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Effects of acid treatment on the trace metal content of chromatographic silica: bulk analysis, surface analysis and chromatographic performance of bonded phases

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Abstract

A series of studies has been carried out on the effect of refluxing silica chromatography particles for 0.5 h and 18 h in water, dilute hydrochloric acid and dilute hydrofluoric acid. The bulk and surface trace metal concentrations were measured by inductively-coupled plasma atomic emission spectroscopy, static secondary ion mass spectrometry (SSIMS) and X-ray photoelectron spectroscopy. Diffuse reflectance Fourier transform infrared spectroscopy was used to determine changes in “isolated” and “bonded” silanol groups. The chromatographic behaviour of a series of weakly basic analytes was investigated on C₈ and C₁₈ bonded phases manufactured from the acid-treated silicas. The different reflux treatments all resulted in a reduction in the numbers of isolated silanols compared with the untreated silica and SSIMS analysis suggested that the HF-treated silicas had undergone a more efficient surface rehydroxylation. Bulk trace metals were removed most effectively by the HF treatment, with the multivalent elements (Ti and Al) being the most difficult to remove. Surface specific analysis suggested that trace metals were removed more rapidly from the surface of the silica compared to the bulk matrix and that the acid treatments resulted in halide contamination of the silica surface. Evidence is presented to suggest that the bulk metal content of the silica is not representative of the concentration of metals at the chromatographic surface. The chromatographic investigations showed that the HF-treated silica gave substantially better performance towards weak bases than the HCl-treated silicas. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The surface of chromatographic silica used in reversed-phase liquid chromatography is often sub-

jected to a rehydroxylation procedure prior to the chemical bonding of alkyl groups. A variety of methods of rehydroxylation has been reported, which generally involve heating of the silica followed by hydrothermal treatment with acids or bases [1–5]. The rehydroxylation stage is known to affect the number and types of silanols present on the surface of the silica, resulting in a reduction of isolated,

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strongly acidic silanols and an increase in the proportion of bonded silanols [1,2,6]. A marked improvement in the chromatographic performance of bonded silicas towards ionised organic bases is usually observed following silica surface rehydroxylation [7] which is attributed to the reduction of unwanted ion-exchange interactions with acidic surface silanols. A reduction in the level of trace metals from the silica matrix following the use of dilute mineral acids (for example HCl or HF) for silica surface rehydroxylation has been noted [3,8–10] and there is now substantial evidence to suggest that the acidity of isolated surface silanols can be directly affected by the presence of trace metals in the silica matrix [3,7,11,12].

Several studies have established the presence of a wide range of metallic impurities in chromatographic grade silicas [1,8,9]. Certain metals, such as sodium, calcium, iron, aluminium and titanium, have been found in concentrations of hundreds or even thousands of ppm. Despite the observed correlation between high trace metal content and unwanted adsorption of bases, it is interesting to note that a marked improvement in the chromatographic performance of bonded silicas towards bases is often achieved even though substantial levels of trace metals are still measurable in the bulk silica matrix [7]. The question therefore arises as to why chromatographically accessible adsorption sites for bases appear to have been removed from the silica surface despite the presence of metals in the silica. There are a number of possible explanations for this: (1) reduction of metal concentration rather than complete removal is sufficient to reduce adsorptive sites; (2) better surface rehydroxylation leads to a more homogeneous surface coverage and effective screening by the bonded phase; (3) the reduction in surface concentration of the trace metals is a more important factor rather than that of the bulk metal content.

Much of the existing work on trace metal content has been focused on measuring the metals in the bulk silica phase. It is evident that functionalities at or near the surface of the silica must be responsible for chromatographic effects, and consequently bulk measurements of metal content may not truly reflect the surface species available to interact with solutes. The surface analytical techniques of static secondary ion mass spectrometry (SSIMS) and X-ray photoelectron

spectroscopy (XPS) have been applied to the study of chromatographic silicas [13–21] but this work has been limited to studies of alkyl bonded silicas or semi-quantitative studies of surface functionalities. XPS can, however, provide a quantitative elemental analysis of the silica surface whilst SSIMS gives structural information relating to surface-bound species. Both techniques have a sampling depth of a few nanometres and have sufficient sensitivity to supply information relating to silanols and the more abundant trace metals such as sodium, iron, aluminium and titanium. Therefore, it was postulated that detailed surface analysis of silicas following acid rehydroxylation has the potential to reveal subtle changes in the outer few nanometres of the silica surface, which may not be detected by bulk analysis.

In this paper we investigate the bulk and surface metal concentrations of sol–gel prepared silica following mineral acid rehydroxylation. We also study the nature of silanol-related species on the surface of these silicas and the chromatographic behaviour of representative C₁₈ and C₈ bonded phases manufactured from the acid-treated silicas.

2. Materials and methods

2.1. Preparation of acid-treated base silicas

The base silica was prepared by the gelation of a colloidal silica sol under controlled conditions as previously described [22]. After emulsification, washing and sintering, the base silica was classified to ensure the particle size distribution was within the normal specification (4.5–5 µm average). The base silica was then split into six individual batches each of which was rehydroxylated by refluxing in water, 0.1% HCl or 0.1% HF for 30 min or 18 h. A portion of the untreated silica was kept as a control sample for bulk and surface analysis of metals and silanols. Five µm C₁₈ and C₈ bonded silicas were prepared from the batches of hydrated base silicas using *n*-dimethyloctadecylsilyl chloride and *n*-dimethyloctylsilyl chloride (monofunctional reagents). The chlorosilane (40%, v/w, in toluene) was reacted with 10.0 g of the base silica with 10% (w/w) of pyridine and refluxed for 6 h. The reaction product was dried in a vacuum oven for 12 h, allowed to cool, washed

in hexane (100 ml), acetone (100 ml), acetone–water (50:50) (100 ml) and acetone (100 ml). The final products were oven dried at 80°C prior to use. A portion of each of the batches was endcapped using trimethylchlorosilane (TMS) under similar conditions to the *n*-alkyl bonding procedure already described. The packing materials were slurry-packed into 10 cm×4.6 mm I.D. stainless steel columns using acetone as a packing and slurry solvent, at a pressure of 8000 p.s.i. (1 p.s.i.=6894.76 Pa). Prior to the chromatographic testing the columns were conditioned with methanol–water (70:30). The pore size and pore volume of the silica particles was determined using mercury porosimetry (Micrometrics 9300 Analyzer), and the surface area was measured by BET single point analysis (Micrometrics Flow-sorb 2300). The carbon loading (% C) for the silicas was obtained from an EC-12 carbon determinator (Leco, St. Joseph, MI, USA). The measured pore size, pore volume, surface area and bulk % C of each of the batches of silica are shown in Table 1.

