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## SYNTHESIS OF SILVER AND COPPER(II) SILICA GELS FOR THE LIQUID CHROMATOGRAPHIC SEPARATION OF OLEFINIC HYDROCARBONS IN THE GROUP ANALYSIS OF LIGHT AND HEAVY PETROLEUM COMPOUNDS

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### SUMMARY

The separation between the saturated and olefinic groups of compounds in petroleum was improved by carrying out both adsorption and charge-transfer chromatography on a single column packed with a silica gel chemically modified with silver nitrate. The preparation of the modified silica and column conditioning were investigated in order to obtain reproducible stationary phase characteristics and chromatographic performance. Samples of light, heavy or wide-boiling-range gasolines, vacuum distillates before and after cracking, vacuum residues and various test compounds were studied with pentane as the mobile phase. The results compared favourably with those obtained with highly activated bare silicas of specific surface area 550 and 800 m<sup>2</sup>/g or copper(II)-modified silicas, used with either *n*-pentane or the perfluoroalkane Fluorinert FC 72 as the mobile phase. For all the samples containing olefins, at least a baseline separation between the saturates and the olefins was observed, while the aromatics were recovered by column back-flushing. The resolution within the olefinic group remained low, which allows more accurate quantitation. Lastly, with modified silica, the water content of the mobile phase and stationary phase is a much less critical parameter than with bare silica, for complete separation is maintained up to a water content of *ca.* 15 ppm in *n*-pentane.

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### INTRODUCTION

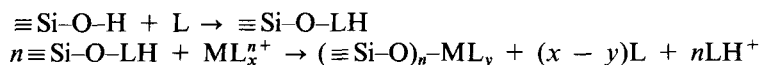
Adsorption chromatography on silica gel as the stationary phase is now a routine method for the group separation of light petroleum into saturated, olefinic and aromatic compounds<sup>1-4</sup>. In a recent paper<sup>5</sup> we discussed the influence of the specific surface area of the silica gel and the nature of the mobile phase and its water content on the separation. It was shown that the best results could be obtained with two phase systems, *i.e.*, a perfluoroalkane mobile phase (water content 2-3 ppm) with

a silica gel of specific surface area about 500 m<sup>2</sup>/g for light gasolines and a pentane mobile phase (water content 8–10 ppm) with a silica gel of very high (*ca.* 800 m<sup>2</sup>/g) specific surface area for heavier gasolines. However, several difficulties remained, especially as far as heavy petroleum samples are concerned, because of their low olefin content, poor solubility in the potential mobile phases, increasing complexity with increasing boiling temperature range and sample-to-sample discrepancies in the response factors of a given class.

An alternative to adsorption liquid chromatography on bare silica gel might be the combination of adsorption and charge-transfer chromatography on silver-modified silica gels, as first suggested by McKay and Latham<sup>6</sup> and Matsushita *et al.*<sup>7</sup>. The olefinic compounds are much more strongly retained on such a phase, owing to their ability to form charge-transfer complexes with the  $\pi$ -electron acceptor silver ions<sup>8</sup>. Hence, the separation of the alkanes from alkenes is greatly improved. However, the separation between the olefinic and aromatic compounds is simultaneously reduced, as the aromatic compounds give less stable silver complexes than the olefinic compounds. It follows that the separation of the alkanes and alkenes from the aromatic compounds must be performed on a bare silica gel column prior to the separation of the alkenes from the alkanes on a silver-modified silica column<sup>6,7</sup>. This two-column procedure was recently used by Norris and Rawdon<sup>9</sup> in supercritical fluid chromatography with flame ionization detection.

The known procedures for modifying silica gel with silver can be classified as treatments of a pre-packed column<sup>10,11</sup> or in a batch<sup>6,7,12–16</sup> and they lead to either simple coating of a silver salt at the surface of the silica gel<sup>6,7,10,11,13,16</sup> or chemical bonding between a siloxane moiety and a silver atom with removal of a hydrogen ion<sup>12,14,15</sup>. In the case of bonding (equivalent to the formation of superficial silver silicate<sup>14</sup>) the procedure might involve either a straightforward exchange between hydrogen and silver ions or a two-step exchange via an intermediate ion<sup>12,14,15</sup>.

For the purpose of group separations of petroleum samples, an *in situ* coating of silica gel with a silver nitrate solution in acetonitrile was successfully employed during preliminary work in our laboratory<sup>5</sup>, but the results were not sufficiently reproducible. This was probably due to the difficulty in eliminating acetonitrile totally from the packed columns and suggests why batch procedures with acetonitrile<sup>7</sup> or water<sup>6</sup> solutions were previously preferred. For this, a silica superficially modified by the formation of silver silicate seems more attractive for stability reasons. Such a phase was obtained by using a two-step batch procedure consisting of an alkaline pre-treatment, followed by a reaction with silver nitrate in methanol<sup>12,14,15</sup> or water<sup>17</sup>. In the latter instance, the maximum load capacities were reported to be 0.5 and 0.95 mequiv./g for silver and copper(II) ions, respectively. However, this procedure was time consuming and probably reduced the specific surface area of the silica owing to its excessive solubility in the alkaline medium. This is why we have investigated a new straightforward procedure, in which an electrically neutral, weakly basic ligand, L, of silver ions was added to the silver solution. The main equilibria occurring during the modifying process with a metallic cation M<sup>n+</sup> can be written as follows:



This procedure was prompted by that previously described for copper(II) ions by Foucault and co-workers<sup>18-20</sup> in ligand-exchange chromatography. However, in order to achieve a charge-transfer mechanism with the olefinic and aromatic compounds, the ligand, L, must be removed from the modified silica gel, *i.e.*, it must be volatile. Some other desirable characteristics of the ligand are basicity, stability of  $ML_x^+$  complexes and ready exchange between  $LH^+$  and  $ML_x^+$  ions, all of which determine the extent of metal loading of the silica gel. Vydra and Markova<sup>21</sup> determined a value close to 0.75 mequiv./g for both ions when 0.25 M aqueous ethylenediamine was used. With a molar aqueous ammonia solution, Foucault and co-workers<sup>18,19</sup> obtained a copper(II) loading of 1.4 mequiv./g. Compared with ethylenediamine, higher silver and copper loadings are expected with ammonia, which gives less stable complexes.

