Immobilization of pyrazole compounds on silica gels and their preliminary use in metal ion extraction

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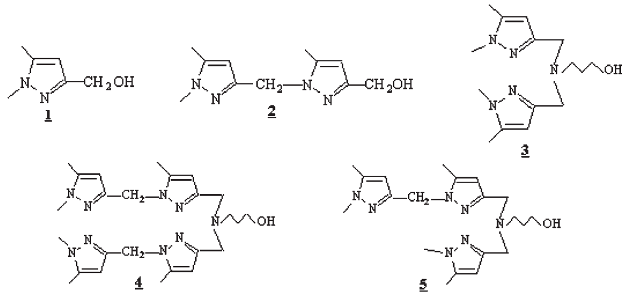
A series of acyclic pyrazole derivatives was prepared by condensation reactions. These compounds were covalently immobilized on silica gel through a flexible 3-glycidoxypropyltrimethoxysilane spacer arm. These materials were used as sorbents for the recovery of heavy and alkali metal ions from aqueous solutions. They exhibit good selectivity between heavy metal ions and alkali ions with an affinity especially high towards mercury. The comparison with liquid-liquid extraction shows that the capacity is not affected by the grafting of the pyrazole rings on the surface of silica. In addition, the solid-liquid process is more convenient in terms of facility of use.

Introduction

The selective preconcentration and separation of trace metal ions have been important subjects in analytical and environmental chemistry. Most of the recent works on the separation of metal ions using macrocyclic ligands have involved either the extraction of metal ions into organic solvents or the transport of the metal through liquid membranes. In order to avoid marginal losses of these materials, which are difficult and expensive to prepare, a convenient method is to immobilize the ligand on the surface of a solid material (organic resin or silica gel) by covalent bonding and to proceed by solid-liquid extraction. Various kinds of ligands have been immobilized on silica gel and used for separation purposes: crown ethers,[1–4] aza crowns,[1–7] thia crowns,[8] *N*-(2-pyridyl)acetamide,[9] 2,2′,6′,2″-terpyridine,[10] 2-pyridine methanol,[10] 2-aminomethyl pyridine[10] and 2,2′-bipyridine,[11] are some examples.

This paper reports the immobilization on a solid silica matrix of a series of pyrazole compounds containing varying numbers of pyrazole rings (Scheme 1). These compounds were covalently bonded to a silica gel through a rather long spacer arm in order to facilitate the contact between the pyrazole and the metal ion. The resulting materials were used for the extraction of transition, alkali and alkaline earth metal ions from water. The results are compared to those obtained with the analogous free pyrazole compounds in liquid-liquid extraction, with respect to capacity and selectivity.



Scheme 1

Experimental

Chemicals

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification.

The following intermediates: 3-hydroxymethyl 1,5-dimethylpyrazole (**1**); 3-chloromethyl 1,5-dimethylpyrazole (**6**) and 3(5)-carboxymethyl 5(3)-methylpyrazole (**7**) were prepared as reported by Tarrago and co-workers.[12]

Spherical porous silica (Silicagel Si60, 0.063–0.200 mm) was obtained from E. Merck. It was extensively washed with water and dried at 160 °C for 24 h before use. Its specific area was 293 m^2 g^{-1} as determined by the BET method (nitrogen adsorption). 3-Glycidoxypropyltrimethoxysilane was obtained from Janssen Chimica.

Syntheses

Synthesis of the pyrazole compounds (Scheme 2). Compounds **2**–**5** and **8**–**10** were prepared as described in a previous work.[13]

Synthesis of epoxy-substituted silica (Scheme 3). Various procedures have been described in the literature for the coupling of an epoxysilane to silica[14–16] and a modification of one of these was used in this work.[15] All equipment was rigorously dried. To porous silica (10 g), dried at 200 °C for 24 h and then stirred in 300 ml of toluene previously dried over metal sodium, were added 240 μl of triethylamine (potassium hydroxide dried) and 13.3 ml of 3-glycidoxypropyltrimethoxysilane.

