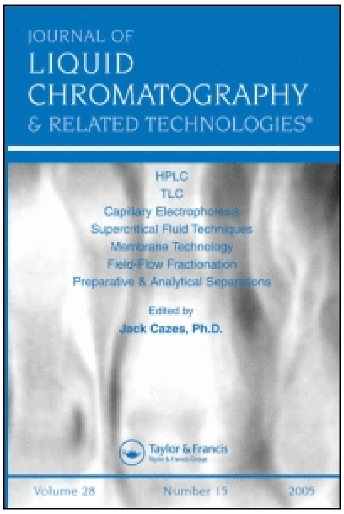

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# Comparative Study of the Reactivity and Selectivity Characteristics of Three Silica Gel Phases—Immobilized-8-Hydroxyquinoline for Separation and Pre-concentration of Chromium (III) from Water Samples

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# Comparative Study of the Reactivity and Selectivity Characteristics of Three Silica Gel Phases—Immobilized-8-Hydroxyquinoline for Separation and Pre-concentration of Chromium (III) from Water Samples

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## ABSTRACT

8-Hydroxyquinoline (8HQ) was used to modify the silica gel surface via the physical adsorption method (phase I), as well as a chemical immobilization approach (phases II and III). The loading process of 8-hydroxyquinoline on the surface of silica gel is simple, direct, and based on only a one step reaction procedure. The three synthesized silica gel phases (I–III) were analytically compared according to their metal-uptake, extraction, and selective properties toward a series of di- and trivalent

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metal ions. The study of the selectivity characters incorporated into these modified silica gel phases revealed that silica gel phase (I) is the highest selective one for Cr (III), with a minimum interference of the other metal ions, and silica gel phase (III) is the highest selective one for Cu (II) but with a high pronounced interference from other metal ions as Cr (III), Ni (II), and Co (II) ions. Silica gel phase (II) was found to be the lowest in metal capacity values, as well as selectivity study and kinetics of the chemical binding processes. The applications of silica phase (I) as a potential selective solid phase extractor for separation and pre-concentration of Cr (III) from natural tap water spiked with 1.0 and 4.0 ppb Cr (III) were successfully accomplished via a pre-concentration micro-column with percentage extraction and pre-concentration of 100% ± 1.5∼2.0%. The possible use of phase (I) for the direct determination of real Cr (III) concentration in sea water samples was also performed via a pre-concentration micro-column, and the results showed an actual concentration range of 0.320–1.67 ng mL$^{-1}$ of Cr (III) in the studied samples.

*Key Words:* Silica gel phases; Immobilized 8-hydroxyquinoline; Cr (III) pre-concentration.

## INTRODUCTION

8-Hydroxyquinoline (8HQ) is widely known and used as an analytical and spectroscopic reagent for qualitative and quantitative determination of various metal ions.[1] This behavior is mainly attributed to the capability of 8HQ to act as a chelating compound for binding, extraction, and complex formation with transition metal ions,[2] as well as rare earth elements.[3] These properties have led to the immobilization of 8HQ on the surface of organic and inorganic solid supports, in order to apply these modified phases in the solid phase extraction technique (SPE) for metal ions removal from different aqueous and non-aqueous samples.[4–8] Examples of the organic matrices selected for the immobilization of 8HQ are polyacrylonitrile hollow fiber membranes for determination and pre-concentration of rare earth elements in sea water[9] and cellulose-8HQ for multielemental analysis in biological samples by on-line pre-concentration micro-column coupled to simultaneous ICP-AES,[10] as well as other organic polymeric resins.[11–13] However, these modified organic species with 8HQ revealed high exchange capacity toward the various tested metal ions, but they suffered from low stability, especially in acidic solution, and low overall kinetic rate of the metal exchange process, as well as the swelling properties of most modified resins.[1] On the other hand, silica gel and glass beads are examples of the inorganic solid supports, which afford several advantages over the organic ones, such as high pronounced mechanical and