We report here an extensive study of a silver-modified silica gel, obtained by chemically bonding silver ions to silica in an aqueous ammonia medium. Column conditioning with this phase was tested and the chromatographic behaviour of such a column with respect to test compounds and light and heavy petroleum samples is presented. The results are compared with those obtained on bare silicas and copper(II)-modified silicas.

## EXPERIMENTAL

### *Apparatus and materials*

The chromatographic system was assembled from commonly available items, described in detail previously<sup>5</sup>. It included a back-flushing device and double detection by differential refractometry and UV absorbance. All separations were performed at ambient temperature.

The silica gels were LiChrosorb Si 60, 7  $\mu\text{m}$ , specific surface area 500  $\text{m}^2/\text{g}$  (E. Merck, Darmstadt, F.R.G.) and an experimental Spherosil, 5  $\mu\text{m}$ , specific surface area 800  $\text{m}^2/\text{g}$  (a gift from Rhône-Poulenc Recherches, Vitry-sur-Seine, France). The silica gels were modified with copper(II) sulphate pentahydrate or silver nitrate of analytical-reagent grade (Merck).

The solvents used in the mobile phase were *n*-pentane of Chromasol or Spectrosol grade (SDS, Peypin, France) and Fluorinert FC 72, a perfluorinated alkane (3 M, St. Paul, MN, U.S.A.). The water content was measured by the Karl Fisher titration method (Automate Bizot et Constant, Prolabo, Paris, France). The solvents were dried with 3 Å molecular sieves.

Saturated, olefinic and aromatic hydrocarbon test solutes were injected: *n*-pentane, *n*-hexane, *n*-heptane (from SDS), *n*-octane, *n*-decane, *n*-dodecane, *n*-hexadecane, *n*-pentacosane (Fluka, Buchs, Switzerland), cyclohexane, 3-methylpentane (SDS); 1-hexene, 1-octene, 1-nonene, 1-decene, 1-hexadecene, 2-methyl-2-butene (Fluka), cyclohexene, cyclooctene, 2,5-dimethyl-2,4-hexadiene (Aldrich, Milwaukee, WI, U.S.A.); benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,3,5-trimethylbenzene, naphthalene, biphenyl (from Merck), all of analytical-reagent grade. The column dead volume was estimated from the retention time of pentane, eluted with dichloromethane as mobile phase.

The petroleum samples studied were a light gasoline, produced by fluid catalytic cracking (FCC), having a boiling range (b.r.) below 130°C; a heavy FCC gasoline

cut (b.r. 130–260°C); a so-called complete gasoline (b.r. below 260°C), containing saturated and olefinic compounds up to *ca.* C<sub>14</sub> and mono- and polyaromatic hydrocarbons; a fraction distilled under vacuum (b.r. below 550°C) called “distillate” in the following text; a fraction similar to the previous one (b.r. below 550°C) but having undergone a cracking process and named “cracked distillate” in the following text; and lastly a deasphalted oil residue from distillation at 550°C.

#### *Preparation of copper(II)-modified silica columns*

Stainless-steel columns (25 cm × 0.48 cm I.D.) were packed with LiChrosorb Si 60 by the slurry technique. About 2 g of silica gel were needed. The columns were equilibrated with water, then a 20-ml stainless-steel packing vessel was connected to the column and filled with 0.2 M copper sulphate in 1 M aqueous ammonia solution. This solution was percolated through the columns at a flow-rate of 1 ml/min with a pump fed with water. During the process, the colour and pH of the effluents were monitored. The simultaneous breakthrough of ammonia and copper(II) ions appeared after *ca.* 10 ml. A total volume of *ca.* 70 ml was passed through the columns, then the columns were washed with *ca.* 20 ml of ethanol. Subsequently, the interstitial ethanol was displaced by a stream of nitrogen at room temperature, and the columns were activated in an oven for 4 h at 120°C under a stream of nitrogen. Subsequently, they were ready to be equilibrated with the mobile phase.

#### *Preparation of silver-modified silica columns*

With the more strongly oxidizing silver ions, washing with reducing organic solvents such as alcohols should be avoided. Moreover, the lower stability of silver silicate, compared with copper silicate, dictates the use of a batch procedure, which allows the removal of ammonia under vacuum and mild heating.

An amount of 10 g of LiChrosorb Si-60 was suspended in 100 ml of 0.18 M silver nitrate in 0.5 M aqueous ammonia solution and allowed to react for 10 min in the dark with ultrasonic stirring. The mixture was allowed to settle for *ca.* 20 min prior to being filtered through a funnel, equipped with a sintered-glass disc (Porosity No. 4) under suction. The powder was washed with 250–300 ml of water and 100 ml of acetone and then transferred into a stoppered round-bottomed flask, wrapped in aluminium foil to protect it from light. The vessel was connected to a rotary evaporator and the powder was dried for 4 h at 50°C under vacuum. After this treatment, the white silver-modified silica must be kept dry and in the dark.