2.2. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis

Samples were analysed as replicates on a Plasma 400 ICP-AES instrument (Perkin-Elmer). The metals

chosen for investigation were zinc, cobalt, nickel, iron, chromium, magnesium, copper, titanium, calcium, aluminium, sodium and potassium. British Chemical Standard high-purity silica (BCS-313 silica) was used for the validation of the ICP-AES methodology and was supplied by the LGC (Teddington, UK). Hydrofluoric acid (40%) was Aristar grade and supplied by Fisons (Loughborough, UK). Concentrated nitric acid (99.999+% purity) was supplied by Sigma. All elemental standards were prepared from atomic absorption grade standards and were supplied by either BDH (Poole, UK) or Aldrich (Poole, UK). All other reagents were of analytical grade or better.

A sample of microparticulate silica (approximately 0.25 g,) was transferred to a PTFE digestion vessel. A solution of hydrofluoric acid (40%, 8 ml) and concentrated nitric acid (2 ml) was added and the vessel was agitated to ensure wetting of the sample. The sealed and capped digestion vessel was placed into a microwave digestion system (MSD-81D microwave; CEM) and was digested on 100% power for 5 min then 50% power for a further 5 min. Each metal concentration was adjusted to account for the carbon loading of the bonded silicas to obtain a true metal concentration per gram of silica. The reproducibility of the method was assessed from the inter-

Table 1
Bulk % carbon, surface area, pore size and pore volume of each batch of silica

Silica treatment	% C	Surface area (m ² /g)	Pore size (Å)	Pore volume (cm ³ /g)
Untreated silica	0.07	174	120.5	0.60
Water (30 min)	0.08	171	122.3	0.58
Water (18 h)	0.06	149	137.1	0.59
HCl (30 min)	0.07	188	115.0	0.58
HCl (18 h)	0.07	156	131.0	0.59
HF (30 min)	0.10	194	112.8	0.59
HF (18 h)	0.05	174	120.3	0.58
C ₁₈ bonded (HCl)	8.21	111	114.2	0.42
C ₁₈ /TMS bonded (HCl)	9.25	108	107.9	0.37
C ₈ bonded (HCl)	6.44	126	110.6	0.45
C ₈ /TMS bonded (HCl)	6.55	123	110.5	0.44
C ₁₈ bonded (HF)	11.13	102	106.7	0.36
C ₁₈ bonded/TMS (HF)	11.29	99	106.3	0.35
C ₈ bonded (HF)	6.42	129	110.0	0.45
C ₈ bonded/TMS (HF)	6.55	126	109.5	0.43

and intra-day precisions of the main elements of interest using British Chemical Standards high-purity silica. The inter-day relative standard deviations (RSDs) were found to be Fe (1.6%), Mg (4.5%), Ti (8.2%), Ca (3.9%), and Al (5.7%), the intra-day RSDs were Fe (1.2%), Mg (1.3%), Ti (1.9%), Ca (2.9%) and Al (1.0). The limit of quantitation for each element was taken as a value of three times the standard deviation of the instrumental noise.

2.3. X-Ray photoelectron spectroscopy

XPS spectra were obtained on a VG Scientific ESCALAB Mk II electron spectrometer using Al K α X-rays. Operating conditions have been published elsewhere [14]. The silica powders were slurried with methanol and transferred onto copper foil which had been previously cleaned by sonication in acetone for 30 min. The prepared samples were allowed to dry for 3–4 min before insertion into UHV conditions. A survey scan and narrow scans for Si 2p, C 1s, O 1s, Na 1s, Fe 2p_{3/2}, Cl 2p, F 1s and Cu 2p_{3/2} were performed. Peak areas were taken from the narrow scans and percentage composition calculated using the manufacturer's standard software, which incorporated Scofield sensitivity factors.

2.4. Static secondary ion mass spectrometry

Spectra were obtained on a VG SIMS Lab instrument equipped with a fast atom bombardment (FAB) argon primary beam, operating at 80 mA and 2 keV. The silica samples were prepared for analysis by placing the dry particles in a sample dish. Despite the use of an atom beam, some charging of the samples was encountered which was compensated for using an electron flood gun. For each sample both positive and negative secondary ion spectra were collected in the region m/z 0–200, whilst maintaining static SIMS conditions. A plot of m/z versus intensity was produced for each sample allowing trace elements and fragments attributable to the silica surface to be identified.

2.5. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)

A Bruker IFS88 Fourier transform infrared spec-

troscopy (FT-IR) instrument with mercury cadmium telluride detector operating at 1 cm^{-1} spectral resolution was used with a diffuse reflectance attachment and environmental chamber with a ZnSe window (SpectraTech, Warrington, UK). One hundred scans were averaged for each analysis and samples were scanned in the range 3900–3000 cm^{-1} . Samples (0.1 g), as loosely packed powders, were maintained at 20°C and water was removed under vacuum at 10^{-3} Torr for 17 h (1 Torr = 133.322 Pa). The sharp IR band at 3760–3735 cm^{-1} was used to indicate the presence of isolated and geminal silanols, and the broader band at 3620–3200 cm^{-1} was used to indicate the presence of bonded silanols [7].

2.6. Chromatographic studies

The chromatographic experiments were performed using Gilson 305 high-performance liquid chromatography (HPLC) pumps, a Gilson 805 Manometric Module, a Gilson 231/401 autoinjector, a Gilson 116 variable-wavelength UV detector and a Gilson 714 HPLC system controller and data processor. Mobile phases were degassed by helium sparge before use. Columns were maintained at 30°C. A single test mix was used in the studies: pyridine, 3-aminopyridine, 3-cyanopyridine, 3-acetylpyridine, 3-chloropyridine and 3-bromopyridine. Injections of 20 μl of a 100 $\mu\text{g}/\text{ml}$ stock solution in water produced satisfactory peaks with a detection wavelength of 205 nm. A mobile phase of methanol–aqueous 0.005 *M* sodium phosphate buffer, pH 7.0 (10:90) was used in all the chromatographic studies. Each compound was injected four times. Mean retention times (t_R), peak asymmetry factors and plate numbers were calculated using the proprietary Gilson 714 software. Retention factors (k) were calculated after determining t_0 by baseline disturbance using the standard formula $k = (t_R - t_0) / t_0$.

3. Results

3.1. ICP-AES analysis of bulk metal content

The bulk metal contents of the untreated base silica and each batch of rehydroxylated silica are

Table 2
ICP-AES determination of trace metals in base silicas

Silica treatment	Metal concentration (ppm)												
	Zn	Co	Ni	Fe	Cr	Mg	Cu	Ti	Ca	Al	Na	K	Total
Untreated	7	0.1	6	227	14	37	4	55	99	290	5159	58	5956
30 min water	8	0.3	6	237	14	43	5	57	142	302	3699	45	4558
18 h water	6	0.5	6	224	13	34	2	55	58	289	3424	43	4155
30 min HCl	7	0.3	6	235	15	28	2	57	41	288	2830	34	3543
18 h HCl	6	0.5	6	228	14	48	2	56	106	292	2572	41	3372
30 min HF	4	0.7	3	122	5	13	2	50	36	229	2059	31	2555
18 h HF	5	0.4	0.8	180	2	34	1	40	44	280	3294	18	3899

shown in Table 2. For the untreated silica, sodium (5159 ppm, 0.52%) is the metal present in the highest concentration, with aluminium (290 ppm, 0.029%), iron (227 ppm, 0.023%), calcium (99 ppm, 0.0099%), potassium (58 ppm, 0.0058%) and titanium (55 ppm, 0.0055%) also contributing significantly. The range of concentrations of the individual metals is typical of other published data for sol–gel derived chromatographic silicas [1,7,8]. However, the relative contributions from individual metals can vary considerably between different types of chromatographic silica with silicas derived from organosilanes having extremely low concentrations of contaminating metals.

