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Characterization of the surface properties of Mg/Al oxides by the solvation parameter model

Zhiping Zhang, Shigang Zhang, Jiping Chen*, Zhongmin Liu, Xinmiao Liang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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Abstract

The oxides of different Mg/Al ratios (Mg/Al = 0, 0.1, 5, 10 and ∞) were prepared, and the characterization of these oxides was attempted by estimating characteristic interaction parameters based on the solvation parameter model. The magnitudes of the regression coefficients varied with the increase of Mg/Al ratio. For the oxide of Mg/Al = 0.1 and Al₂O₃, the contribution of these characteristic interactions for solutes' retention was similar to that of the common silica, and the dipolarity/polarizability (π^*), the solute hydrogen bond donating (α_2^{H}) and accepting (β_2^{H}) abilities played an important role. Yet, the retention behavior at a higher Mg/Al ratio (Mg/Al = 5, 10 and MgO) drastically changes, and $V_i/100$ (the intrinsic molar volume), π^* , α_2^{H} and β_2^{H} all favored the solutes retention. By comparison of the regression coefficients on various normal-phase (NP) and reversed-phase (RP) columns, a new model was developed to correlate the solute retention factors on Mg/Al = 5, 10 and MgO columns with the data of NP and RP columns.

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1. Introduction

Metal oxides, e.g., zirconia, titania and alumina [1–4] and their derivatives [5–7], recently have deserved much attention from chromatographers based on their chemical and thermal stability. Additionally, these oxides have higher retention and selectivity as well as more excellent column efficiency in contrast to polymeric materials [4]. However, MgO is rarely used as packing material although it has been found many exceptionally important applications in catalysis [8-11], refractory materials [12], paints [13], superconductors [14], toxic waste remediation [15], etc. In the early studies, many researchers [16–18] have found that olefinic bonds and aromatic groups can be preferentially held on MgO relative to other groups, and the solutes' retention increases with the increase of olefinic bonds. It is well known that the main differences between various polycyclic aromatic hydrocarbons (PAHs) are the numbers of olefinic bonds, and MgO may be a favorable material for the separation and enrichment of different PAHs, especially for the low concen-

0021-9673/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.chroma.2006.02.069 tration of toxic PAHs in environmental samples. Despite that, MgO from different sources are variable, and most of the commercial chromatographic MgO are fine powders [16], which to a certain extent restrict its application in liquid chromatography (LC). Binary metal oxides may be an alternative to make up the defects of MgO. At present, Al₂O₃ has been widely used in the sample preparation due to its stability, easily controlled shape and well-known surface characteristics, and hence Mg/Al binary oxides are likely to be a perfect material in the preparation process of environmental samples. Moreover, Mg/Al oxides have high specific surface area, thermal stability and strong basicity [10,11,19] that provide a robust basis for their wide applications.

Prior to develop a new adsorbent, it is important to study the retention interactions between the stationary phase and solutes. The solvation parameter model proposed by Kamlet et al. [20], as an important tool to elucidate the interactions between solutes and stationary phases, has been widely used in many adsorption equilibrium processes [21–25] for studying the retention characteristics of various adsorbents. For example, Park et al. [23] used the solvation parameter model to characterize chromatographic properties of the NP-LC stationary phases in terms of the type and relative strength of the stationary phase interactions with solutes, such as Hypersil silica, Lichrospher Diol, Hypersil

^{*} Corresponding author. Tel.: +86 411 84379562; fax: +86 411 84379562. *E-mail address:* chenjp@dicp.ac.cn (J. Chen).

APS NH_2 and various CN stationary phases. These authors also employed the model in the characterization of stationary phases in RP-LC [24]. Pyo et al. [25] investigated the chromatographic properties of an octyldecylsilane bonded phase in packed capillary column supercritical fluid chromatography with the model.