For the packing of 25 cm × 0.48 cm I.D. columns, 2.4 g of silver-modified silica gel were dispersed in 40 ml of carbon tetrachloride or Fluorinert FC 72. The slurry was homogenized in an ultrasonic bath for 10 min and rapidly poured into a conical stainless-steel packing vessel. The columns were packed under 500 bar pressure with isooctane as pumping solvent for 10 min. The columns (containing *ca.* 2 g of silver-modified silica) were finally activated in an oven at 120°C under a stream of nitrogen and then they were ready to be equilibrated with the mobile phase. To prevent the silica from turning dark brown by formation of silver hydroxide with the release of water molecules, the drying step should not exceed 2 h, otherwise the silica pores may become partially clogged, which would lead to a loss of chromatographic retention for all compounds.

*Analytical characterization of the silver-modified silicas*

The nitrogen and silver contents of the modified silica gels were determined before any washing from a mass balance of the reaction mixture. A 1-ml sample of the starting ammoniacal silver nitrate solution was titrated first with 0.1 *M* nitric acid and then with 0.1 *M* hydrochloric acid in order to determine the initial ammonia and silver concentrations, respectively. The equivalence points were obtained with a Model Mini 80 pH/millivoltmeter (Tacussel, Villeurbanne, France), Tacussel glass and silver electrodes and a Tacussel RDJ/C8 calomel reference electrode with a double internal compartment, containing potassium chloride and potassium nitrate. A further 1-ml sample of solution was similarly analysed after the reaction with the silica gel had taken place. This sample was carefully filtered through a 0.5- $\mu\text{m}$  Millex-SR filter unit (Millipore, Bedford, MA, U.S.A.). The silver content of the modified silicas after washing and drying was determined by titration with 0.1 *M* hydrochloric acid of a 0.2-g sample, suspended in 20 ml of water and 2 ml of concentrated nitric acid. The corresponding nitrogen contents were obtained by elemental microanalysis performed on 0.3-g modified silica samples.

## RESULTS AND DISCUSSION

*Silver loading of the silica gel*

The influence of silver nitrate and ammonia concentrations on the silver loading was studied with LiChrosorb Si 60 (7  $\mu\text{m}$ ), using a batch procedure, as described under Experimental. The amounts of ammonia and silver ions loaded on the silica were determined from a mass balance, as described. The initial silver nitrate concentration was varied first by keeping the ratio of ammonia to silver concentrations in the range 2.6–2.8. It was found that the silver concentration in solution at equilibrium must be higher than 0.12 *M* in order to attain the maximum silver loading. This value clearly shows a much lower affinity of silver compared with copper(II) ions, for which the maximum loading was reached with solutions as dilute as 0.02 *M*<sup>18,19</sup>. As for the ratio of initial concentrations of ammonia and silver, it must be taken into account that the sorption of ammonia is higher than that of silver ions. Therefore, the ammonia concentration in the solution decreases more than the silver concentration. As a consequence, it can be predicted from theory and verified experimentally that this ratio should be higher than 2.6, in order to avoid the precipitation of silver hydroxide at the end of the reaction. On the other hand, this ratio should not exceed 2.8; otherwise, the sorption of ammonia could increase at the expense of the silver loading.

Using this set of operating conditions, the silver loading reproducibly obtained was 0.58 mequiv./g with a nitrogen content of 1.9–2.0 mequiv./g. As expected, it was also observed that acid pre-treatment of the silica gel with an equimolar mixture of concentrated nitric and sulphuric acids for 1 h markedly improved the silver loading up to *ca.* 0.7 mequiv./g. Lastly, it must be noted that the copper loading obtained under the operating conditions described was 1.3 mequiv./g. The surface of the resulting modified silica gel must present the following functional moieties:

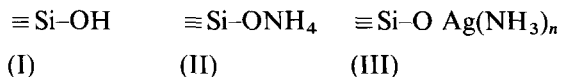


TABLE I

## EFFECT OF CONDITIONING OF SILVER-MODIFIED SILICA GEL ON NITROGEN CONTENT AND CHROMATOGRAPHIC PROPERTIES

Column, 15 × 0.48 cm I.D.; stationary phase, LiChrosorb Si 60, modified with 0.50 mM/g silver; Mobile phase, *n*-pentane (8 ppm of water); flow-rate, 1 ml/min. Test solutes: (1) *n*-hexane; (2) 1-hexene; (3) benzene.

Parameter	Solute	Conditioning		
		Vacuum (4 h, 50°C)	Vacuum (4 h, 50°C) + oven (2 h, 120°C)	Vacuum (4 h, 50°C) + oven (6 h, 120°C)
Nitrogen content (mM/g)	—	0.7	0.2	0.14
Capacity factor	1	0.1	0.2	0.3
	2	0.4	0.7	1.5
	3	0.9	1.5	2.2
Efficiency (plate number)	1	4000	4500	3500
	2	1000	250	150
	3	1300	1000	700

where *n* depends on the ammonia concentration in solution. By analogy with the results reported for copper-modified silicas<sup>22</sup>, the most likely value must be 1. With a specific surface area of 550 m<sup>2</sup>/g (LiChrosorb Si 60) and assuming a total silanol group density of 5 per nm<sup>2</sup> (ref. 23), the distribution among the three types of sites must be 57% of Type I, 30% of Type II and 13% of Type III. After the washing step, the remaining silver loading was 0.50 mequiv./g.

*Conditioning of silver-modified silica gels*

The silver-modified silica gels were conditioned so as to remove ammonia and water as completely as possible. Prior to packing the column, the material was kept in a rotary evaporator at 50°C under vacuum, then the packed columns were dried in an oven at 120°C under a stream of nitrogen. The nitrogen content remaining depended on the drying time of the column. The column efficiency and the chromatographic retentions of test solutes were also measured with *n*-pentane, containing 8 ppm of water as the mobile phase. The results are given in Table I. It will be noted that the vacuum treatment was not adequate to eliminate ammonia totally. The capacity factors increased with increasing drying time, whatever the nature of the compounds, but this increase was greater for the olefinic compounds. This was consistent with an increase in retention by both adsorption and charge-transfer mechanisms. A significant decrease in efficiency due to tailing was observed with the olefinic and aromatic compounds. This effect could be due to slow kinetics of the breaking of charge-transfer complexes. From these results, it appears that the drying time should not exceed 2 h. With longer times, the separation between the olefinic and aromatic compounds decreased and the efficiency became too low.