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thermal strength, high resistance to swelling process, as well as rapid overall exchange kinetics.[14] Among these reported efforts are the immobilization of 8HQ on the surface of fluorinated metal alkoxide glass for the determination of trace elements in sea water by ICP-MS.[15] The determination and pre-concentration of metal ions in seawater samples by graphite furnace atomic absorption spectrometry on 8HQ-silica gel phases were also reported.[16–18] The pre-concentration and purification of rare earths in natural water samples was also studied and evaluated.[19]

Other analytical applications of silica gel phases-immobilized 8HQ were also reported, such as the chromatographic separation of aromatic amines,[20] as well as metal ions.[21] In addition, the determination of metal ions by capillary zone electrophoresis with on-column chelation[22] and flow injection anodic stripping voltammetry was also accomplished.[23]

In this paper, a comparative study is presented for evaluation of the reactivity and selectivity characters toward different metal ions, which are incorporated into three modified silica gel phases and synthesized via one step reaction of loading 8HQ on the silica surface by both physical and chemical immobilization techniques. A strong emphasis was also aimed on finding the optimum condition for selective solid phase separation of different metal ions by the three silica gel–8HQ phases.

## EXPERIMENTAL

### Reagents and Materials

8-Hydroxyquinoline, 3-chloropropyltrimethoxysilane, 3-amino-propyl-trimethoxysilane, and metal salts were purchased from Aldrich Chemical Company, USA. Silica gel (60–300 mesh, 60 Å-pore diameter) was purchased from Riedel-Dehaën, Germany. Organic solvents were dried according to conventional methods.

All metal ion solutions were prepared with doubly distilled water and the buffer solutions were prepared from 1.0 M-sodium acetate to which different volumes of 1.0 M-hydrochloric acid were added, and the pH-value of the resulting solution was adjusted by the use of a pH-meter.

### Preparation of Silica Gel Phases (I–III)

Silica gel was first activated by refluxing in concentrated hydrochloric acid for 4-hours to remove any adsorbed trace species, then filtered, washed repeatedly with doubly distilled water to neutral filtrate, and the active silica gel phase was then dried in an oven at 160°C for 8-hours to remove surface adsorbed water molecules.

Ten grams of the dry silica gel was suspended in 200 mL of dry and hot toluene, mixed with 20 mL of 3-chloropropyltrimethoxysilane or (3-aminopropyltrimethoxysilane), and the reaction mixture was refluxed for 8 hours. The product, Si—Cl or (Si—NH$_2$)[24,25] was filtered off, washed with toluene, ethanol, and diethyl ether, and dried in an oven at 70°C for 6 hours.

Silica gel-physically adsorbed-8HQ (phase I) was prepared by the direct reaction of 10 g of active silica gel and 1.45 g (~10 mmol) of 8HQ already dissolved in 200 mL of dry and hot toluene. This mixture was refluxed for 4 hours and the silica gel phase (I) was then filtered, washed with toluene, ethanol, and diethyl ether, and dried in an oven at 70°C for 6 hours.

The two chemically modified silica gel phases (II) and (III) were prepared as follows. The silica gel phase (II) was synthesized by dissolving 1.45 g (~10 mmol) of 8HQ in 200 mL of dry and hot toluene, to which 10.0 g of Si—Cl phase was suspended. The silica gel phase (II) was filtered, washed, and dried, as in phase (I). To prepare silica gel phase (III), 5-formyl-8-hydroxyquinoline was first synthesized according to Reimer-Tieman reaction of 8HQ and chloroform as previously reported.[26] 1.60 g (~10 mmol) of 5-formyl-8-hydroxyquinoline was dissolved into 200 mL dry and hot toluene. 10.0 g of Si—NH$_2$ phase was then added to this mixture and refluxed for 4-hours and the silica gel phase (III) was filtered, washed, and dried, as described for both silica gel phases (I) and (II).

