{A})}{K_{\mathrm{d}}(\mathrm{B})}$$

where, as $\alpha_{A/B}$ is the separation factor for cation A vs. cation B, K_d(A) is the distribution coefficient value of cation A and K_d(B) is the distribution coefficient value of cation B. The separation factor $\alpha_{A/B}$ can be determined from the individual concentration distribution coefficient of A and B in a mixture of these two cations and is considered to equal the same value if calculated from two different individual solutions of A and B. This means, that the separation factor ($\alpha_{A/B}$) can be directly determined from the distribution coefficient (K_d) of the two interacting metal ions with the modified silica gel phase.

Silica gel phase-chemically immobilized dithiocarbamate (**I**) was found to give the highest determined K_d value for Hg(II) as 15,580, followed by Cu(II) with a value of 10,094. This means, that this modified silica gel phase is highly selective for Hg(II) and Cu(II). The other tested metal ions were found to exhibit little affinity to bind with silica gel phase (**I**). Their K_d-values were found to be very close to those reported for active silica gel phase.[7] The selectivity incorporated into this silica gel phase via the immobilization of dithiocarbamate moiety on the surface of silica gel phase was reported as the separation factor ($\alpha_{A/B}$) for Hg(II) and Cu(II) vs. Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), and Pb(II). These values are listed in Table 2 and clearly show evidence to support the selectivity of this silica phase for extraction of Hg(II) and Cu(II) from these interfering metal ions. On the other hand, the application of this silica gel

Table 2. The separation factor ($\alpha_{A/B}$) for the different metal ions by the modified silica gel phase (**I**).

Metal ion	Separation factor	
	Hg(II)	Cu(II)
Mg(II)	471.1	305.9
Ca(II)	1,554.5	1,009.4
Cr(III)	1,110.3	721.0
Mn(II)	818.2	531.3
Fe(III)	444.1	288.4
Co(II)	485.7	315.4
Ni(II)	575.8	373.9
Zn(II)	39.1	25.36
Pb(II)	129.5	84.1
Cd(II)	10	6.5
Cu(II)	1.5	—

phase (**I**) for selective extraction and separation of Hg(II) from Cu(II) cannot be accomplished due to the low separation factor of $\alpha_{\mathrm{Hg/Cu}} = 1.5$.

The same trend of high affinity of Hg(II) and Cu(II) was also observed by modified silica gel phase (**II**) similar to that determined by silica gel phase (**I**). The selectivity of the modified silica gel phase for Hg(II) extraction from the other interfering ions is evident in Table 3 and based on the high separation factor of Hg(II) vs. other interfering metal ions. This silica gel phase can also be used for selective extraction of Cu(II) from other interfering ions such as Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and Pb(II). A possible interference of Cu(II) can be expected in the selective extraction or separation of Hg(II) by the modified silica gel phase (**II**), due to the low selectivity factor $\alpha_{\mathrm{Hg/Cu}} = 2.1$.

Table 4 compiles the data of the separation factor ($\alpha_{\mathrm{A/B}}$) for the same series of metal ions by the modified silica gel phase (**III**). Four metal ions, viz., Hg(II), Cu(II), Cd(II), and Zn(II) were found to be highly extracted by this silica gel phase (**III**). The separation factors of these four metal ions vs. other tested metal ions show that Hg(II) and Cu(II) can be easily separated from other interfering metal ions. Cd(II) can be separated from the other interfering metal ions, except Zn(II) and Ni(II), due to low separation factors of 1.3 and 2.7, respectively. Zn(II) can be selectively extracted from all other interfering metal ions, except Ni(II) and Cd(II), as listed in Table 4. This modified silica gel phase (III) is showing the same trend as silica gel phases

Table 3. The separation factor ($\alpha_{\mathrm{A/B}}$) for the different metal ions by the modified silica gel phase (**II**).

Metal ion	Separation factor	
	Hg(II)	Cu(II)
Mg(II)	646.2	307.7
Ca(II)	1,208.1	575.3
Cr(III)	1,157.7	551.3
Mn(II)	2,137.4	1,017.8
Fe(III)	375.5	178.8
Co(II)	817.1	389.1
Ni(II)	142.6	67.9
Cd(II)	112.1	53.4
Pb(II)	427.6	203.6
Zn(II)	29.6	14.1
Cu(II)	2.1	—

Table 4. The separation factor ($\alpha_{A/B}$) for the different metal ions by the modified silica gel phase (**III**).

Metal ion	Separation factor			
	Hg(II)	Cu(II)	Cd(II)	Zn(II)
Mg(II)	750	300.0	97.2	74.2
Ca(II)	1,014.8	405.9	131.5	100.6
Cr(III)	609	243.6	78.9	60.4
Mn(II)	1,087.3	434.9	140.9	107.8
Fe(III)	237.8	95.1	30.8	23.6
Co(II)	76.5	30.6	9.9	7.6
Ni(II)	21.0	8.4	2.7	2.1
Pb(II)	197.8	79.1	25.6	19.6
Cu(II)	2.5	—	—	—
Cd(II)	7.7	3.1	—	—
Zn(II)	10.1	4.0	1.3	—

(**I**) and (**II**), giving impossible selective separation or extraction of Hg(II) from Cu(II).