TABLE II

CAPACITY FACTORS OF SATURATED, OLEFINIC AND AROMATIC TEST SOLUTES ON MODIFIED AND UNMODIFIED SILICA GELS

Stationary phases: Spherosil (800 m<sup>2</sup>/g); LiChrosorb-Cu = LiChrosorb Si 60 (550 m<sup>2</sup>/g) superficially modified with copper sulphate; LiChrosorb-Ag = LiChrosorb Si 60 superficially modified with silver nitrate. Mobile phase: *n*-pentane (8 ppm of water) or perfluoroalkane Fluorinert FC 72 (2-3 ppm of water).

Compound	Spherosil- <i>n</i> -pentane <sup>24</sup>	LiChrosorb-Cu- FC 72	LiChrosorb-Cu- <i>n</i> -pentane	LiChrosorb-Ag- <i>n</i> -pentane
<i>Alkanes</i>				
<i>n</i> -Pentane		0.5		
<i>n</i> -Hexane	0.06		0.1	0.2
<i>n</i> -Heptane	0.06	0.9	0.1	0.2
<i>n</i> -Octane	0.06	1.1	0.1	0.2
<i>n</i> -Decane	0.07	1.4	0.1	0.2
<i>n</i> -Dodecane	0.05	1.7	0.1	0.2
<i>n</i> -Hexadecane	0.01	2.4	0.1	0.2
<i>n</i> -Pentacosane				0.2
Cyclohexane	0.18	0.6	0.1	0.2
<i>Alkenes</i>				
2-Methyl-2-butene	0.7			0.6
1-Hexene	0.4	0.2	0.2	0.7
1-Octene	0.4	3.5	0.2	0.7
1-Decene	0.4		0.2	0.7
1-Hexadecene	0.3		0.2	0.7
Gulthenes (C <sub>20</sub> -C <sub>24</sub> )	0.2			
Cyclohexene	0.7		0.3	0.9
Cyclooctene	0.6	4.3	0.3	4.0
2,5-Dimethyl-2,4-hexadiene	2.0	> 14	0.5	1.8
<i>Aromatic</i>				
Benzene		> 14	0.8	1.5
Toluene	2.5	> 14	0.9	1.6
<i>p</i> -Xylene	2.7		0.9	1.8
<i>m</i> -Xylene	2.8		0.9	1.9
1,3,5-Trimethylbenzene	3.1			2.1
<i>o</i> -Xylene	3.1		1.0	2.3
Naphthalene			4.6	4.6
Biphenyl			9.5	10.4

*Chromatographic behaviour of test compounds*

Table II gives the chromatographic retention data for saturated, olefinic and aromatic hydrocarbons, measured on LiChrosorb Si 60, superficially modified with silver nitrate, as previously described under Experimental. The mobile phase was *n*-pentane. A weak eluent, such as the perfluoroalkane Fluorinert FC 72, was not advisable for group separations of petroleum samples, as neither the olefinic nor the aromatic compounds were eluted. For the sake of comparison, retention data obtained with Spherosil, a bare silica gel of very high specific surface area (800 m<sup>2</sup>/g), and with LiChrosorb Si 60, superficially modified with copper sulphate, are also given. Spherosil, used with *n*-pentane as the mobile phase, was earlier the most useful

phase system for heavy petroleum samples, because it involved both adsorption and exclusion mechanisms<sup>5</sup>.

With *n*-pentane and LiChrosorb Si 60, modified to either copper or silver silicate, all the alkanes were eluted at the same time. Unlike the Spherosil-*n*-pentane phase system, this system gave no evidence of exclusion phenomena with heavy molecules, such as *n*-pentacosane. This means that the pores were not clogged by any