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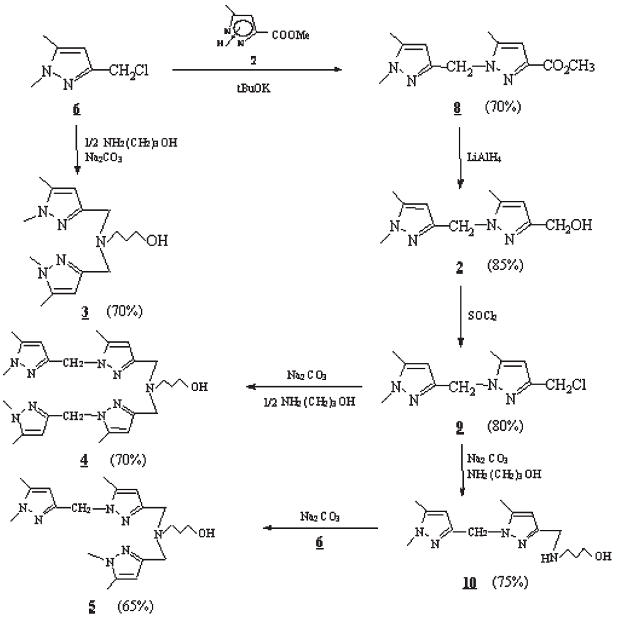
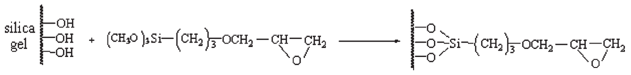


Scheme 2



Scheme 3

The mixture was stirred and refluxed under nitrogen overnight. Then the substituted silica was filtered off and washed on a glass filter funnel with toluene, acetone and diethyl ether (150 ml of each) and finally dried.

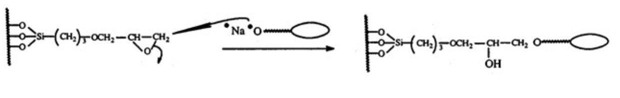
Synthesis of silica-gel-bound pyrazole (Scheme 4). After converting the hydroxy-substituted pyrazole compound (**1**–**5**) to the alcoolate derivative using sodium metal in tetrahydrofuran, the resulting salt (0.8 mmol) was added to a suspension of epoxy-substituted silica (1 g) in 30 ml of dimethylformamide (DMF). The mixture was stirred and refluxed under nitrogen for 24 h. The solid material was filtered and the residue was washed with DMF, toluene, water (distilled and deionized), methanol, dichloromethane (150 ml of each) and finally dried.

Methods

Spectroscopic measurements. At the different steps of the synthesis, the samples were characterized by IR and solid state NMR spectroscopy (CP MAS CXP 300 MHz).

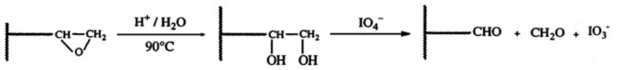
Surface area. Specific areas were determined by the nitrogen adsorption-desorption method using a Thermoquest Sorpsomatic 1990.

Determination of the epoxy groups. The amount of epoxy spacer grafted on silica was determined by three different methods: (i) elemental analysis of carbon; (ii) reaction with sodium thiosulfate and determination of sodium hydroxide[16–18] according to Scheme 5: 200–300 mg of epoxy-substituted silica were vigorously shaken with 10 ml of 6×10^{-3} M sodium thiosulfate to constant pH and the released hydroxyl groups were titrated with 0.1 M hydrochloric acid; and (iii) hydrolysis followed by determination with sodium periodate[16,19] (Scheme 6): 50 mg of the sample were treated with 20 ml of concentrated sulfuric acid at 90 °C for 1 h; after cooling and addition of 20 ml of 0.01 M sodium periodate, the mixture was left in the dark for 48 h and then the excess of periodate was titrated.



Scheme 4

Scheme 5



Scheme 6

Procedure for the batch method. A 100 mg sample of silica-bound pyrazole and 5 ml of an aqueous solution of a given metal ion (6.48×10^{-3} mol l^{-1}) were gently shaken for 24 h. The final solution was filtered and the residual metal ion was determined using an atomic absorption spectrometer (AAS). All the experiments were performed at 25 °C. The samples can be regenerated by washing with a solution of hydrochloric acid (6 N). Solutions of metal ions were prepared by dissolution of the chloride, nitrate or sulfate salt. Water was purified by demineralization with a IonMiser Model 6c after double distillation.