### Metal Capacity Determination

The metal capacity values determination[27] for the three newly synthesized silica gel phases (I–III) was accomplished in various buffer solutions and shaking time values, by the batch equilibrium technique as follows. Typically, 50 ± 1 mg of the silica gel phase was equilibrated with 1.0 mL of 0.1 molar metal ion solution and 9.0 mL of the selected buffer solution (pH 1–6) in a 50 mL volumetric flask. This mixture was then shaken at room temperature for 30 min. After equilibration, the mixture was filtered through filter paper, washed with 50 mL of doubly distilled water, and the unextracted metal ion was determined by complexometric titration and/or atomic absorption spectrophotometry.

### Metal Ions Selectivity Measurements by the Three Modified Silica Gel Phases (I–III)

To 100 mg of the three newly synthesized silica gel phases (I–III), 10 mL of buffered metal ions mixture (pH 6) containing eight metal ions, viz. Cr (III), Mn (II), Ni (II), Co (II), Cu (II), Zn (II), Cd (II), and Pb (II), ~0.1 molar each, were added and automatically shaken for 30 min. After equilibration, the extracted metal ions on the surface of silica gel phase were filtrate and washed with 50 mL of doubly distilled water. The filtrates and washings were subjected to further dilution process in order to meet the detection conditions of the atomic absorption spectrophotometric analysis. A standard solution containing the same eight metal ions was also prepared for the quantitative evaluation.

### Selective Solid Phase Separation and Pre-concentration of Cr (III) from Natural Tap Water Via a Pre-concentration Micro-Column[28,29]

Two drinking tap water samples were spiked with Cr (III) to maintain the concentration of Cr (III), ~4.0 and 1.0 ppb each. One liter of this water sample was then passed over a pre-concentration micro-column packed with 1.0 g of the physically adsorbed silica gel phase (I) with a flow rate of 10 mL per minute. The pre-concentrated Cr (III) on the surface of silica gel phase (I) was then eluted by running of 5.0 mL of concentrated hydrochloric acid. The eluting solution was subjected to atomic absorption analysis for the determination of the Cr (III) pre-concentrated.

### Selective Solid Phase Separation and Direct Determination of Cr (III) in Natural Sea Water Via Pre-concentration with Phase (I)

Seven samples, one liter each, were collected from the heavily industrial area at El-Max, North coast of Egypt and based on different depths and locations. Each sample was passed over a micro-column packed with 1000 mg of the modified silica gel phase (I) with a flow rate of 5 mL min$^{-1}$. The adsorbed Cr (III) on the surface of phase (I) was then eluted by 5.0 mL concentrated hydrochloric acid and subjected to atomic absorption analysis.

### Apparatus

Infrared spectra were recorded from KBr pellets with a Perkin-Elmer 1430 ratio recording spectrophotometer. The pH measurements were carried out with an Orion pH-meter model EA 920 calibrated against two standard buffer solutions of pH 4.0 and 9.2. The atomic absorption measurements of all tested metal ions were accomplished by the use of a Perkin-Elmer 2380 atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

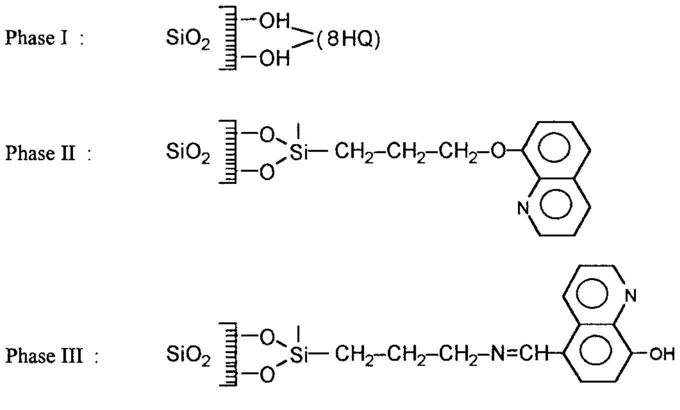
### Surface Coverage Values and Structural Identification

The determination of the surface coverage values (mmol $g^{-1}$) of the newly modified silica gel phases with 8HQ was mainly based on and accomplished by the application of metal probe testing method.[24] This method is based on determination of the maximum metal capacity value of the tested metal ions and these were found to correspond to Cr (III) for the modified silica gel phases (I) and (II) and Cu (II) for phase (III). The found mmol $g^{-1}$ values are 0.696, 0.585, and 0.633 for the silica gel-loaded–8HQ phases (I), (II), and (III), respectively. The possible structure of these three synthesized silica gel phases (I–III) are presented in Scheme 1 and based on the infrared studies of these phases.