The distribution coefficients of Hg(II), Cd(II), and Cu(II) were found to be the highest values of the modified silica gel phase (**IV**). These three metal ions were subjected to the evaluation of the separation factor ($\alpha_{A/B}$) vs. other tested

Table 5. The separation factor ($\alpha_{A/B}$) for the different metal ions by the modified silica gel phase (**IV**).

Metal ion	Separation factor		
	Hg(II)	Cd(II)	Cu(II)
Mg(II)	482.4	107.2	22.4
Ca(II)	1,584.5	352.1	73.6
Cr(III)	1,008.5	224.1	46.8
Mn(II)	1,109.3	246.5	51.5
Fe(III)	792.5	176.1	36.8
Co(II)	616.1	136.9	28.6
Ni(II)	221.9	49.3	10.3
Zn(II)	49.5	11.0	2.3
Pb(II)	28.8	6.4	1.3
Cd(II)	4.5	—	—
Cu(II)	21.5	4.8	—

metal ions and these are listed in Table 5. Hg(II) and Cd(II) can be selectively separated from other interfering metal ions such as Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co (II), Ni(II), Zn(II), and Pb(II). Cu(II), on the other hand, can be selectively extracted from these metal ions, except Zn(II) and Pb(II). Phase (**IV**) was found to be the only modified phase that can be used for selective separation and extraction of Hg(II) from Cu(II).

REFERENCES

1. Liu, P.; Pu, Q.; Su, Z. Analyst **2000**, *125*, 147.
2. Mahmoud, M.E. J. Liq. Chromatogr. Rel. Technol. **2002**, *25*, 1187.
3. Warwick, P.E.; Croudace, I.W.; Howard, A.G. Anal. Chem. **2002**, *72*, 3690.
4. Howard, M.; Jurbergs, H.A.; Holcomb, J.A. Anal. Chem. **1998**, *70*, 1604.
5. Nesterenko, P.N.; Jones, P. J. Chromatogr. A **1997**, *770*, 129.
6. Ma, W.X.; Liu, F.; Li, K.A.; Chen, W.; Tong, S.Y. Anal. Chim. Acta **2000**, *416*, 191.
7. Osman, M.M.; Kholeif, S.A.; Abou Al-Maaty, N.A.; Mahmoud, M.E. Microchim. Acta **2002**, *143*, 25.
8. Swaile, D.F.; Sepanik, M.F. Anal. Chem. **1991**, *63*, 179.
9. Pyell, U.; Stork, G. Fresenius J. Anal. Chem. **1992**, *343*, 576.
10. Mahmoud, M.E.; Soliman, E.M. J. Liq. Chrom. Rel. Technol. **2003**, *26*, 3045.
11. Dudler, V.; Lindoy, L.F.; Sallin, D.; Sclaaepfer, C.W. Aust. J. Chem. **1987**, *40*, 1557.
12. Izatt, R.M.; Bruening, R.L.; Breuning, M.L.; Tarbet, B.J.; Krakowiak, K.E.; Bradshaw, J.S.; Christensen, J.J. Anal. Chem. **1988**, *60*, 1826.
13. Kimura, K.; Nakajima, M.; Shono, T. Anal. Lett. **1980**, *13*, 741.
14. Anthemidis, A.N.; Zachariadis, G.A.; Strais, J.A. Talanta **2002**, *58*, 831.
15. Roy, P.K.; Rawat, A.S.; Rai, P.K. Talanta **2003**, *59*, 239.
16. Mahmoud, M.E.; Gohar, G.A. Talanta **2000**, *51*, 77.
17. Mahmoud, M.E. Anal. Chim. Acta **1999**, *398*, 297.
18. Pu, Q.; Sun, Q.; Hu, Z.; Su, Z. Analyst **1998**, *123*, 239.
19. Ueda, K.; Koshino, Y.; Yamamoto, Y. Anal. Lett. **1985**, *18*, 2345.
20. Garcia, M.F.; Garcia, R.P.; Garcia, N.B.; Medel, A.S. Talanta **1994**, *42*, 1833.
21. Mahmoud, M.E.; Osman, M.M.; Amer, M.E. Anal. Chim. Acta **2000**, *413*, 33.
22. Seshadri, T.; Kettrup, A. Fresenius Z. Anal. Chem. **1982**, *318*, 1.
23. Seshadri, T.; Haupt, A.-J. Anal. Chem. **1988**, *60*, 47.
24. Soliman, E.M. Anal. Lett. **1997**, *30*, 1739.

25. Jabson, E.; Baiker, A.; Wokaun, A. J. Chem. Soc. Faraday Trans. **1990**, *86*, 1131.
26. Hagenhoff, B.; Benninghoven, A.; Barthel, H.; Zoller, W. Anal. Chem. **1991**, *63*, 2466.
27. Chapman, J.R. In *Practical Organic Mass Spectrometry*; John Wiley & Sons: Chichester, 1993; Chapter 8.
28. Unger, K. In *Porous Silica*; Elsevier: Amseterdam, 1979; Chapter 6.

Received September 22, 2003
Accepted December 8, 2003
Manuscript 6231

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 19:29 23 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081JLC120037366