The effects of the acid rehydroxylation treatments are presented in terms of the change in the metal concentration (ppm) compared to the untreated control batch of silica (Fig. 1). A general pattern of changes in the reduction of bulk metal concentration is apparent from these plots with the HF-treated silicas showing a more consistent and greater level of metal depletion than either the water- or HCl-treated batches. The 18 h treatment time does not consistently result in a greater extent of metal depletion and, unexpectedly; many of the metals show greater depletion at 30 min compared to 18 h. It is also apparent that some of the trace metals actually increase their concentration following water and HCl treatment, though not with the HF treatment. The reason for this is unclear, but the very small differences involved (often less than 10 ppm) are close to the inter- and intra-day precisions of the ICP-AES method (1.8 to 8.2%, depending on the individual metal) and therefore may be explained by assay

variability. The data clearly demonstrate that HF treatments for either 30 min or 18 h give a consistent reduction of all metals apart from cobalt (which is the metal in lowest concentration, at less than 0.7 ppm) and that this treatment is superior to that of water or HCl reflux in terms of the removal of metal species.

The results reported are in agreement with other studies on the removal of trace metals by acid treatment of silica [1,8,9], which indicate that certain of the metals observed in higher concentrations (sodium, iron, magnesium, calcium) can be removed more easily by acid treatment than others (notably titanium and aluminium). Multivalent metal species such as aluminium or titanium are known to be more tightly bound into the silica matrix [23]. There is strong evidence to suggest that mixed oxides with SiO₂ as the major component and a trace metal as the minor component will be strongly acidic if they contain titanium, aluminium or similar multivalent metals [24]. Clearly, this observation has significance for chromatographic performance of the acid-treated phases, where a small number of highly acidic silanol sites may remain due to the presence of aluminium and titanium. According to Tanabe [24] the presence of trace amounts of sodium in the silica matrix may assist in stabilising the acidity of silica containing aluminium or titanium, but sodium on its own does not appear to influence silanol acidity.

3.2. XPS analysis of surface metal atomic percentage

The percentage compositions obtained by XPS

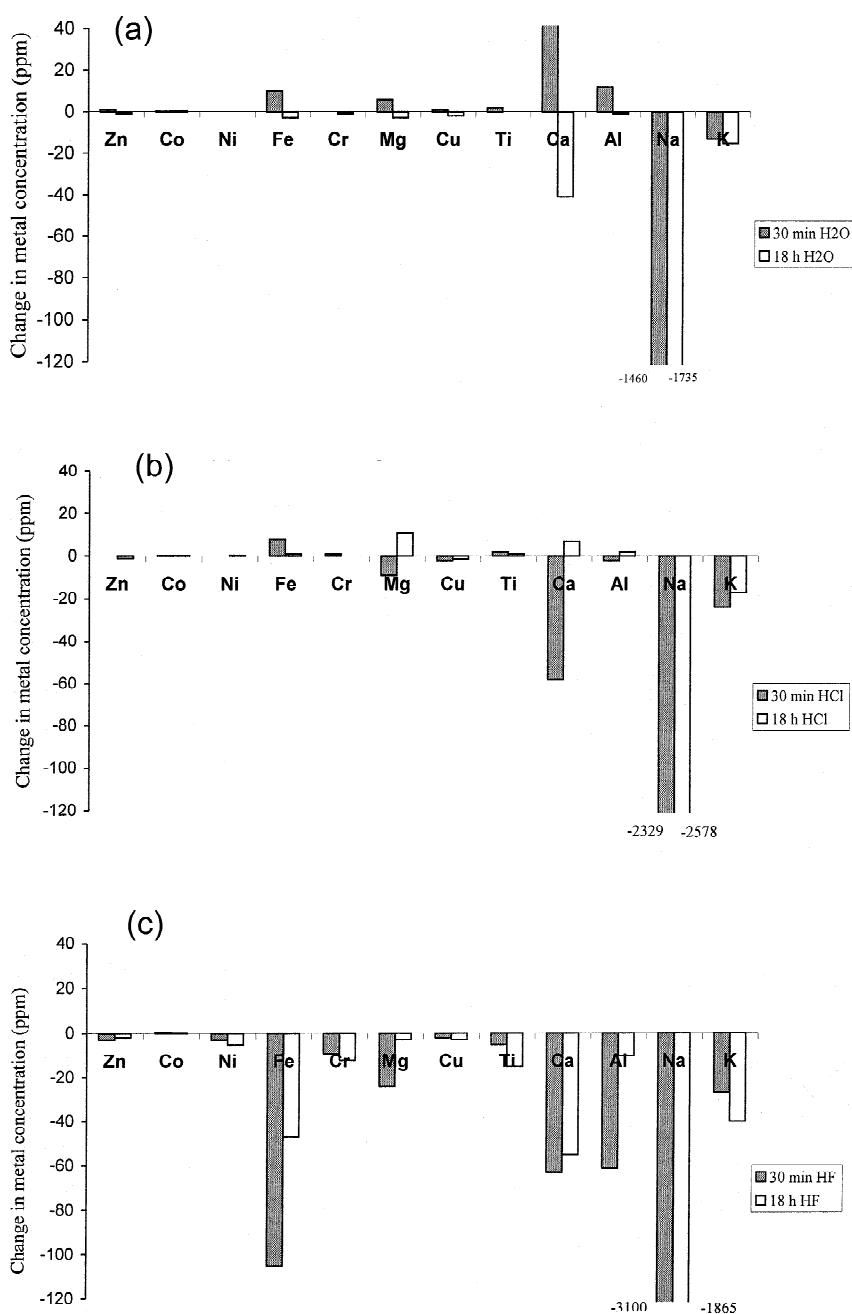


Fig. 1. (a) Effect of boiling in water on metal content of base silicas. (b) Effect of boiling in HCl on metal content of base silicas. (c) Effect of boiling in HF on metal content of base silicas.

surface analysis of the water- or acid-treated silicas compared to the untreated control are shown in Table 3. XPS is significantly less sensitive than bulk

analysis (limit of detection approximately 0.1% depending on the sample and the element being determined) and, consequently, most of the trace