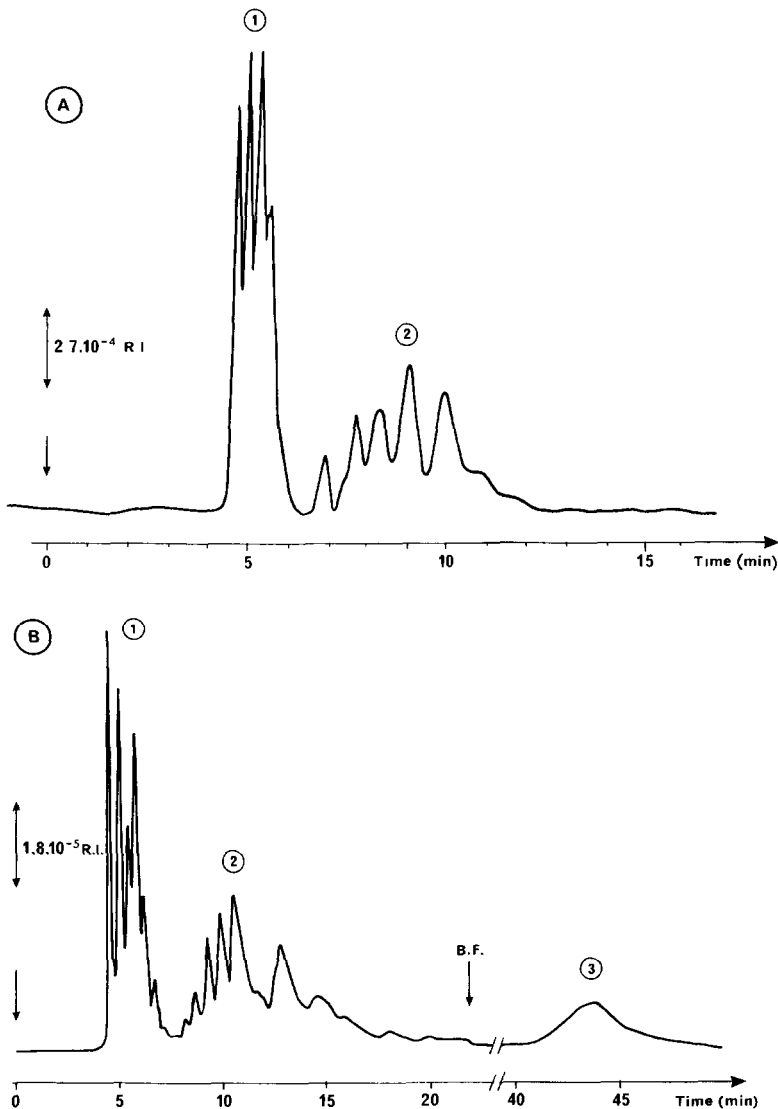


Fig. 1. Separations of a light gasoline sample on (A) bare and (B) copper-modified LiChrosorb Si 60 silica gel with perfluoroalkane Fluorinert FC 72 (water content 2 ppm) as the mobile phase. Column, 25 cm  $\times$  0.48 cm I.D.; flow-rate, 1 ml/min; refractive index detection; B.F. = back-flushing. Peaks: (1) alkanes; (2) alkenes; (3) aromatic compounds.



compounds derived from the modifying process. On the whole, the results for the alkanes were not very different from those obtained with unmodified silicas. This was expected on theoretical grounds; however, the retention values of alkanes seemed slightly low with the Spherosil-*n*-pentane phase system. This might be explained by the fact that they had been obtained earlier in the course of another series of experiments<sup>24</sup>.

With regard to the olefinic compounds, it is clearly apparent that the strongest retention was obtained with the silver-modified silica gel, the olefinic complexes being more stable with silver than with copper. On the silver-modified silica, the capacity factors increased with increasing stability constants of the silver-olefin complexes, and the elution order was branched olefins < linear olefins < cyclic olefins. This order is in agreement with the rules laid down by Hartley<sup>8</sup> on the basis of steric and electronic considerations. Cyclooctene exhibited a surprisingly high retention. This behaviour was also reported by Weiss<sup>25</sup> for the *trans*-isomer. With 1-alkenes, no influence of the alkyl chain length was evidenced. This resulted in very close retention values in the olefinic group, which is very favourable for a group analysis. Unfortunately, conjugated dienes and monoaromatic hydrocarbons displayed similar retentions: conjugated dienes gave more stable silver complexes, but the adsorption contribution to their retention was less. Finally, it should be kept in mind that the separation between alkane and alkene groups increased stepwise on passing from bare Spherosil to the copper-modified material and thence to silver-modified silica gels.

#### *Group analysis of petroleum compounds*

As was recently discussed<sup>1-5</sup>, for light FCC gasoline samples, the mobile phase should be a perfluorinated alkane so that refractive index detection can be used for the accurate quantitation of the lightest alkanes. However, the very low eluent strength of these solvents causes a high resolution within the saturated and especially olefinic groups, which is detrimental to their accurate quantitation. With silica gels of very high specific surface area, such as Spherosil (800 m<sup>2</sup>/g), some of the alkanes are even baseline-resolved, and the olefinic separation pattern is very scattered<sup>5</sup>. A separation of more practical relevance was obtained with a silica of lower specific surface area, such as LiChrosorb Si 60 (550 m<sup>2</sup>/g). In Fig. 1 the results obtained with bare or copper-modified LiChrosorb Si 60 and Fluorinert FC 72 are compared. It can be seen that the separation between the two groups was similar, but the retentions and resolution within each group were markedly higher on copper-modified silica; this behaviour was expected for the alkenes but was surprising for the alkanes. Further, olefins were not eluted by Fluorinert FC 72 from silver-modified silica.

A major drawback of Fluorinert FC 72 is its poor solvent properties for petroleum products, especially for olefinic and aromatic compounds. Hence, even with light gasolines, *n*-pentane was used as the mobile phase if the content of the lightest alkanes was low or of minor concern. However, it was found in adsorption chromatography<sup>5</sup> that no satisfactory separation between the saturated and olefinic groups could be obtained unless a silica gel of very high specific surface area (*e.g.*, 800 m<sup>2</sup>/g) was used. Moreover, the water content of the mobile phase is a very critical parameter, and *n*-pentane containing less than *ca.* 10 ppm of water must be used. Fig. 2A shows that the separation between the saturated and olefinic compounds