It is clear from the data given that high surface coverage of the silica gel phases was accomplished by a very simple and direct method based on only a one step reaction.

### Evaluation of the Metal Capacity Values

The values of the metal capacity of these three silica gel phases-loaded–8HQ (I–III) were determined for a series of metal ions {Mg (II), Ca (II), Cr



*Scheme 1.* Structures of the three phases.

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(III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Pb (II), Hg (II), and Ba (II)} by the batch equilibrium technique, under the influence of pH-value of metal ion and shaking time values. This study is an important and essential one in order to configure the optimum pH-value of the metal ions. This was found to be pH 6 for most metal ions, as given in Table 1.

The data of this study are compiled in Table 1 and simply show a direct comparison of the reactivity of three synthesized silica gel-loaded–8HQ (I–III) toward metal-uptake. It is evident that Cr (III) is the highest extracted metal ion by both phases (I) and (II) with $\mathrm{mmol\,g^{-1}}$ values of 0.696 and 0.585, respectively, followed by Ni (II) as 0.433 and 0.400 $\mathrm{mmol\,g^{-1}}$. The silica gel-immobilized 8HQ phases (I) and (II) were also found to be similar for most of the tested metal ions in all the buffer solutions (pH 1–6). However, the silica gel phase (III) was found to be quiet different in the metal-uptake properties if compared to the other two silica gel phases (I) and (II) judging from the highest metal capacity values, which were found to be 0.633 $\mathrm{mmol\,g^{-1}}$ for Cu (II) followed by Cr (III), Hg (II), and Co (II) as 0.600, 0.567, and 0.417 $\mathrm{mmol\,g^{-1}}$, respectively. In addition, the values of the metal capacity given in Table 1 indicate that silica gel phase (II) is the lowest in the extraction of most tested metal ions compared to both silica gel phase (I) and (III). This trend and performance of phase (II) may be attributed to the reactivity of phase (II) as monodentate in metal binding, and mainly dependent on the presence of the nitrogen donor atom as the active one in this phase, while the oxygen donor

*Table 1.* Metal capacity values expressed in $\mathrm{mmol\,g^{-1}}$ of the silica gel phases (I–III).[a]

| Metal ion | Optimum pH value | Phase (I) | Phase (II) | Phase (III) |
|---|---|---|---|---|
| Mg (II) | 6.0 | 0.133 | 0.133 | 0.133 |
| Ca (II) | 6.0 | 0.100 | 0.100 | 0.233 |
| Cr (III) | 6.0 | 0.696 | 0.585 | 0.600 |
| Mn (II) | 6.0 | 0.233 | 0.167 | 0.200 |
| Fe (III) | 4.0 | 0.316 | 0.200 | 0.200 |
| Co (II) | 6.0 | 0.167 | 0.100 | 0.417 |
| Ni (II) | 6.0 | 0.433 | 0.400 | 0.233 |
| Cu (II) | 6.0 | 0.333 | 0.283 | 0.633 |
| Zn (II) | 6.0 | 0.200 | 0.167 | 0.267 |
| Cd (II) | 6.0 | 0.233 | 0.167 | 0.267 |
| Ba (II) | 6.0 | 0.217 | 0.217 | 0.300 |
| Hg (II) | 6.0 | 0.250 | 0.233 | 0.567 |
| Pb (II) | 6.0 | 0.200 | 0.200 | 0.167 |

[a] Values are based on triplicate analyses.