Table 3
XPS analysis of base and C₈/C₁₈ bonded silicas

Silica treatment	XPS elemental composition						
	% C	% O	% Si	% Na	% Cl	% F	% Fe
Untreated	2.2	65.0	31.0	0.8	0.7	0.3	n.d.
Water (30 min)	0.6	67.6	31.3	0.4	n.d.	0.1	n.d.
Water (18 h)	1.4	66.1	32.5	n.d.	n.d.	n.d.	n.d.
HCl (30 min)	0.9	65.9	32.2	0.4	0.4	0.2	n.d.
HCl (18 h)	1.5	66.3	31.6	0.3	0.2	0.1	n.d.
HF (30 min)	1.0	64.9	32.4	0.4	n.d.	0.1	1.2
HF (18 h)	1.4	66.5	26.7	1.9	n.d.	n.d.	3.5
C ₁₈ bonded (HCl treated)	27.5	45.3	26.9	0.0	0.2	0.1	0.0
C ₈ bonded (HCl treated)	14.7	54.6	30.2	0.0	0.3	0.2	0.0
C ₁₈ bonded (HF treated)	27.9	47.5	24.0	0.0	0.0	0.2	0.4
C ₈ bonded (HF treated)	14.3	57.9	26.7	0.0	0.4	0.1	0.6

metals are undetectable by surface analysis, with only sodium and iron being measurable. XPS also permits the determination of the chlorine and fluorine surface concentrations resulting from the dilute HCl and HF treatments. Fig. 2 shows the depletion of trace elements by the different reflux conditions. The surface concentration of sodium in the untreated silica measured by XPS (0.8%) is slightly higher than the bulk sodium measured by ICP-AES (0.5%). However, following refluxing for 30 min, the XPS measured sodium (0.4%) is in reasonable agreement with the bulk analysis (0.2–0.4%). This suggests that excess sodium may have been present on the surface of the untreated silica, which was subsequently removed by the refluxing treatments. The observation of chlorine (0.7%) by XPS on the untreated silica suggests that the excess sodium on the surface may have been present as sodium chloride, perhaps deriving from the process of manufacture. The 18 h treatment samples did not give as consistent results as the 30 min ones, and the anomalously high value for sodium in the 18 h HF treatment may be explained by the formation of sodium fluoride on the surface of the silica (note the very high level of fluorine observed in this sample at 3.5%). The XPS measured iron concentrations range between 0.3 to 0.1%, which is a factor of 10 higher than the bulk concentration (0.02%), which suggests that iron is preferentially located at or close to the silica surface. The surface iron concentration is reduced by all the

reflux treatments of the silica, but only 18 h in HCl or water remove the metal completely. These results are not consistent with the bulk measurements, where water treatment appears to have little effect in reducing bulk iron.

It can be seen that the acid-treated silicas contain lower surface concentrations of sodium, chlorine and iron than the control material. This confirms that boiling in water or dilute acid, for even a short period of time, will result in a reduction of surface contaminants. This is in agreement with work previously reported by Kaiser and Batich [16]. Treatment with water alone for 18 h reduces the contaminants to a level which are not detectable by XPS. The quantitative surface data support the argument that the metals at or close to the surface are preferentially removed by acid treatment. Boiling in dilute HCl is not so effective, with detectable levels of sodium and iron remaining and the level of chlorine being higher than that in the water boiled silica. With dilute HF treatment, there is an initial reduction in sodium after 30 min, but extended boiling results in an increase in sodium to a level higher than the control. Also, although HF is effective in the removal of iron and chlorine, it does introduce substantial fluorine contamination on to the silica surface. A possible, but unconfirmed, explanation is that the dissolved metals may be re-deposited on the silica surface during reflux in the form of very insoluble fluorides of aluminium, iron and zirconium.

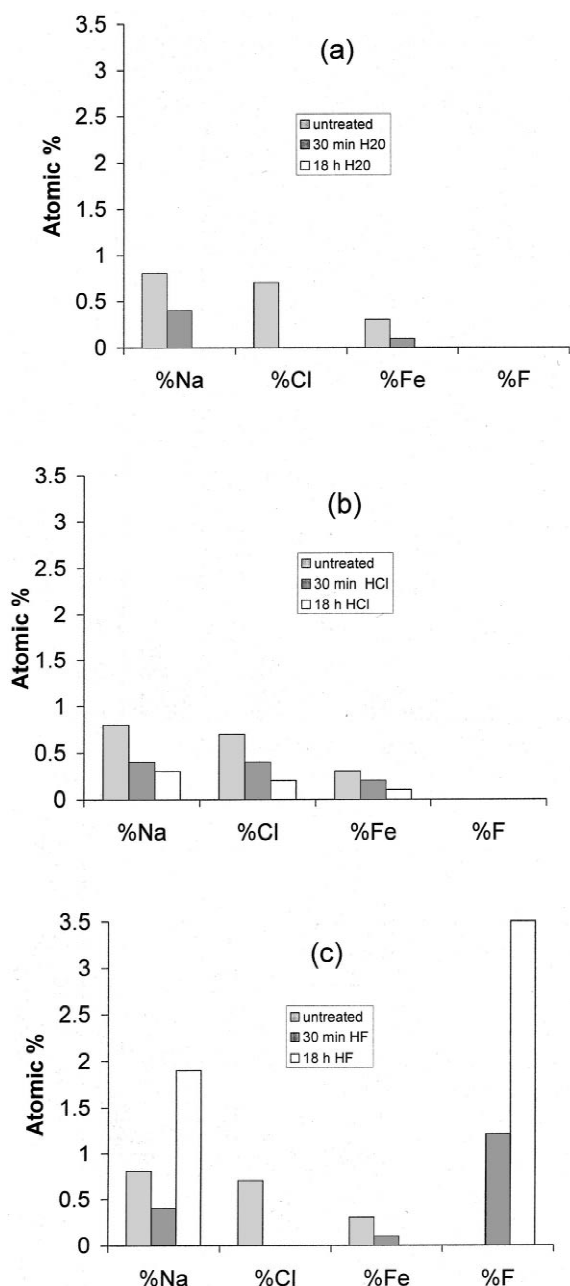


Fig. 2. XPS analysis of surface atomic percentage on base silicas boiled in (a) water, (b) 0.1% HCl and (c) 0.1% HF.

It could be argued that the presence of excess fluorine in the HF-treated silicas, and also the high chlorine content of the HCl-treated silicas was due to insufficient washing of the silica following the acid

treatments. However, the XPS analysis of the 30 min HF- and HCl-treated C_{18} bonded silicas reveals 0.4% fluorine in the HF-treated bonded phase (no chlorine detected) and 0.2% chlorine in the HCl-treated bonded phase (no fluorine detected). This observation suggests that the presence of chlorine and fluorine on the silica surface may reflect a strong adsorption, or some kind of incorporation of the elements into the surface matrix of the silica gel.