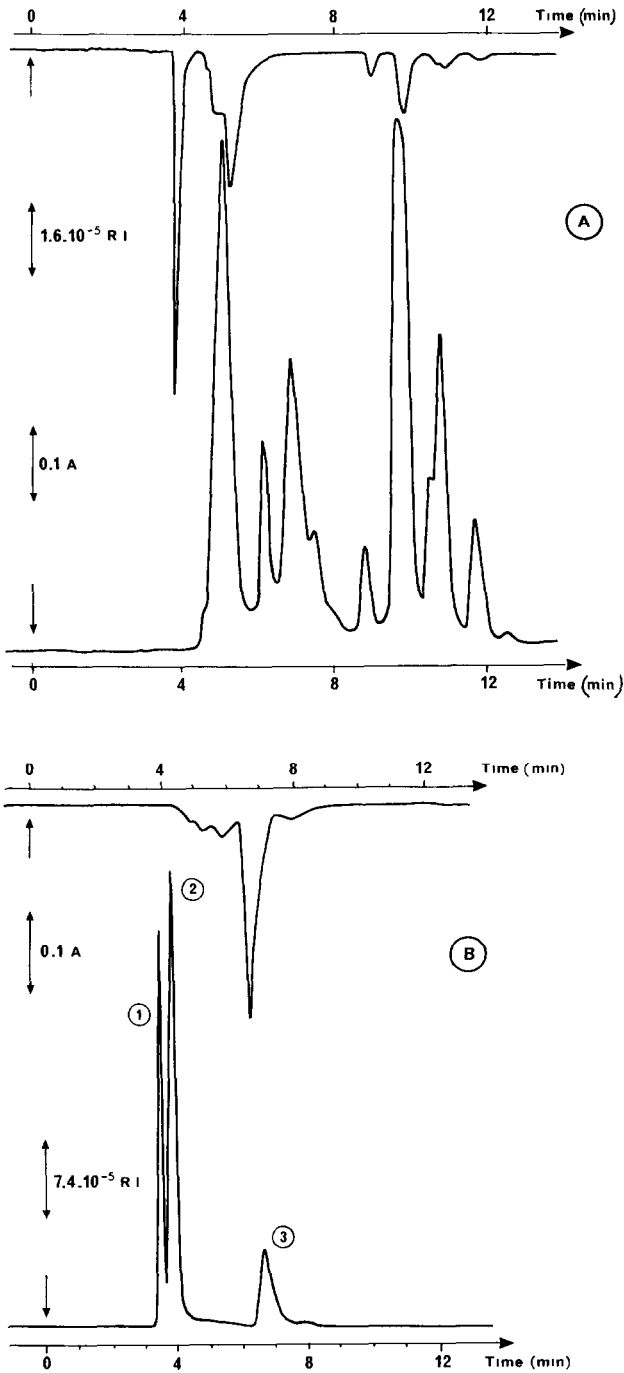


Fig. 2. Separations of a light gasoline sample on (A) silver- and (B) copper-modified silica gels with *n*-pentane as the mobile phase. Water content: (A) 18 ppm; (b) 8 ppm. Refractive index detection and UV detection at (A) 210 nm and (B) 254 nm; other operating conditions and peak identification as in Fig. 1.

remained good on a silver-modified silica gel with a water content in *n*-pentane of *ca.* 18 ppm. Using far-UV detection at 210 nm, the separation pattern failed to return fully to the baseline after 8–9 min. This can be ascribed to the strong retention of conjugated dienes (Table II). However, taking into account the low diolefin content of light gasolines (<0.5% according to gas chromatographic measurements), this slight drawback should not overshadow the great advantages of the method. On a copper(II)-modified silica gel (Fig. 2B), the alkene group was impressively gathered

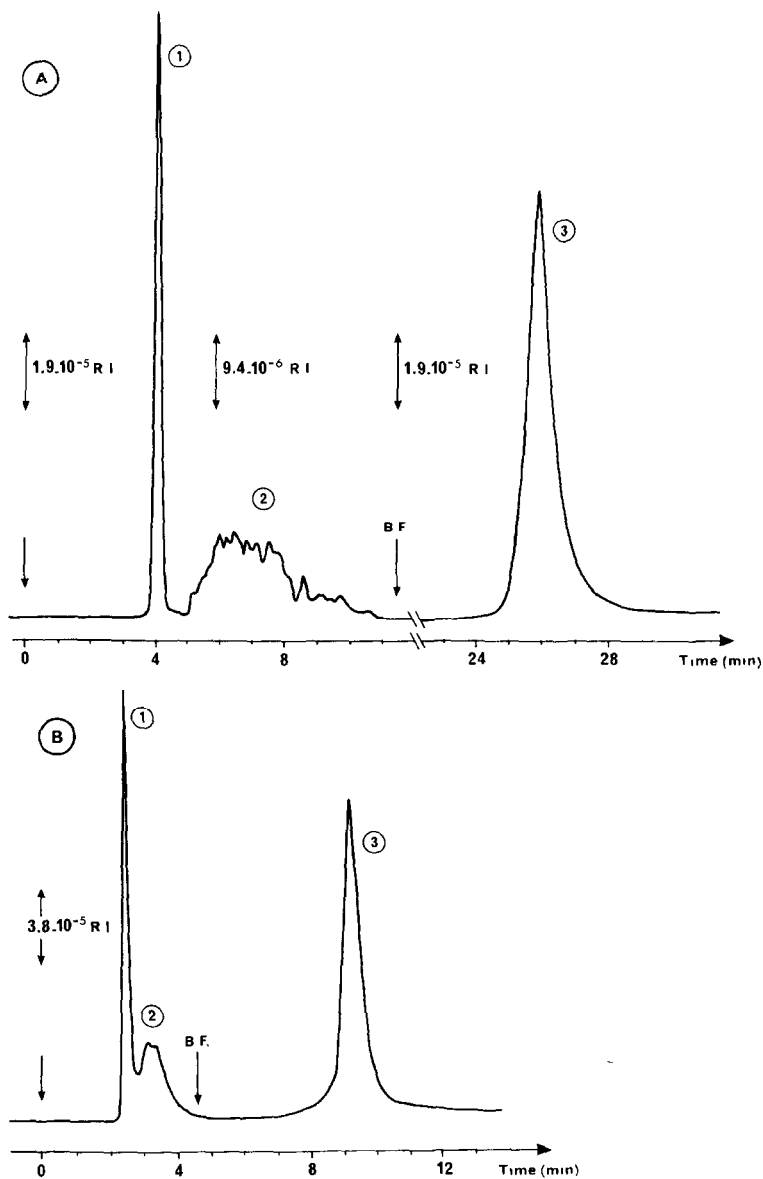


Fig. 3.

