Journal of Chromatography, 626 (1992) 159–164
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 461

Iron(III) ion-modified chromatographic silica preparations and characterization

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(First received June 5th, 1992; revised manuscript received June 26th, 1992)

ABSTRACT

Stable, reproducible, iron(III) ion-modified silica stationary phases were prepared in aqueous media by a batch process. The catalytic activity of this modified stationary phase for oxidation of hydroquinone to benzoquinone was considerably greater than that of earlier iron(III) ion-modified silicas from non-aqueous media. Capacity factors of selected solutes were used to compare the retention properties of the aqueous iron(III) ion-modified silica with those of the unmodified silica. The capacity factors for solutes containing hydroxyl groups tended to increase with the iron(III) ion-modified silica relative to those for the unmodified silica column, whereas the capacity factors for carbonyl-containing compounds (esters, ketones and aldehydes) became smaller or were unaffected.

INTRODUCTION

Modification of chromatographic silica with metal ions has attracted interest as a possible means of obtaining materials with special retention properties for selective separations and, less frequently, with catalytic activities for chromatographic reactor applications [1–4]. A number of reviews are available on classical liquid chromatographic studies of a variety of metal ions associated with silica [5–8]. More recently, attempts to influence column selectivity in high-performance liquid chromatography (HPLC) by attaching metal ions to silica surfaces have also been reported [9–15]; these include the use of Ag^+ [9], for "argentation" chromatography, a standard approach to resolving *cis–trans* isomers.

The finding in several laboratories that the catalytic activity of iron(III) ion-contaminated silica columns can complicate hydroquinone-type analyses [16–18] led to studies of the application of homogeneous, iron(III) ion-doped silica in LC reactors for catalyzed hydroquinone oxidations [2,4], but only limited attention was paid to retention effects. Shortcomings with respect to reproducibility at the time of *in situ* and batch treatments for attaching iron(III) ions to silica in non-aqueous media led to the present study of the use of aqueous media for silica modification.

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0021-9673/92/$05.00

EXPERIMENTAL

The standard HPLC system [2,4,19] employed incorporated a Beckman Model 110B solvent-delivery pump, a Beckman Series 210 four-port sample valve with a 20-μl sample loop, a Perkin-Elmer LC-55 variable-wavelength spectrophotometer set at 254 nm, the column and an HP 3396A integrator.

To prepare the iron(III) ion-modified silica, *ca.* 2.0 g of Spherisorb S10W HPLC silica were mixed with potassium acetate–water (0.98 g in 250 ml) and stirred at room temperature with a magnetic stirrer for 48 h. After centrifugation and washing with water three times to remove excess of salt, the silica was mixed with 50 ml of (2.5 m*M*) iron(III) chloride solution and stirred at room temperature for 48 h. After centrifugation, the product was washed three times with water, methanol and 2-propanol. The resulting yellowish, iron(III) ion-doped silicas were suspended in 2-propanol for column packing. Alltech stainless-steel columns (10 cm × 4.6 mm I.D.) were slurry-packed at about 6000 p.s.i. using an in-house slurry-packing apparatus [20]. Two columns packed from different batches showed reproducible properties, with capacity factors agreeing to within 2%.

Inductively coupled plasma analysis of different iron-modified silica batches showed that about 2000 ppm of iron were attached to the silica (from the Soil and Plant Analysis Laboratory, University of Wisconsin, Madison Extension, Madison, WI, USA). Surface area measurements showed that this aqueous treatment did not change the specific surface area of the silica (195 ± 5 m^2/g). The apparent density did change: the density of the unmodified silica was 0.47 g/ml, whereas that of the iron-modified silica was 0.51 g/ml, using the method of Verzele *et al.* [21], indicating that the prolonged stirring produced some break-up of the silica particles. The pressure drop across the column for the iron-modified silica column was increased to about 350 p.s.i. compared with 250 p.s.i. for the unmodified silica column, at a flow-rate of 1.0 ml/min, in accord with the density increase.

The hydroquinone oxidation reaction was carried out in the iron(III) ion-modified silica column as described previously [2,4] at 25.0°C with *tert.*-butanol–hexane (8:92) as the mobile phase at flow-rates of 1.0–5.0 ml/min.

Capacity factors of the solutes were compared for the iron-modified silica columns and in-house packed silica column with two *tert.*-butanol–hexane mobile phase (4:96 and 8:92). Triplicate injections were used for solutes or solute mixtures at a flow-rate of 1.0 ml/min, and the temperature was controlled at 25.0°C, with a column jacket [4]. For aniline derivatives, a mobile phase of methanol–hexane (2:98) was used to obtain reasonable elution volumes. The capacity factor (k') was based on $k' = (V_R - V_m)/V_m$, where V_R is the solute retention volume and V_m is the void volume, based on unretained toluene elution for the systems studied here.