3.3. SSIMS analysis of surface species

SSIMS spectra were obtained for the untreated base silica, all the acid-treated silicas and the C_8 and C_{18} bonded phases manufactured from the HF- and HCl-treated silicas. It is not proposed to discuss SSIMS analysis of the alkyl components of the bonded silicas since we have previously published similar data elsewhere [13,14]. Fig. 3 shows typical positive and negative ion SSIMS spectra (0–100 m/z), respectively, obtained for the untreated silica and the HCl- and HF-treated silicas. The positive ion spectra showed the following characteristic low mass silica-based ions, which were common to all the base silicas: Si^+ (m/z 28), SiH^+ (m/z 29), $SiOH^+$ (m/z 45). In addition, the spectra identified the main positive ion contaminants present on the silica surface: Na^+ (m/z 23), Fe^+ (m/z 56), K^+ (m/z 39) and Al^+ (m/z 27). Characteristic ions in the negative ion spectra were O^- (m/z 16), OH^- (m/z 17), SiO_2^- (m/z 60), SiO_3^- (m/z 76), SiO_3H^- (m/z 77) as well as the main negative ion surface contaminant of Cl^- (m/z 35) [note that F^- (m/z 19) was observed on the HF-treated silicas]. The spectra of the bonded silicas (not shown) were dominated by low mass alkyl/silica fragments, but it was readily possible to distinguish the silica-based and metal/halide contaminant peaks from the alkyl components.

It was possible to obtain a semi-quantitative indication of the changes in surface species as a result of the different acid hydrolysis treatments by comparing the relative SSIMS ion intensities for the individual surface species. This was done by using the total sum of all the positive ion peak areas from m/z 0–100 as a reference for each silica sample (Table 4). Details of this approach are published elsewhere [14]. The spectra from the HCl- and HF-treated silicas showed similar peaks to that in the

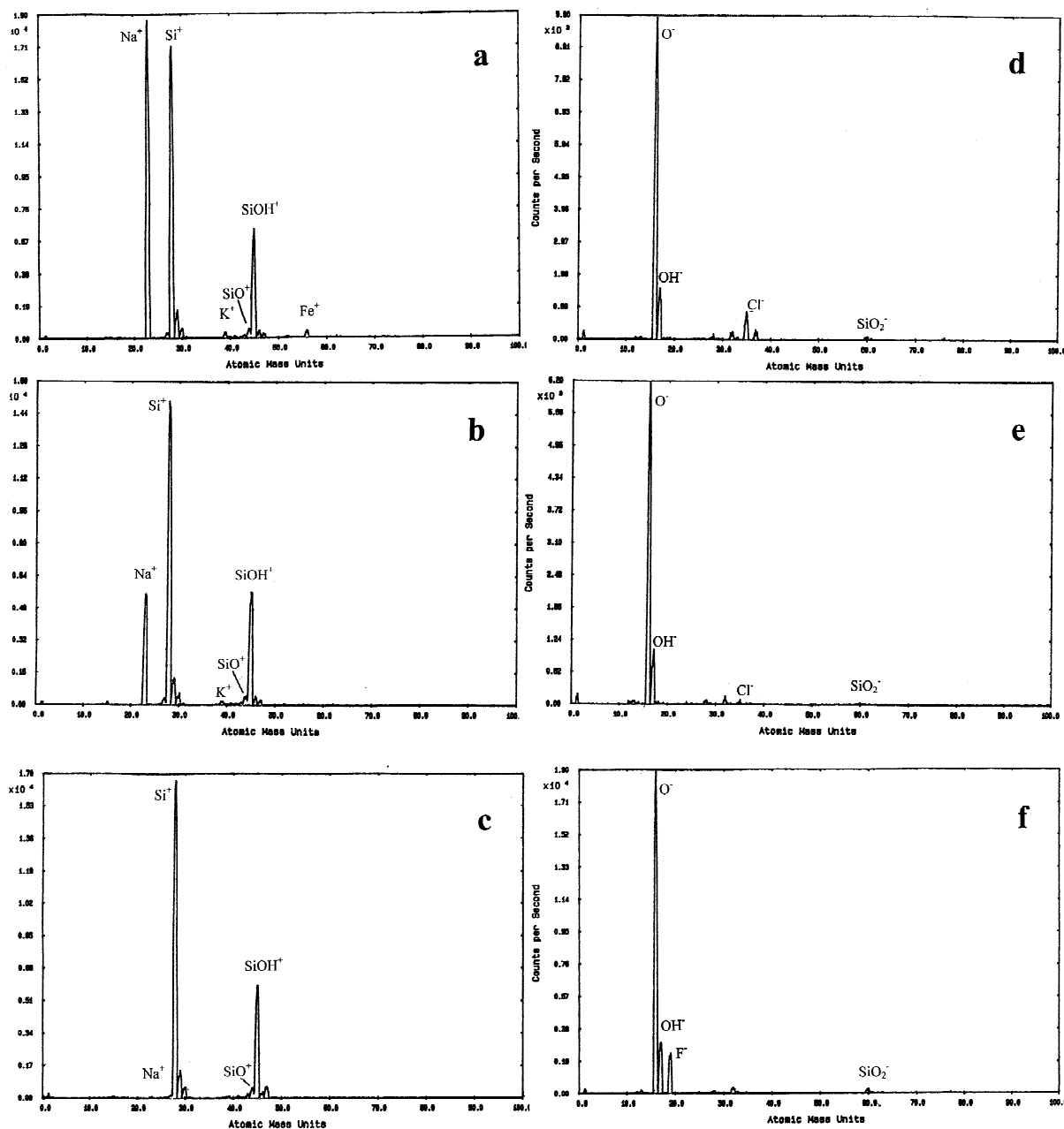


Fig. 3. SSIMS spectra (m/z 0–100) recorded for untreated and acid-washed silicas: (a) positive ion spectrum for untreated silica, (b) positive ion spectrum for HCl-washed silica, (c) positive ion spectrum for HF-washed silica, (d) negative ion spectrum for untreated silica, (e) negative ion spectrum for HCl-washed silica, (f) negative ion spectrum for HF-washed silica.

control base silica, but with significant changes in the levels of contamination present. Both HCl- and HF-treated silicas showed a significant reduction

(compared to the Si signal) in the levels of sodium, chlorine, aluminium, potassium and iron. However, the HF-treated silica gave a relatively high level of

Table 4
Relative intensities of trace metals and silanol relevant ions determined by SSIMS