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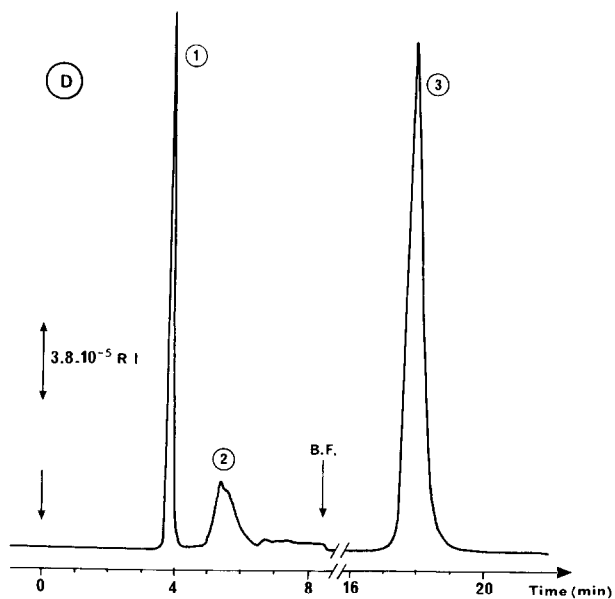
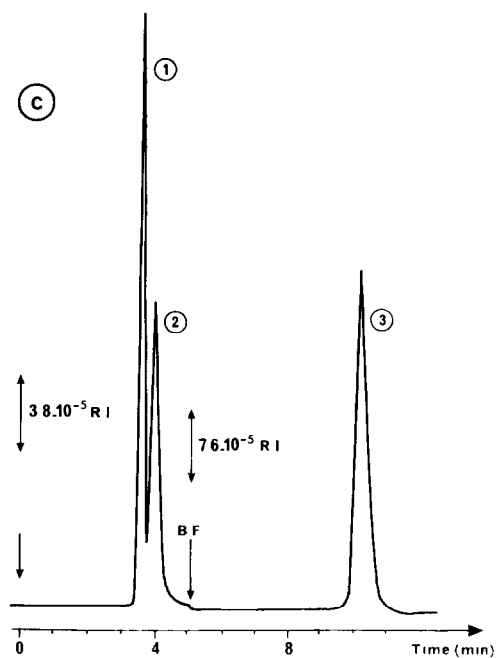


Fig. 3. Separations of a complete gasoline sample on bare and modified silica gels with *n*-pentane (water content 8 ppm) as the mobile phase. Stationary phases: (A) Spherosil; (B) LiChrosorb Si 60; (C) copper-modified LiChrosorb Si 60; (D) silver-modified LiChrosorb Si 60. Other operating conditions and peak identification as in Fig. 1.

together compared with unmodified and silver-modified silica gels, which is an asset for peak integration, particularly at a low alkene content.

The same comparisons were made with a more complex mixture, a sample of complete gasoline. Perfluorinated alkanes are not advocated as the mobile phase for such samples because the solubility is too poor. The separations with *n*-pentane are shown in Fig. 3. As expected, the separation between the alkane and alkene groups was a little less, and the best results were achieved on silver-loaded LiChrosorb Si 60. Of course, as in the preceding instances, the aromatic compounds could be focused in a single peak by column back-flushing.

The same operating conditions were then used for still heavier petroleum samples. Fig. 4 shows the separation of a cracked distillate sample. In this instance,

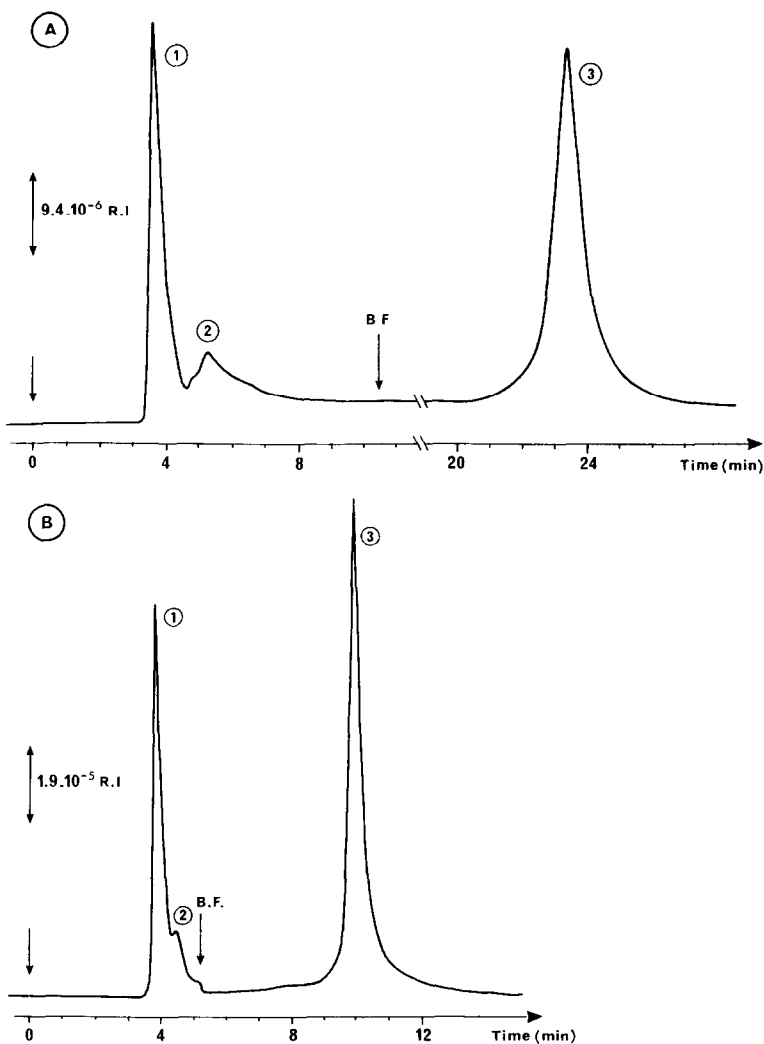


Fig. 4.