Procedure for the liquid-liquid extraction method. A 7×10^{-5} mol l^{-1} aqueous solution of the metal salt (50 ml) was added to 50 ml of a methylene chloride solution of a given pyrazole compound (7×10^{-5} mol l^{-1}). The mixture was gently shaken and the equilibrium was reached after 2 h. The residual concentration of metal was determined as above.

Results and discussion

Characterization of epoxy-substituted silica gel

The grafting of the epoxy groups on the silica surface was attested to by the disappearance of the large ν_{OH} adsorption around 3300 cm^{-1} and the appearance of a sharp $\nu_{C–H}$ band at 3030 cm^{-1}.

After hydrolysis of the epoxy groups to diols with diluted sulfuric acid (pH2, 90 °C, 1 h), the presence of the spacer arm on the silica gel was asserted by ^{13}C solid state NMR spectroscopy. The peaks were attributed as shown in Fig. 1.

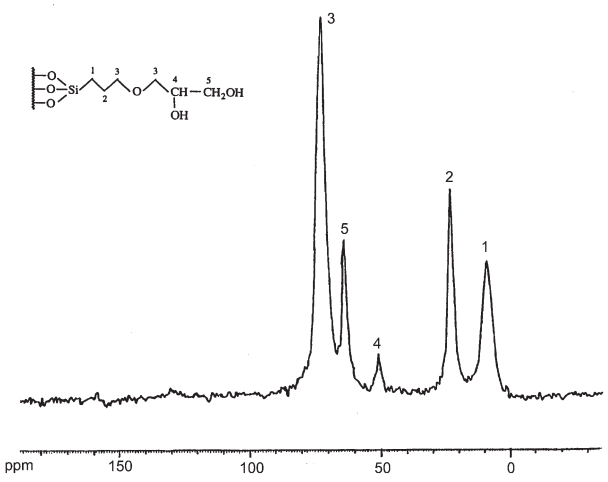


Fig. 1 ^{13}C solid state NMR spectrum (300 MHz) of hydrolyzed epoxy-substituted silica.

Epoxy content of substituted silica

The results of the determination of the amount of epoxy groups as described in the Experimental section are given in Table 1. Elemental analysis and titration with thiosulfate gave results in very good agreement. On the contrary, results from the periodate method are significantly lower and are attributed to an incomplete hydrolysis of the epoxy groups. For the calculation of the amount of pyrazole ligands bound to silica, only the results of the two first methods were considered.

Characterization of silica-gel-bound pyrazole

The amount of pyrazole grafted per gram of silica support was obtained in two ways: (i) from elemental analysis of nitrogen and (ii) from the determination of the unreacted epoxy groups by the thiosulfate method. The results were in good agreement (Table 2). The amount of pyrazole ligands is rather low compared to the number of available epoxy groups (maximum yield 40% for sample S1) and decreases with increasing number of pyrazole rings. This is probably due to steric hindrance but is rather unexpected considering the length of the spacer arm.

The successive grafting reactions on the surface of silica did not significantly modify its properties since the specific areas of all the samples, S1–S5, are in the range of 270–320 $m^2 g^{-1}$ (Table 3).

Table 1 Determination of the epoxy groups per gram of support

	Epoxy groups/μmol g^{-1} of support
Elemental analysis of carbon	787
Thiosulfate method	772
Periodate method	500

Table 2 Determination of the pyrazole ligand concentration

Sample[a]	Elemental analysis/ μmol g^{-1}	Thiosulfate method/ μmol g^{-1}	Ave. concentration/ mg g^{-1}
S1	325	335	41
S2	209	214	46
S3	210	215	61
S4	109	115	53
S5	113	120	44

[a] The number refers to the corresponding pyrazole compound in Fig. 1.

Complexing properties

The complexing properties of the above pyrazole-modified silica towards various metal ions were evaluated by the batch method. No extraction from the aqueous solution was observed for calcium, cesium, potassium, sodium and lithium. For mercury, cadmium and lead, the results are expressed in terms of μmol of metal bound per g of sorbent, mg of metal per g of sorbent and the yield of complexation is expressed as μmol of metal per μmol of pyrazole ligand (Table 3).

Native silica exhibits some complexing properties towards mercury and cadmium but not with lead. This disappears when going to epoxy-substituted silica S_e and thus can be attributed to the native hydroxyl groups.