According to the solvation parameter model [26,27], logarithmic retention factors of solutes can be described as Eq. (1).

$$\log k' = \log k'_0 + rR_2 + m\frac{V_i}{100} + s\pi^* + b\beta_2^{\rm H} + a\alpha_2^{\rm H}$$
(1)

where $\log k'_0$ is the multiple regression intercept, and the subscript 2 designates a solute property; R_2 is the excess molar refraction; $V_i/100$ is the intrinsic (van der Waals) molar volume, π^* is the dipolarity/polarizability, $\alpha_2^{\rm H}$ and $\beta_2^{\rm H}$ are the solute hydrogen bond (HB) donating and accepting abilities, respectively. The coefficients, r, m, s, b, and a describe the differences between the solute-stationary phase interactions and the solute-mobile phase interactions [6]. However, in many previous reports [22,28], the value of the coefficient r shows less contribution for solutes' retention relative to other coefficients. Due to this reason or others, Eq. (2) is often applied to characterize the retention interactions between solutes and different stationary phases.

$$\log k' = \log k'_0 + m \frac{V_i}{100} + s\pi^* + b\beta_2^{\rm H} + a\alpha_2^{\rm H}$$
(2)

A positive sign of the coefficients in Eq. (2) would mean that the corresponding molecular interaction is stronger in the stationary phase than in the mobile phase. On the contrary, it indicates that the molecular force favors in the mobile phase [21]. If the mobile phase is fixed, these parameters will characterize the difference of retention interactions between solutes and stationary phases.

In the present paper, the retention interactions between different Mg/Al oxides and solutes are discussed by the investigation of the regression coefficients in Eq. (2). On this basis, a new model was developed to correlate the solute retention factors on the oxide of Mg/Al=5, 10 and MgO columns with the data of normal-phase (NP) and reversed-phase (RP) columns.

2. Experimental

2.1. Preparation of Mg/Al oxides

The various Mg/Al oxides were prepared according to the following procedure:

Solution A: MgCl₂·6H₂O and Al(NO₃)₃·9H₂O with Mg²⁺/Al³⁺ molar ratios of 0, 0.1, 5, 10 and ∞ were dissolved in deionized water (500 mL) to give the solutions with a Mg²⁺ concentration of 1.5 M.

Solution B: NaOH and Na₂CO₃ were dissolved in deionized water (300 mL) to form the mixed base solution. The concentrations of the base were related to the concentrations of metal ions in solution A as follows: $[Al^{3+}]/[OH^{-}] = 1:3$ and $[Mg^{2+}]/[CO_3^{2-}] = 1:1$.

At room temperature, solution A was added into the vigorously stirred solution B in an hour, and the resulting slurry was aged under such a condition for 4 h. Then the precipitate was filtered and washed with deionized water. After that, the product was dissolved in 1250 mL of deionized water followed by spraying and calcining in the air (heating from room temperature to 550 °C at the rate of 1 °C/min followed by holding for 2 h).

 SiO_2 with a diameter of 5 μ m was purchased from Qingdao Haiyang Chemical Group Co.

2.2. Apparatus

All chromatographic data were performed on a Waters 510 chromatograph equipped with a single pump, a Waters 2487 Dual Absorbance Detector (Waters, USA) operated at 254 nm detection wavelength and a Rheodyne injector (Model 7725, Rheodyne, USA) with a 20 μ l sample loop. A computer-based DL 800 workstation was used not only to control the instrumentation, but also to collect chromatographic data.

2.3. Chromatographic conditions

Mg/Al oxides were packed into the stainless-steel tubes (100 mm × 4.6 mm I.D) by slurry packing method. The column was placed in a thermostated jacket, and the temperature was controlled at 30 ± 0.1 °C. The eluent used was 1.0% (v/v) isopropanol–hexane, and the flow rate was 0.6 ml min^{-1} . The retention time of tetrachloroethene was used as dead time (t_0), and the retention factor (k') was calculated by $k' = (t - t_0)/t_0$ from the mean retention time of duplicate measurements. The elution liquids, *n*-hexane and isopropanol (HPLC grade), were purchased from Shandong Yu Wang Ltd., and the solutes used were of analytical grade or better.

3. Results and discussion

3.1. Chromatographic properties of Mg/Al oxides

For the investigation of the interactions between solutes and Mg/Al oxides and SiO₂, a series of probe solutes with different properties were injected and their retention factors were determined. The injected solutes, their solvachromatic parameters and their retention factors using 1.0% (v/v) isopropanol–hexane as the mobile phase are shown in Table 1. From these results, Eq. (2) allows the computation of the regression coefficients as given in Table 2. For all of the solutes set, the correlation coefficients (*R*) is above 0.92, which indicates that the goodness-of-fit of the equations is good enough.