Solvents were of HPLC grade from Burdick and Jackson. Reagents were purchased from Aldrich and used without further purification.

RESULTS AND DISCUSSION

The aqueous solution treatments for preparing iron-modified silica outlined under Experimental were effective and reproducible. The modified silica packed column was stable. After more than 2 months of continued use, no significant changes in

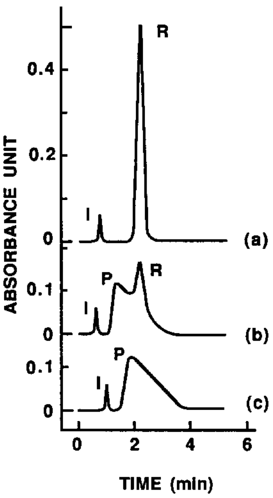

Fig. 1. Chromatograms of 2.5 m*M* hydroquinone on (a) a bare silica column at a flow-rate of 4.0 ml/min and on an iron(III) ion-modified silica column at flow-rates of (b) 4.0 and (c) 2.0 ml/min. Mobile phase, *tert.*-butanol–hexane (8:92); sample size, 20 μl. I = Inert standard (toluene); P = benzoquinone product from hydroquinone oxidation in the column; R = hydroquinone reactant.

column retention properties were observed. Some specific properties of the iron(III) ion-modified silica and its characteristics are discussed below.

Comparison of catalytic activities of columns

The iron-modified silica prepared in aqueous solution was found to possess significantly higher catalytic activity for hydroquinone oxidation than earlier modified silicas prepared with non-aqueous media [2,4]. Fig. 1 shows (a) a chromatogram of hydroquinone obtained using an unmodified silica column, and the results of injection of hydroquinone to the iron(III) ion-modified silica column at flow-rates of (b) 4.0 and (c) 2.0 ml/min. In Fig. 1a, only a hydroquinone peak is eluted, without any indication of benzoquinone formation. Hydroquinone is oxidized at a significant rate in the iron(III) ion-modified silica column, as indicated by the benzoquinone product wave in the chromatogram. In Fig. 1b some unreacted hydroquinone is still apparent in the chromatogram, whereas at a flow-rate of 2.0 ml/min with a longer residence time (Fig. 1c)

TABLE I

COMPARISON OF CAPACITY FACTORS FOR SOLUTES ON UNMODIFIED AND IRON(III)-MODIFIED SILICA STATIONARY PHASES WITH *tert.*-BUTANOL–HEXANE (4:96) AS MOBILE PHASE

No.	Solute	Silica column	Iron(III)-modified silica column	Change (%)
Hydroxylic materials				
1	Phenol	0.71	0.83	+17
2	2-Nitrophenol	0.23	0.39	+70
3	3-Nitrophenol	0.98	1.32	+35
4	4-Nitrophenol	1.99	2.54	+28
5	2,4-Dinitrophenol	3.66	9.86	+169
6	2-Methoxyphenol	0.71	1.69	+138
7	3-Methoxyphenol	1.04	1.16	+12
8	4-Methoxyphenol	1.57	1.77	+13
9	2-Ethoxyphenol	0.49	1.40	+185
10	4-Ethoxyphenol	1.17	1.38	+18
11	*sec*-Phenethyl alcohol	1.55	1.60	+3
12	4-Cresol	2.05	2.45	+19
13	Cinnamyl alcohol	2.07	2.40	+16
14	Benzyl alcohol	2.32	2.46	+6
15	4-Nitrobenyl alcohol	8.64	10.72	+24
16	2-Phenoxyethanol	2.88	3.48	+21
17	3-Methyl-2-buten-1-ol	2.87	2.95	+3
18	Hydroquinone	9.06	–[a]	
Esters, ketones and aldehydes				
19	Methyl benzoate	0.27	0.25	−7
20	3-Tolyl acetate	0.28	0.22	−21
21	4-Tolyl acetate	0.29	0.23	−21
22	4-Nitrobenzyl chloride	0.38	0.31	−18
23	2-Naphthaldehyde	0.44	0.35	−20
24	1,4-Naphthoquinone	0.82	0.57	−30
25	Acetophone	0.87	0.76	−13
26	Diethyl phthalate	1.02	0.68	−33
27	Cinnamaldehyde	1.15	0.85	−26
28	4-Nitrophenyl acetate	1.45	1.23	−15
29	4-Nitrobenzaldehyde	1.54	1.40	−9
30	Benzoquinone	1.68	1.65	−2
31	3-Methyl-2-butenal	2.83	2.61	−8
32	1-Benzoylacetone	0.41	0.35	−15
Toluene retention volume (ml)		1.419	1.422	