Silica treatment		Relative ion intensity							
		<i>m/z</i> 23	<i>m/z</i> 56	<i>m/z</i> 27	<i>m/z</i> 19	<i>m/z</i> 35	<i>m/z</i> 28	<i>m/z</i> 44	<i>m/z</i> 45
Acid reflux	Bonding	Na ⁺	Fe ⁺	Al ⁺	F ⁻	Cl ⁻	Si ⁺	SiO ⁺	SiOH ⁺
Untreated	–	36.13	1.45	1.01	0.21	4.68	33.24	1.01	12.43
HF	–	0.58	0.47	1.12	3.98	1.06	20.89	1.96	16.33
HCl	–	4.04	1.14	0.81	0.85	1.09	12.11	1.14	4.55
HF	C ₁₈	0.55	2.64	3.85	2.87	0.55	2.11	0.55	0.87
HF	C ₁₈ /TMS	0.53	1.81	2.49	2.86	0.98	2.94	0.75	1.85
HF	C ₈	0.56	1.12	3.54	2.93	0.38	3.73	0.93	2.03
HF	C ₈ /TMS	0.21	1.10	4.71	5.18	0.96	14.96	1.56	4.26
HCl	C ₁₈	1.00	1.79	2.68	0.76	1.24	2.68	0.57	1.00
HCl	C ₁₈ /TMS	0.30	1.81	3.29	0.44	0.68	2.70	1	1.88
HCl	C ₈	0.50	1.49	4.59	0.43	0.60	4.57	1.25	4.52
HCl	C ₈ /TMS	0.53	1.43	4.07	0.79	0.54	3.90	1.22	3.74

fluorine not observed in the control sample. These results are in general agreement with and support the conclusions made from the quantitative surface analysis data obtained by XPS. It is particularly notable that sodium is a major contaminant on the untreated silica surface, but is partially removed by HCl treatment, and almost completely by HF treatment. This observation again suggests that sodium is a loosely-bound surface contaminant, possibly physically rather than chemically adsorbed to the surface.

Relatively few detailed SSIMS studies of trace components on chromatographic silicas have been carried out. Buszewski [25] studied several commercial silicas by SSIMS (positive ion only) and observed sodium, magnesium, calcium and titanium as the main trace metals. Following a washing procedure with 20% HCl the author claimed a 3.1 to 27.4% decrease in these metals based on changes in SSIMS ion intensity, but the level of accuracy of this result must be questioned in view of the known semi-quantitative nature of SSIMS [26].

The relative intensities of the silica-based ions can give an indication of the proportion of silanols present on the surface of the base silicas. It can be seen that the HF-treated silica shows higher intensities for the ions Si⁺, SiO⁺ and SiOH⁺ compared to the HCl-treated silica. This suggests that the HF-treated silica may undergo a more efficient rehydroxylation process to produce a greater silanol popula-

tion. SSIMS analyses of the bonded phases derived from the acid-treated base silicas show that the HF-treated phases have a lower proportion of silanol related ions compared to the HCl-treated phases, suggesting that a more efficient bonding process was achieved with the HF-treated phases. However, these data are not completely consistent with the shielding of silanols since the TMS endcapped phases have a higher intensity of SiO⁺ and SiOH⁺ than the non-endcapped phases.

3.4. DRIFT

There has been some controversy over the assignment of IR bands to silanols functionalities on the silica surface, and this has been reviewed [7,27]. For the purpose of this work, the IR band at 3760–3735 cm⁻¹ was used to indicate the presence of isolated (including geminal) silanols, and the broader band at 3620–3200 cm⁻¹ was used to indicate the presence of bonded silanols. The ratio of isolated to bonded silanols was calculated by determining the area under the peaks in each of the IR bands, and this was plotted against the batch of silica (Fig. 4). The background water spectrum, observed as a broad band between 3000 and 4000 cm⁻¹ was not completely removed, despite the vacuum treatment, and its level was observed to be variable between samples. No correction was made for this difference

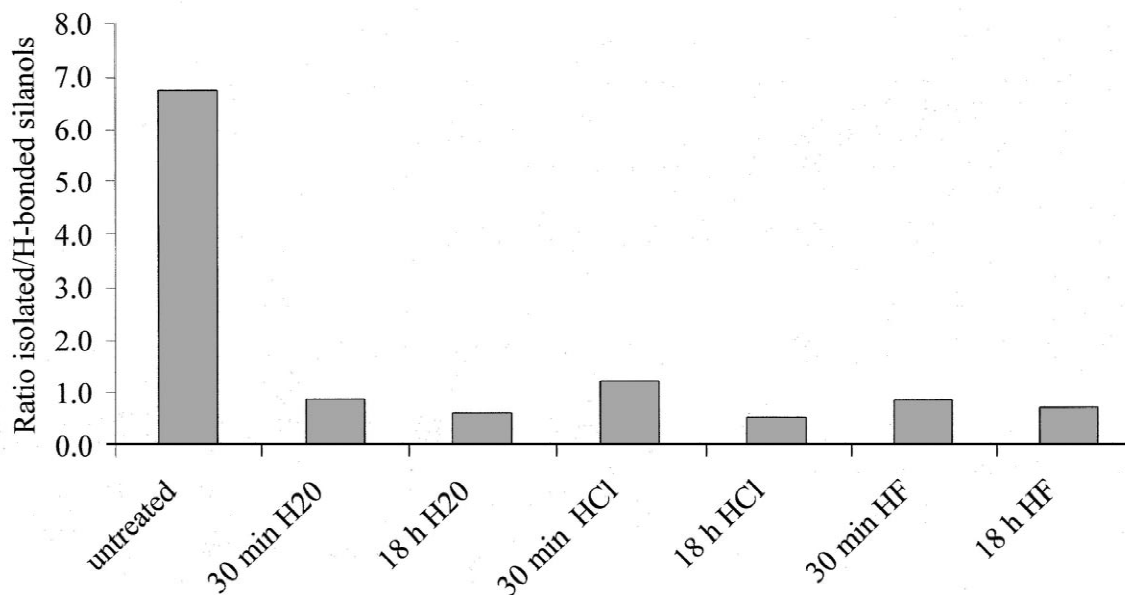


Fig. 4. Ratio of isolated:H-bonded silanols determined by DRIFT.

in background and it is possible that this may have introduced unwanted variability into the measurement of areas under the selected IR bands. It is evident that all the different rehydroxylation procedures result in a substantial decrease in the proportion of isolated silanols compared with bonded silanols. However, there appeared to be little difference between the rehydroxylation procedures, with all resulting in an 80–90% reduction in the ratio of isolated to H-bonded silanols. It is likely that any subtle differences in silanol content would not be detected by IR spectroscopy, and no attempt was made to assign bands to individual peaks within the defined bands. The main conclusion from the IR investigation is that boiling in water, dilute HCl or dilute HF all result in an apparent decrease in the intensity of IR bands associated with isolated silanols. This observation is in agreement with results from other studies on DRIFT analysis of acid-treated silicas [7,27].

3.5. Chromatographic studies

The test solutes were chosen from a series of 3-substituted pyridines known to have strong secondary interactions with ionised silanols on the types

of silicas used in this study [22]. The primary aim of the chromatographic experiments was to compare the extent of unwanted secondary interactions of a series of weak organic bases on the HCl- and HF-treated phases. From previous studies [14,22] it is known that pyridine and 3-amino pyridine (the most basic of the analytes) are the most sensitive solutes to secondary interactions, and this was also apparent in the present investigations.

The retention of the solutes on the HF-treated bonded phases was reproducible, with the order of retention corresponding to the log *P* values of the pyridines, on all the bonded and endcapped phases (Fig. 5). However, the HCl-treated columns showed more variability in retention order between the bonded and endcapped phases, suggesting that the different bonded groups introduced differential access to the ionised silanols on the HCl-treated silica surface.