According to the multiple regression results of log k' against the solvatochromatic parameters, the magnitudes of the coefficients m, s, b and a vary significantly with the types of the oxides, indicating that there are various factors rendering the difference of solutes retention on these oxides. As shown in Table 2, the signs of the coefficients s, b and a are all positive for these oxide columns, which means that the retention behaviors of these solutes increase with the increase of the solute polarizability/dipolarity (π^*), HB donating ($\alpha_2^{\rm H}$) and HB accepting abilities ($\beta_2^{\rm H}$). At the same time, the results also indicate that the magnitudes of the net attractive polar interactions [23]

Table 1
Solvatochromic parameters [29,30] of the probe solutes and their retention factors on SiO2 and various Mg/Al oxide

Chemicals	<i>V_i</i> /100	π^*	$\beta_2^{\rm H}$	$\alpha_2^{\rm H}$	k'						
					SiO ₂	Al ₂ O ₃	Mg/Al = 0.1	Mg/Al = 5	Mg/Al = 10	MgO	
Benzene	0.491	0.59	0.10	0.00	0.03	0.12	0.00	0.00	0.01	0.13	
Anthracene	1.015	0.80	0.20	0.00	0.05	0.16	0.01	0.16	0.45	1.05	
Pyrene	1.156	0.90	0.25	0.00	0.07	0.19	0.02	0.47	1.30	3.16	
Bromobenzene	0.624	0.79	0.06	0.00	0.05	0.18	0.01	0.02	0.02	0.14	
Nitrobenzene	0.631	1.01	0.30	0.00	0.30	0.38	0.05	0.03	0.10	0.21	
Aniline	0.562	0.73	0.50	0.26	4.78	6.15	0.30	0.99	1.77	1.73	
Benzyl alcohol	0.634	0.99	0.52	0.39	6.99	12.34	1.59	3.09	3.55	4.31	
Naphthalene	0.753	0.30	0.15	0.00	0.04	0.14	0.01	0.02	0.02	0.14	
Fluorine	0.960	0.26	0.20	0.00	0.04	0.15	0.01	0.05	0.13	0.44	
Chlorobenzene	0.581	0.71	0.07	0.00	0.04	0.18	0.21	0.01	0.03	0.13	
p-Chloro-aniline	0.653	0.73	0.40	0.31	2.73	13.96	0.72	2.03	3.58	5.66	
Acetophenone	0.690	0.90	0.49	0.00	0.56	0.41	0.04	0.38	0.09	0.22	
Anisole	0.630	0.73	0.22	0.00	0.10	0.36	0.01	0.01	0.02	0.22	
Pyridine	0.470	0.87	0.64	0.00	10.23	2.15	0.06	0.09	0.16	0.24	
3-Methyl-pyridine	0.570	0.84	0.67	0.00	9.34	2.15	0.06	0.06	0.14	0.23	
m-Bromo-nitrobenzene	0.764	1.06	0.26	0.00	0.24	0.37	0.05	0.05	0.09	0.22	
<i>m</i> -Bromo-aniline	0.659	0.84	0.40	0.31	4.56	9.42	0.79	2.34	4.13	6.01	
<i>p</i> -Methyl-aniline	0.660	0.69	0.51	0.26	4.93	7.61	0.26	0.67	1.14	1.38	

Table 2

Multiple regression results for SiO2 and various Mg/Al oxides

Oxides	R	SD	$\log k'_0$	m	S	b	a	n
SiO ₂	0.99	0.18	-1.48 ± 0.26	-0.81 ± 0.25	0.35 ± 0.22	3.74 ± 0.28	2.02 ± 0.34	18
Al ₂ O ₃	0.98	0.17	-0.73 ± 0.24	-0.47 ± 0.24	0.13 ± 0.21	1.67 ± 0.26	3.62 ± 0.32	18
Mg/Al = 0.1	0.92	0.34	-1.50 ± 0.56	-0.84 ± 0.52	0.68 ± 0.41	0.84 ± 0.5	3.97 ± 0.64	17
Mg/Al = 5	0.96	0.26	-3.60 ± 0.42	2.03 ± 0.40	0.50 ± 0.32	1.61 ± 0.42	4.44 ± 0.48	17
Mg/Al = 10	0.97	0.25	-3.65 ± 0.36	2.38 ± 0.36	0.56 ± 0.31	1.50 ± 0.39	4.52 ± 0.48	18
MgO	0.96	0.20	-2.14 ± 0.29	1.78 ± 0.28	0.28 ± 0.25	0.36 ± 0.31	3.68 ± 0.38	18