For the three metals considered, the yield of extraction was calculated as the number of moles of the metal ion compared to the number of moles of pyrazole groups. For each metal under study, the yield increases with the number of pyrazole rings and is a maximum for sample S4, which has four pyrazole rings and a symmetrical structure. The yield decreases when going from mercury to cadmium or lead. The maximum yield (52%) is attained for sample S4 and mercury. In most cases, the complexing ability is rather far from the maximum theoretical value (for example 22.3 mg g^{-1} for S4 and mercury or 36.6 mg g^{-1} for S1 and cadmium).

Another interesting point is to compare the yields of solid-liquid and liquid-liquid extraction (Table 4). Solid sorbents are clearly as efficient as the liquid-liquid extraction process, which shows that the formation of the pyrazole-metal complex is not affected by the grafting on the silica surface. The length and the flexibility of the spacer arm are sufficient to allow a good accessibility to the complexation sites.

The results obtained with the S4 sample above can be compared with those from the cyclic analog of S4, also immobilized on silica, which was studied in a previous work.[20] For the latter, the yields calculated as above were better (70%, 46% and 46% for mercury, cadmium and lead, respectively) due to the cyclic structure. The cyclic compound was also able to complex lithium, sodium, potassium, calcium and cesium, unlike the acyclic one.

The yields of extraction are very close to those obtained with the same pyrazole compounds bound on a Merrifield resin[13] instead of silica. This is rather surprising since it was expected that the more hydrophilic nature of the silica support would make the complexation easier. This suggests that the spacer arm is long enough to render the influence of the hydrophilic or hydrophobic matrix negligible.

Regeneration of the samples

All the samples were easily regenerated by soaking the sample in 6 N HCl for afew minutes (5 ml of 6 N HCl per g of

Table 3 Sorption capacities toward mercury, cadmium and lead

			Capacity towards mercury			Capacity towards cadmium			Capacity towards lead		
Sample[a]	Specific area/ $m^2 g^{-1}$	Pyrazole ligand conc./ μmol g^{-1} of support	μmol g^{-1}	mg g^{-1}	Yield[b] (%)	μmol g^{-1}	mg g^{-1}	Yield[b] (%)	μmol g^{-1}	mg g^{-1}	Yield[b] (%)
S_0[c]	293	0	16.2	3.2	–	13	1.4	–	0	0	0
S_e[c]	311	0	0	0	0	0	0	0	0	0	0
S1	321	330	48.6	9.7	15	19.4	2.2	6	22.7	4.7	7
S2	317	211	70	14	33	0	0	0	16.2	3.3	5
S3	279	212	85	17	40	42.4	4.8	20	44.5	9.2	21
S4	271	112	58	11.6	52	22.4	2.5	20	35.8	7.4	32
S5	298	117	45	9	39	12.9	1.45	11	10.5	2.2	9

[a] The number refers to the corresponding pyrazole compound in Fig. 1. [b] Yield of complexation calculated as: μmol of metal per μmole of pyrazole. [c] S_0: native silica; S_e: epoxy modified silica.

Table 4 Comparison of the % yields of extraction for liquid-liquid (LLE) and solid-liquid (PS) extraction (calculated as μmol of metal per μmol of pyrazole)

	Mercury		Cadmium		Lead	
Sample	PS[a]	LLE[a]	PS[a]	LLE[a]	PS[a]	LLE[a]
S1	15	13	6	6	7	0
S2	33	35	0	5	5	0
S3	40	42	20	21	21	15
S4	52	55	20	15	32	26
S5	39	38	11	10	9	10

[a] PS: pyrazole silica; LLE: liquid-liquid extraction.

Table 5 Complexation/regeneration using sample S4 and mercury

Cycle number	Capacity/μmol g^{-1}
1	58
2	60
3	57
4	62

support). After washing, the complexing properties were measured again. Table 5 shows the results obtained for sample S4 with mercury when undergoing four cycles of complexation/regeneration.

Conclusion

These sorbents based on silica-bound pyrazole rings exhibit a large difference of affinity between heavy metal ions and alkali ions. Their affinity is especially high for mercury. This is not surprising if the high donor properties of nitrogen towards this metal are considered. Amino polymers coated on silica surfaces were also reported to be very good sorbents for mercury.[21]

Further experiments are in progress using these sorbents in column systems with various metal ions. The selectivity of the complexation is also under study using mixtures of metal ions in the solutions.

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