Comparing the asymmetry factors for pyridine and 3-amino pyridine on the HCl- and HF-treated silicas, a similar pattern emerges for both the C₈ and C₁₈ bonded phases (Fig. 6). Overall, the HF-treated silica gave a substantially better peak symmetry compared with the HCl-treated, with the peak symmetry being correlated well with the basicity of the solutes.

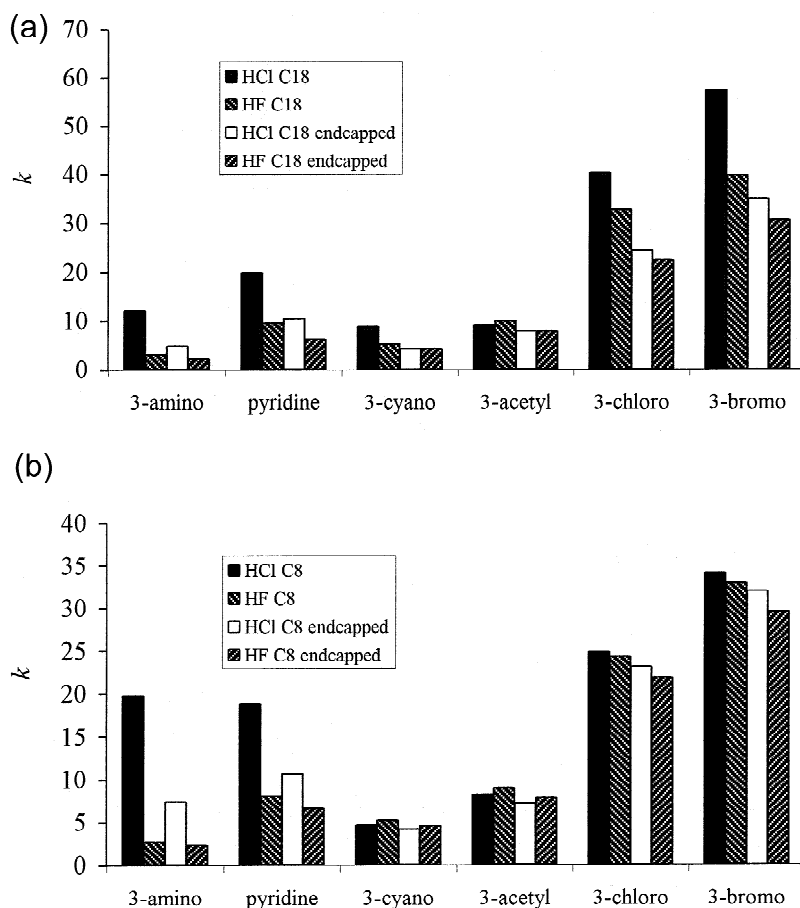


Fig. 5. (a) Retention behaviour of test analytes on C_{18} bonded phases following HCl and HF treatment. (b) Retention behaviour of test analytes on C_8 bonded phases following HCl and HF treatment.

Following endcapping of the silicas, the improved results with the HF-treated phases is enhanced further, whereas the HCl-treated phases show no change in performance or give more asymmetrical peak shapes. These observations are supported by the data on efficiency (Fig. 7), where it is again evident that the bonded phases based on the HF-treated silica give a consistently improved performance compared with the HCl-treated. However, all the basic analytes still show evidence of secondary interactions with silanols, even in the endcapped phases, with asymmetry factors of between 2 and 3 and efficiencies of less than 3000 plates/column. It is postulated that the relatively high level of aluminium (and, to a

lesser extent, titanium) remaining after HF treatment, may leave a residue of acidic silanols on the surface of the silica, which can only be partly masked by bonding and endcapping of the silica. As mentioned before, these metals are known to form highly acidic mixed oxides with silica [24] and are particularly difficult to remove from the silica matrix.

The chromatographic studies with the weak organic bases demonstrated that the bonded phases based on the HF-treated silica give more consistent retention behaviour, improved efficiencies and better peak symmetries than with the HCl-treated phases. These results are in agreement with previous investigations [2,28] which demonstrated that refluxing

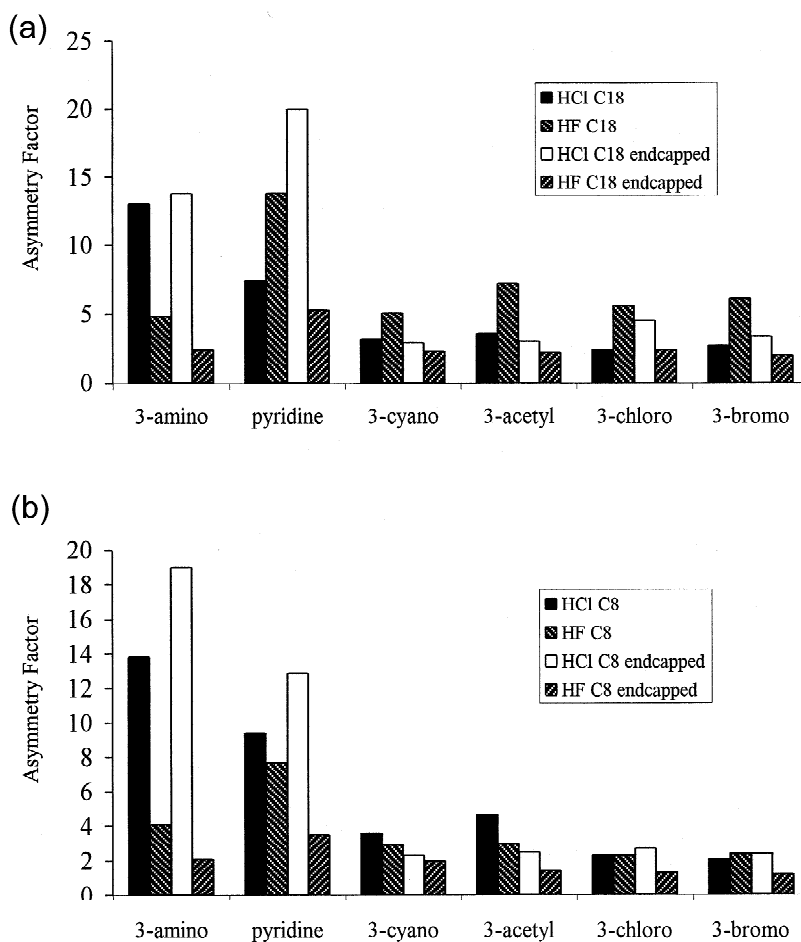


Fig. 6. (a) Asymmetry factors of test analytes on C_{18} bonded phases following HCl and HF treatment. (b) Asymmetry factors of test analytes on C_8 bonded phases following HCl and HF treatment.

silica with HF can improve the chromatographic quality of bonded phases.