Note: where *R* is correlation coefficient, SD is the standard deviation of the regression and *n* is the number of regression probe solutes.

between the solute and the Mg/Al oxides and SiO₂ are greater than those between the solute and the mobile phase, which are in good agreement with the previous reports on NP-LC columns [6,21,23]. After careful observation of these data, it can be also seen that the dominant interaction on SiO₂ column is the HB accepting abilities, whereas the HB donating abilities on different Mg/Al oxides make a great contribution to solutes' retention. These results suggest that the surface basicity on these Mg/Al oxides is larger than that on SiO₂ column, and the solutes with stronger HB acidities have larger retention behavior on Mg/Al oxides. In addition, it can be also seen in Fig. 1 that as the Mg content is increased from 0 to 60.3% in the Mg/Al oxides, the coefficients s, b and a remain relatively constant although the coefficient b has a slight change, indicating that the variation of the Mg content has less influence on the dipolarity/polarizability and the HB donating and accepting abilities of these Mg/Al oxides.

Comparison of the magnitudes of *m*, it can be clearly seen in Fig. 1 that this coefficient significantly changes with the increase of the Mg content. As shown in Table 2, the values of the coefficients *m* on Al₂O₃, Mg/Al = 0.1 and SiO₂ columns are negative, which agree with the chemical sense [6,21,23]. According to the definition of the coefficient in NP-LC, *m* represents the difference in cohesive energy density between the stationary and

mobile phases [31]. When a solute is transferred from the mobile phase onto the stationary phase, it will replace the pre-adsorbed mobile phase molecules on the stationary surface and the amount of the molecules replaced is roughly proportional to the size of the solute molecule. An increase in the solute size requires more energy for endoergic interactions by solutes with active sites



Fig. 1. Plot of the regression coefficients vs. the Mg content in Mg/Al oxides.

on the adsorbent surface. This will lead to a decrease of solute retention with the increase of solute size on NP-LC columns [23]. Furthermore, the hydrophobility of the mobile phase in NP-LC is greater than the stationary phase, which results in the increase of the solubility of organic solutes in mobile phase. Therefore, the sign of the coefficient m is negative in NP-LC systems.

With the increase of Mg/Al = 5, 10 and ∞ , it is interesting that the values of *m* are all positive. By the investigation of the retention interactions of Al₂O₃ and SiO₂ in normal-phase systems using the solvation parameter model, Park et al. [32] also observed that the coefficient *m* was positive. They suggested that this term $V_2/100$ crudely approximated an increase in dispersive interactions between adsorbents and the solutes as the solutes increased in size and hence polarizability, and dipole–dipole and dipole-induced interactions were reflected in the π^* term. Whereas, the coefficient *s* for the oxides of Mg/Al = 5, 10 and MgO are rather less relative to the coefficient *m*, indicating that the polarizability/dipolarity is not the main factor resulting in the increase of the solute retention with the increase of solute size. To our knowledge, it should be attributed to the surface properties of Mg/Al oxides.