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atom is considered as weakly or inactive based on the ethereal nature. The other two silica gel phases (I) and (III) are considered, and found to be more reactive with metal ions, according to the positioning of the active donor atoms (O, N) on the surface of the modified silica gel phases.[30,31]

The selectivity incorporated into the three silica gel phases (I–III) due to the immobilization of 8HQ, may be interpreted on the basis of the determined mmol $g^{-1}$ values, as summarized in Table 1. It is clear that the silica gel phases (I) and (II) are highly selective for Cr (III), while the silica gel phase (III) is a selective one for Cu (II) but with some expected interference from Cr (III) and Hg (II), as well as other metal ions.

The effect of shaking time is another key factor in the process of evaluation of the three silica gel-immobilized–8HQ. The data collected from this study proved that the metal binding of Cr (III), taken as an example of the tested metal ions, with the silica gel phases (I) and (III) were very fast judging from the percentage extraction of Cr (III) by the two silica phases. It was found that 100% extraction of Cr (III), related to the given metal capacity values in Table 1, was accomplished by both silica gel phases (I) and (III) after only 1 min shaking time, while this value of percentage extraction required 10 min in the case of silica gel phase (II). These observations again confirm and account for the variation in the metal binding and reactivity of these three silica gel phases, as described in the previous section.

### Metal Ions Selectivity Studies by Silica Gel Phases (I–III)

Solid phase extraction (SPE) technique is widely and routinely used in different application areas.[32] The recent interest in SPE is mainly owing to several main factors, such as the direct and simple application of the sample and less or no waste generation, as well as the ability of SPE to interface with other major instrumentation.[28] Selective SPE is also considered of great importance because it allows the extraction and separation of the target analyte from any mixture that contains other and complex species, and this analytical approach leads to the minimization of the analysis time.

In this study, we aimed to perform the selectivity test[30,33] in order to evaluate the selectivity character incorporated into the silica gel phases via the immobilization of 8HQ toward the different tested metal ions. A mixture containing equimolar amounts of eight metal ions, viz. Cr (III), Mn (II), Ni (II), Co (II), Cu (II), Zn (II), Cd (II), and Pb (II) was used, and the data resulted from the atomic absorption analysis of this study are compiled in Table 2. It is evident from the mmol $g^{-1}$ values that the silica gel-physically adsorbed–8HQ phase (I) is the highest selective phase for Cr (III) amongst the three tested silica gel phases (I–III). The value of mmol $g^{-1}$ of Cr (III) determined in the

***Table 2.*** Selective separation of various metal ions by silica gel phases (I–III).[a]

| | Values (mmol $g^{-1}$) | | |
|---|---|---|---|
| Metal ion | Phase (I) | Phase (II) | Phase (III) |
| Cr (III) | 0.657 | 0.241 | 0.334 |
| Mn (II) | 0.053 | 0.055 | 0.039 |
| Ni (II) | 0.067 | 0.077 | 0.301 |
| Co (II) | 0.049 | 0.034 | 0.278 |
| Cu (II) | 0.270 | 0.215 | 0.630 |
| Zn (II) | 0.069 | 0.083 | 0.140 |
| Cd (II) | 0.099 | 0.043 | 0.122 |
| Pb (II) | 0.065 | 0.060 | 0.140 |

[a] Values are based on triplicate analyses.

selectivity study is very close to that reported in the metal capacity determination section, and this behavior can be used to account for the confirmation of the high selectivity of phase (I) for extraction and removal of Cr (III) from other interfering metal ions. However, only Cu (II) was found to show little interference in the selective extraction of Cr (III) by silica gel phase (I) due to the 0.270 mmol $g^{-1}$ value of Cu (II).