[a] Owing to the long residence time in the column, hydroquinone was completely oxidized to benzoquinone.

complete oxidation of hydroquinone was observed. Use of the inert standard method [22,23] gives a pseudo-first-order rate constant of $k_s = 1.34 \cdot 10^{-2}$ s^{-1}, which can be compared with $k_s = 7.54 \cdot 10^{-4}$ s^{-1} at 35°C under similar conditions [2] for an iron (III) ion-doped silica column prepared in non-aqueous media.

A substantial amount of the variation of column activity for hydroquinone oxidation with iron-modified silicas from aqueous and non-aqueous preparation methods can be explained by the amounts of iron(III) ion immobilized on the silica from these two different treatments. Elemental analysis indicated that about 1000 ppm of iron was deposited in the non-aqueous synthesis [2], whereas the aqueous treatment yielded a deposit of about 2000 ppm of iron on the same type of silica surface. However, the doubling of the amount of surface-deposited iron from the aqueous procedure cannot alone account for the observed activity difference, which is about an order of magnitude greater at a lower temperature. Hence it appears that these different treatments also substantially changed the surface properties. This result made it desirable to study the present iron-modified silica further using solute retention comparisons to provide an additional simple means beyond catalytic activity for characterizing iron-modified silica surfaces.

Capacity factors

Capacity factors (k') for selected solutes on the bare silica and iron(III) ion-modified silica columns with *tert.*-butanol–hexane (4:96 and 8:92) mobile phase are shown in Tables I and II, respectively.

Several general features emerge from Table I. For example, for a variety of hydroxyl compounds, such as phenol, nitrophenol, methoxyphenol, ethoxyphenol, *sec.*-phenethyl alcohol, benzyl alcohol and cinnamyl alcohol, the capacity factors are greater on the iron-modified than on the bare silica column. The increase in retention on iron(III) ion-modified silica presumably reflects the relatively strong result

TABLE II

COMPARISON OF CAPACITY FACTORS FOR SOLUTES ON UNMODIFIED AND IRON(III)-MODIFIED SILICA STATIONARY PHASES WITH *tert.*-BUTANOL–HEXANE (8:92) AS MOBILE PHASE

No.	Solute	Silica column	Iron(III)-modified silica column	Change (%)
Hydroxylic materials				
1	Phenol	0.30	0.42	+40
4	4-Nitrophenol	0.79	1.60	+102
11	*sec*-Phenethyl alcohol	0.73	0.86	+18
12	4-Cresol	1.03	1.19	+15
13	Cinnamyl alcohol	1.04	1.19	+14
14	Benzyl alcohol	1.06	1.51	+42
16	2-Phenoxyethanol	1.61	1.87	+16
17	3-Methyl-2-buten-1-ol	1.16	1.50	+29
18	Hydroquinone	5.51	6.33	+15
Esters, ketones and aldehydes				
19	Methyl benzoate	0.22	0.20	−9
20	3-Tolyl acetate	0.22	0.18	−18
21	4-Tolyl acetate	0.23	0.18	−22
24	1,4-Naphthoquinone	0.64	0.45	−29
25	Acetophone	0.68	0.65	−4
26	Diethyl phthalate	0.68	0.45	−33
27	Cinnamaldehyde	0.85	0.64	−24
28	4-Nitrophenyl acetate	1.12	1.04	−7
30	Benzoquinone	1.28	1.28	0
31	3-Methyl-2-butenal	2.08	2.08	0
Toluene retention volume (ml)		1.417	1.420	

TABLE III

COMPARISON OF CAPACITY FACTORS FOR SOLUTES ON UNMODIFIED AND IRON(III)-MODIFIED SILICA STATIONARY PHASES WITH METHANOL–HEXANE (2:98) AS MOBILE PHASE

No.	Solute	Silica	Iron(III)-modified silica	Change (%)
34	Aniline	2.87	5.79	+102
35	3,4-Dichloraniline	4.99	5.33	+6.8
36	4-Chloroaniline	5.82	6.13	+5.3
37	2-Nitroaniline	4.65	4.92	+5.8
38	3-Nitroaniline	11.3	12.3	+8.8
39	4-Nitroaniline	28.5	29.3	+2.8
40	2,4-Dinitroaniline	22.1	23.2	+5.0
41	Formanilide	6.41	7.04	+9.8
42	Acetanilide	10.0	10.5	+5.0
43	4-Toluidine	11.9	12.8	+7.6
Toluene retention volume (ml)		1.415	1.419	

from coordination with the iron(III) ions immobilized on silica. Shahwan and Jezorek [12] found similar effects with an 8-quinolinol–silica gel–iron(III) stationary phase, where the capacity factors for phenolic compounds significantly increased.