4. Conclusions

Data produced by several different analytical techniques support the conclusion that rehydroxylation of a silica support with dilute HF gives a support material with a substantially reduced trace metal content, fewer isolated silanols and a more extensive surface rehydroxylation compared with the HCl-treated silica. The markedly improved chromato-

graphic performance towards weak bases of the HF-treated phases can be attributed to a combination of improved surface coverage of the bonded phase and the reduction in available sites for unwanted ion-exchange interactions with the bases. Evidence is presented from surface analysis of the silicas to suggest that the bulk measurement of trace metals is not an accurate indication of the metal available at the chromatographic surface. Trace metals which are present in substantial concentration in the bulk analysis (for example, sodium) are preferentially removed from the surface of the silica by acid treatment. This observation explains, in part, why

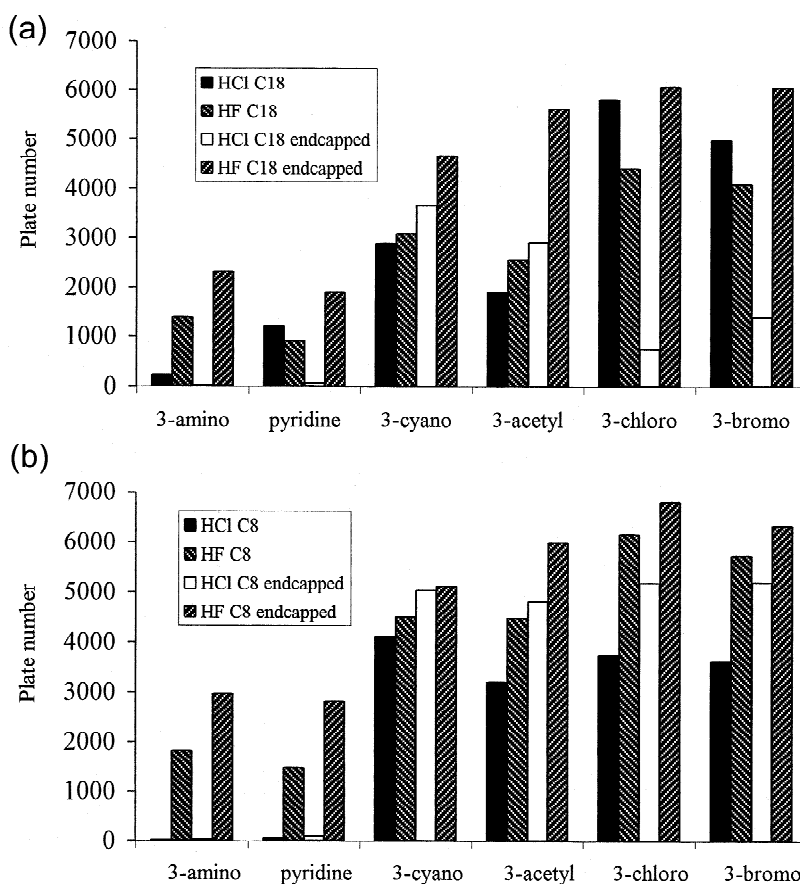


Fig. 7. (a) Plate numbers of test analytes on C₁₈ bonded phases following HCl and HF treatment. (b) Plate numbers of test analytes on C₈ bonded phases following HCl and HF treatment.

silicas with a high bulk metal content can show low levels of adsorptive sites for basic solutes.

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References

- [1] J. Köhler, D.B. Chase, R. D Farlee, A.J. Vega, J.J. Kirkland, *J. Chromatogr.* 352 (1986) 275.
- [2] J. Köhler, J.J. Kirkland, *J. Chromatogr.* 385 (1987) 125.
- [3] J. Nawrocki, *Chromatographia* 31 (1991) 177.
- [4] J. Nawrocki, *Chromatographia* 31 (1991) 193.
- [5] K.K. Unger, B. Lork, K. Pfeiderer, E. Albert, J. Bayer, *J. Chromatogr.* 556 (1991) 395.
- [6] G.B. Cox, R.W. Stout, *J. Chromatogr.* 384 (1987) 315.
- [7] J. Nawrocki, *J. Chromatogr. A* 779 (1997) 29.
- [8] M. Verzele, M. De Potter, J. Ghysels, *J. High Resolut. Chromatogr. Commun.* 2 (1979) 151.
- [9] B. Buszewski, *Chromatographia* 34 (1992) 573.
- [10] J. Nawrocki, D.L. Moir, W. Szezepaniak, *Chromatographia* 28 (1989) 143.
- [11] P.C. Sadek, P.W. Carr, L.W. Bowers, *J. Liq. Chromatogr.* 8 (1985) 2369.
- [12] P.C. Sadek, P.W. Carr, L.W. Bowers, *J. Liq. Chromatogr.* 25 (1985) 489.
- [13] V.A. Brown, D.A. Barrett, P.N. Shaw, M.C. Davies, H.J. Ritchie, P. Ross, A.J. Paul, J. F Watts, *Surf. Interface Anal.* 21 (1994) 263.
- [14] D.A. Barrett, V.A. Brown, M.C. Davies, P.N. Shaw, *Anal. Chem.* 68 (1996) 2170.
- [15] B. Buszewski, *Chromatographia* 29 (1990) 233.

- [16] M.A. Kaiser, C.D. Batich, *J. Chromatogr.* 175 (1979) 174.
- [17] A.F. Carley, L. Moroney, M.W. Roberts, *Faraday Discuss. Chem. Soc.* 15 (1980) 39.
- [18] M.L. Miller, R.W. Linton, *Anal. Chem.* 56 (1984) 2204.
- [19] M.L. Miller, R.W. Linton, *Anal. Chem.* 57 (1985) 2314.
- [20] M.L. Miller, R.W. Linton, G.E. Maciel, B.L. Hawkins, *Surf. Interface Anal.* 7 (1985) 196.
- [21] S.J. Simko, M.L. Miller, R.W. Linton, *Anal. Chem.* 57 (1985) 2448.
- [22] D.A. Barrett, V.A. Brown, P.N. Shaw, M.C. Davies, H.J. Ritchie, P. Ross, *J. Chromatogr. Sci.* 34 (1996) 146.
- [23] W.A. Aue, M.M. Daniewski, E. Pickett, P.R. McCullough, *J. Chromatogr.* 111 (1975) 37.
- [24] K. Tanabe, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis, Science and Technology*, Springer-Verlag, Berlin, 1981, p. 231.
- [25] B. Buszewski, *Chromatographia* 34 (1992) 573.
- [26] J.C. Vickerman (Ed.), *Surface Analysis – The Principal Techniques*, Wiley, Chichester, 1997.
- [27] W.A. Proctor, S.K. Ramirez, K.L. McWilliams, J.L. Huerta, J.J. Kirkland, in: J.J. Pesek, M.T. Matyska, R.R. Abuelafiya (Eds.), *Chemically Modified Surfaces – Recent Developments*, Royal Society of Chemistry, Cambridge, 1996, p. 45.
- [28] J.J. Hetem, *Chemically Modified Silica Surfaces in Chromatography. A Fundamental Study*, Huthig Buch Verlag, Heidelberg, 1993.