The modified silica gel phase (II) was found to also be selective for Cr (III) and its selectivity is lower than that of phase (I). Phase (II) experienced high interference of Cu (II) judging from the relatively close mmol $g^{-1}$ values as 0.241 and 0.215 for Cr (III) and Cu (II), respectively. The value of the mmol $g^{-1}$ of Cr (III) in this test was dramatically decreased compared to that given in Table 1, and this might be due to the incapability of this phase (II) to react with metal ions, as noted previously as only monodentate chelating phase. On the other hand, the selectivity incorporated in the modified silica gel phase (III) was found to be high for Cu (II) with 0.630 mmol $g^{-1}$ value, but with pronounced interference from other metal ions such as Cr (III) (0.233 mmol $g^{-1}$), Ni (II) (0.301 mmol $g^{-1}$), and Co (II) (0.278 mmol $g^{-1}$), as well as from the other tested metal ions.

## Selective Separation and Pre-concentration of Cr (III) from Natural Tap Water by Silica Gel Phase (I)

Two tap water samples were selected as the matrix for the evaluation of the selective separation and pre-concentration processes by silica gel-physically

*Table 3.* Selective pre-concentration of Cr (III) by silica gel phase (I) from natural tap water samples via a micro-column separation.

| Tap water sample (L) | Spiked Cr(III) (ppb) | Phase mass (g) | Elution solution (mL concentration HCl) | Detected Cr(III) (ppb)[a] | Percentage extraction[b] |
|---|---|---|---|---|---|
| 1.0 | 4.00 | 1.00 | 5 | 4.00 ± 0.05 | 100 ± 1.5 |
| 1.0 | 1.00 | 1.00 | 5 | 1.00 ± 0.02 | 100 ± 2 |

[a] Values are corrected based on the dilution factor.

[b] Values are based on triplicate analysis.

adsorbed–8HQ phase (I). The water samples were spiked with 1.0 and 4.0 ppb of Cr (III). Table 3 comprises the results obtained by the atomic absorption analysis of the retained Cr (III) on the packing material, which were correlated and presented as the percentage extracted of Cr (III) from the spiked concentration in each water sample. The values shown in Table 3 clearly represent the excellent selective separation and pre-concentration of Cr (III) by silica gel phase (I). A pre-concentration factor of 200 was achieved in this study.

### Selective Separation and Direct Determination of Cr (III) in Natural Seawater Samples Via Pre-concentration with Phase (I)

The results of this study are compiled in Table 4 and clearly indicate the possible application of modified silica gel phase (I) for pre-concentration of

*Table 4.* Direct determination of Cr (III) in real seawater sample via pre-concentration micro-column with silica gel phase (I).

| Sample number | Sample volume (mL) | Phase mass (mg) | Pre-concentration reagent (mL concentrated HCl) | Pre-concentration factor | Actual Cr (III) concentration (ng mL$^{-1}$) |
|---|---|---|---|---|---|
| 1 | 1000 | 1000 | 5 | 200 | 0.320 |
| 2 | 1000 | 1000 | 5 | 200 | 0.810 |
| 3 | 1000 | 1000 | 5 | 200 | 0.870 |
| 4 | 1000 | 1000 | 5 | 200 | 0.880 |
| 5 | 1000 | 1000 | 5 | 200 | 1.040 |
| 6 | 1000 | 1000 | 5 | 200 | 1.100 |
| 7 | 1000 | 1000 | 5 | 200 | 1.670 |

very low concentration levels of Cr (III) in high salinity sea water samples. The values listed also refer to the presence of Cr (III) in this industrial area with a concentration range of 0.320–1.670 ng $mL^{-1}$. This concentration range is beyond the detection limits assigned for AAS and can not be determined without the use of a pre-concentration technique.[28–30] In addition, the matrix effects due to the dissolved organic and inorganic species in seawater played an insignificant role in such determination process of Cr (III) as shown.

## CONCLUSION

Although the three silica gel phases, studied and evaluated in this work, are immobilized with only one organic modifier (8HQ), their reactivity and selectivity properties for the various tested metal ions were found to be quite different. In addition, the successful application of the silica gel phase (I) as a selective solid phase for separation and pre-concentration of Cr (III) from natural tap water was also extended to sea water, because Cr (III) is well known as an essential trace metal ion for the metabolism of glucose, lipids, and proteins in mammals.[33,34]

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