The capacity factor increase is greater for *ortho*-substituted compounds, such as 2-nitrophenol, 2-methoxylphenol and 2-ethoxyphenol, relative to other phenolic compounds, and still greater for 2,4-dinitrophenol. Formation of a five-member chelated ring structure with silica surface-bonded Fe^{3+} can explain the large increase in the *ortho*-ether phenols. For the nitrophenols, there is probably involvement of the substituent with the aromatic ring that enhances the coordination tendency. This is supported by the retention increase for 2,4-dinitrophenol.

For a wide range of esters, ketones and aldehydes in Table I, such as acetophone, nitrophenyl acetate, methyl benzoate, *trans*-cinnamaldehyde, diethylphthalate, tolyl acetate, 2-naphthaldehyde and 4-nitrobenzaldehyde, the capacity factors are about the same or smaller for the iron-modified silica column relative to the bare silica column.

Similar qualitative elution features are observed in Table II for the *tert.*-butanol–hexane (8:92) mobile phase as for the mobile phase in Table I. Hydroxyl-containing compounds are also eluted considerably earlier from the silica column. Most important, with a higher concentration of *tert.*-butanol modifier in the mobile phase, hydroquinone is eluted before complete conversion to benzoquinone. The net result for hydroxyl-containing compounds was a higher capacity factor on the iron(III) ion-modified silica column than on the bare silica column. Hence the interaction of this type of compound with iron(III) ions on silica is still strong in the more polar solvent.

In addition to the hydroxyl group, we also considered other solute groups that would be expected

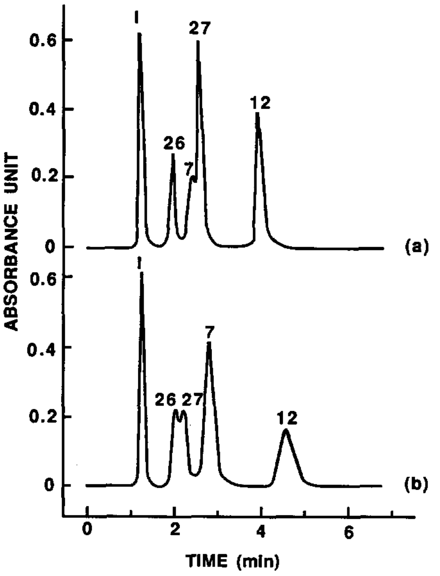

Fig. 2. Chromatograms of the test solutes toluene (I), diethyl phthalate (26), 3-methoxyphenol (7), *trans*-cinnamaldehyde (27) and 4-cresol (12) with *tert.*-butanol–hexane (4:96) as mobile phase at a flow-rate of 1.0 ml/min on (a) a bare silica column and (b) an iron(III) ion-modified silica column.

to interact strongly with iron(III) ions. Table III shows capacity factors for a group of aniline-related compounds, some of which were studied by Kunzru and Frei [10] on cadmium-impregnated silica and by Djerki *et al.* [14]. As can be seen, the k' values also increased with the iron(III) ion-modified silica column, reinforcing the conclusion that coordination with iron can be an overriding factor.

The preferred interactions of the OH group with Fe^{3+} on silica may have applications for selective separations. As an example, Fig. 2 shows chromatograms for a mixture of toluene, 3-methoxyphenol, 4-cresol, diethyl phthalate and cinnamaldehyde. The bare silica column (Fig.2a) and the iron (III) ion-modified column (Fig.2b) were used under the same experimental conditions, with *tert.*-butanol–hexane (4:96) as the mobile phase at room temperature. Both the elution order and chromatographic patterns were altered, illustrating how iron (III) ions associated with silica surfaces can alter solute retentions to advantage to provide resolution and selective separations. Further investigations of applications of metal ion-modified silica columns are in progress.

ACKNOWLEDGEMENTS

We appreciate support of this work by the US Army Research Office and the University of Wisconsin. We also thank Dr. Chawn-ying Jeng for suggestions and experimental help and Mr. Scott Fritsch for assistance with some experiments.

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