Recently, many experimental evidence and model calculations [33-38] have proved the existence of different oxygen vacancies at the surface or sub-surface region of MgO. Different from other covalent oxides, the removal of oxygen atoms in MgO does not lead to the formation of new bonds but rather cavities, which may be filled with electrons trapped by the strong electrostatic potential of ionic crystal [38]. Because the probe solutes in this study are almost aromatic compounds with rich π electrons, especially for these PAHs, the oxygen cavities on the surface of MgO will strongly interact with the π electrons of these aromatic compounds. Consequently, these solutes with more π electrons have larger retention behavior on MgO [16–18], which is clearly seen from the retention factors of PAHs in Table 1. For the various Mg/Al oxides, the basic property of MgO is modified and controlled by the displacement of Mg²⁺ with the guest Al³⁺ ions in the lattices [11]. According to the study of Cavani et al. [19], Al octahedral at higher Al content (Mg/Al < 3) would become adjacent on the basis of geometric considerations, thus leading to Al(OH)₃ nucleation. With the increase of Mg/Al ratio higher than 4, the location of the Mg ion is such that the formation of Mg(OH)₂ is favored. Therefore, the oxide of Mg/Al=0.1behaviors the characteristics of Al_2O_3 , and the coefficient *m* is negative. With the increase of Mg/Al ratio up to 5, the Al³⁺ has less influence on the surface properties of the Mg/Al oxides, and the value of *m* is positive.

3.2. Correlation of solute retention factors with those on both NP- and RP-LC columns

By comparison of the multiple regression coefficients of the linear solvation energy relationships (LSERs) on various NP- and RP-LC columns, the results are given in the support information. According to both NP- and RP-LC columns, the magnitudes of these regression coefficients vary significantly with the type of LC system. From the multiple regression coefficients of 13 kinds of NP-LC columns [6,23,29,39], the results show that the coefficient m is negative and, the values of s, a, b are positive for all NP columns, suggesting that the hydrophobicity of these stationary phases in NP-LC systems is less than that of mobile phases, and the dipolarity/polarizability, the HB donating and accepting interactions between solutes and stationary phases favor the solutes' retention.

Relative to NP-LC columns, these coefficients on various RP columns have much diversity. According to these 38 types of RP columns [6,7,40–44], the values of the coefficient (m) are positive in all cases, and another three coefficients (s, a, b) are almost negative although there are some abnormalities for the coefficient s, which means that the intrinsic molar volume is the most important parameter for the increase of solutes' retention in comparison with other interactions in RP-LC system.

From the results of the above section, it can be obviously seen that not only the values of the regression coefficients m on Mg/Al = 5, 10 and MgO are positive, but the values of the other three coefficients s, a, b are also positive, which suggests that the intrinsic molar volume, dipolarity/polarizability, HB donating and accepting abilities on these columns are all in favor of solutes retention. By the analysis of different types of NP- and RP-columns, it is clear that the main contribution for the increase of solutes' retention in RP-LC is the former one, whereas the latter three terms play an important role in NP-LC. If we connect the respective contribution for the increase of solutes' retention on other types of both NP- and RP-columns together, the contribution terms on the oxides of Mg/Al = 5, 10 and MgO may be made up by them. If this deduction accords with the truth, the retention factors on Mg/Al=5, 10 and MgO should have a good relationship with those on other types of both NP- and RP-columns, which can be described as Eq. (3).

$$\log k'_{\text{Mg/Al} \ge 5} = A + \sum_{i=1}^{n_i} B_i \log k'_{\text{NP}} + \sum_{j=1}^{n_j} C_j \log k'_{\text{RP}}$$
(3)

where A is the multiple regression intercept, and B_i and C_j are constants that reflect the relative contribution of the corresponding retention parameters, n_i and n_j are the numbers of the chromatographic systems that have different selectivities, and log k'_{NP} and log k'_{RP} are the logarithmic retention factors on NP-and RP-LC columns, respectively.

For confirming the above model, the retention factors of a limited number of solutes (No. 1–11) in Table 1 on Mg/Al = 5, 10 and MgO columns were correlated with those on NP-SiO₂ and Al₂O₃ columns and RP-ODS and CN columns [44], and the results are listed in Table 3.

As can be seen from Table 3, when single NP- or RP-LC columns are put into regression the correlation coefficients R^2 are rather low, namely, the values for the Mg/Al = 5, 10 and MgO columns are, respectively, 0.72, 0.63 and 0.56 when both NP-SiO₂ and Al₂O₃ are used as molecular descriptors, the values are 0.65, 0.77 and 0.65 for RP-CN and ODS columns. Nevertheless, when both NP- and RP-LC columns are put into the regression of Eq. (3), the correlation coefficients take place a great change. For the oxides of Mg/Al = 5, 10 and MgO columns, the values

Table 3

Multiple linear regression results or log k on Migrat = 5, to and Migo with Mr - and KF-LC columns												
NP-LC		RP-LC		Mg/Al=5			Mg/Al = 10			MgO		
SiO ₂	Al ₂ O ₃	CN	ODS	R^2	SD	F	R^2	SD	F	R^2	SD	F
+	+	_	_	0.72	0.55	8.8	0.63	0.66	6.8	0.56	0.49	5.1
_	_	+	+	0.65	0.60	6.6	0.77	0.51	13.7	0.65	0.44	7.4
+	_	+	_	0.96	0.20	92.5	0.97	0.20	113.8	0.90	0.24	34.5
+	_	_	+	0.99	0.12	239.1	0.97	0.20	115.9	0.92	0.21	45.2
_	+	+	_	0.97	0.19	103.9	0.95	0.25	69.8	0.94	0.18	66.5
_	+	_	+	0.93	0.27	45.9	0.89	0.36	32.2	0.92	0.22	43.4
+	+	+	_	0.99	0.12	164.1	0.98	0.18	89.6	0.95	0.19	39.8
+	+	_	+	0.99	0.09	277.3	0.97	0.21	69.2	0.94	0.19	37.5
_	+	+	+	0.97	0.18	74.6	0.97	0.21	67.9	0.94	0.19	39.0
+	_	+	+	0.99	0.13	154.2	0.97	0.20	73.1	0.92	0.22	27.1
+	+	+	+	0.99	0.10	179.4	0.98	0.20	57.6	0.95	0.20	25.9

Multiple linear regression	results of $\log k'$	on $Mg/Al = 5$	10 and MgO	with NP- ar	nd RP-LC columns
interpre intera regression	results of log h	$0 \Pi \Pi \Pi = 0$	10 und mgo	within the cu	ia ia no columno

Note: + means that the column is included in the multiple regression, and – indicates that the column is not included. R², correlation coefficient; SD, standard deviation of the regression; F, Fish F-statistic.

of R^2 are all larger than 0.89, and it steadily increases up to 0.99, 0.98 and 0.95 for a total of four columns. The results indicate that the retention interactions between the oxide of Mg/Al = 5(or Mg/Al = 10 and MgO) and solutes in NP-LC can be divided into two types. One exists in NP-columns, and the other can be made up by the interactions in RP-columns. If single NP- or RP-columns are put into regression, it cannot meet the need of the retention interactions on the oxide of Mg/Al = 10 and MgOcolumns.

At the same time, if the retention factors on some commercial NP- and RP-columns are available, it may be an alternative method to get their retention values on the oxides of Mg/Al=5, 10 and MgO with this model. More importantly, because the retention interactions of many commercial NP- and RP-columns, such as SiO₂ and ODS columns, are well-known, it is very convenient to investigate the retention characteristics of Mg/Al oxides (Mg/Al molar ratio larger than 5) by using this model. This will support a possibility on quickly developing a suitable Mg/Al oxide or other materials with the similar surface properties as Mg/Al oxides for the separation and enrichment of different PAHs from environmental samples.

4. Conclusions

Different Mg/Al oxides were characterized by estimating the characteristic interaction parameters for the stationary phases based on the solvation parameter model. Comparison of the interaction parameters for these Mg/Al oxides showed that the intrinsic molar volume, dipolarity/polarizability, solute HB donating and accepting abilities on the oxides of Mg/Al = 5, 10 and MgO all contributed to the solutes' retention in NP-LC system, whereas the latter three terms favored the solutes' retention for the oxide of Mg/Al=0.1 and Al₂O₃ which was in agreement with chemical sense. According to the retention behavior of different solutes in various NP- and RP-LC columns, a new model is suggested to develop for the correlation of solutes' retention on the oxides of Mg/Al=5, 10 and MgO from the data of NP (Al₂O₃ and SiO₂) and RP columns (ODS and CN).

The correlation coefficients indicate that this model has a good enough accuracy to correlate the retention factors on the oxides of Mg/Al=5, 10 and MgO with these on other types of NP- and RP-columns. At the same time, it should be pointed out that only a limited number of probe solutes have been applied to develop this model, and more solutes should be used for the further test of this model.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2006.02.069.

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