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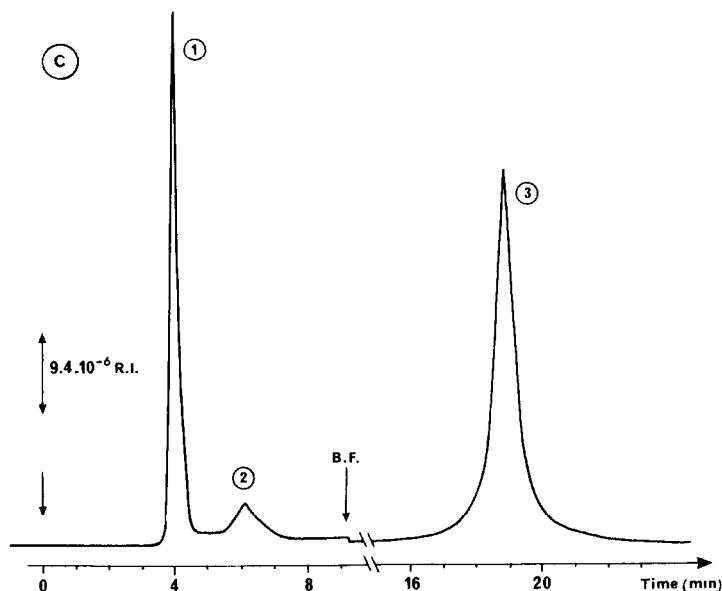


Fig. 4. Separations of cracked distillate sample on bare and modified silica gels with *n*-pentane (water content 8 ppm) as the mobile phase. Stationary phases: (A) Spherosil; (B) copper-modified LiChrosorb Si 60; (C) silver-modified LiChrosorb Si 60. Other operating conditions and peak identification as in Fig. 1.

adsorption chromatography did not afford a complete separation between the alkane and alkene groups, even with silica gels of the highest specific surface area commercially available; copper-modified LiChrosorb Si 60 did not provide better results, whereas the separation succeeded with the silver-loaded stationary phase. The aromatic peak was larger than with the foregoing samples, because of the increased complexity of the mixture. The last samples studied were a distillate and a residue (Fig. 5). The silver-modified silica gel did not allow the detection of olefinic compounds in any of them. A significant shoulder on the trailing edge of the alkane peaks should be noted. This shoulder was more visible when the distillate was chromatographed on Spherosil because of a slight shift of the leading edge of the peak towards shorter retentions. This observation suggests the existence of exclusion phenomena for heavy hydrocarbons, and is in accordance with the fact that the cracking process simultaneously increased the contents in olefinic and light hydrocarbons.

## CONCLUSION

The group analysis of light and heavy petroleum products as saturated, olefinic and aromatic compounds was successfully performed on a silica gel superficially modified with silver silicate with *n*-pentane as the mobile phase. The retention involved both adsorption and charge-transfer complex formation for the olefinic and aromatic compounds. This explains why the separation between the alkane and alkene groups is much greater than with the previously described adsorption methods. This separation was far better than with copper(II)-modified silicas, but unfortu-

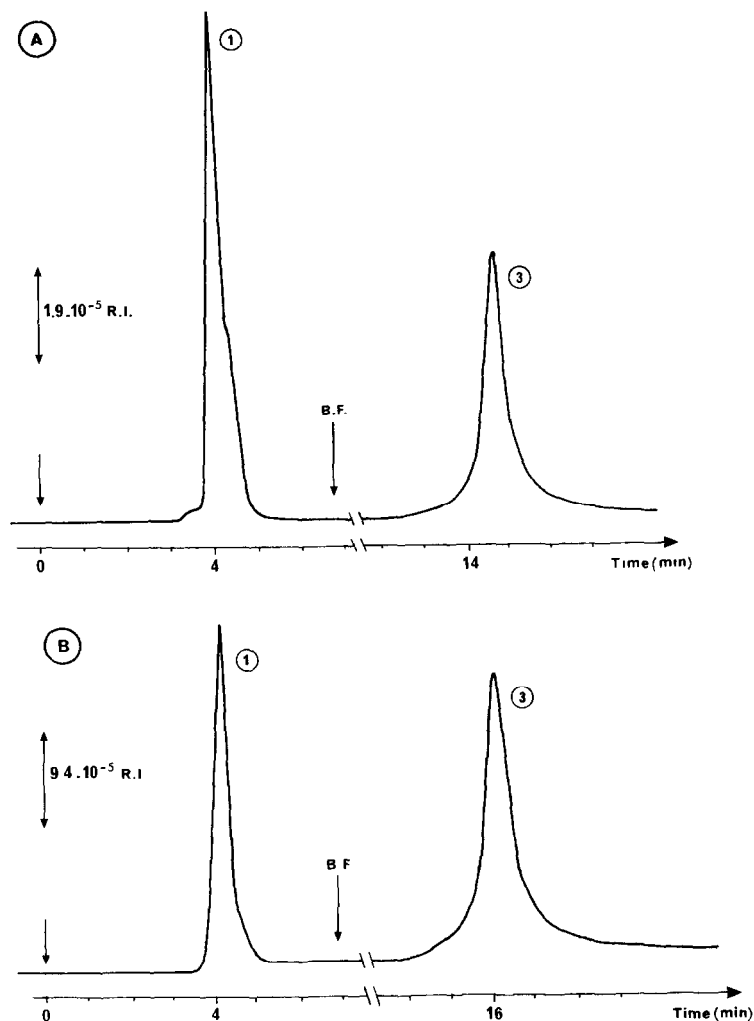


Fig. 5. Separations of (A) distillate and (B) residue samples on silver-modified LiChrosorb Si 60 with *n*-pentane (water content 8 ppm) as the mobile phase. Other operating conditions and peak identification as in Fig. 1.

nately the olefinic compounds were not eluted in the form of peaks as sharp as with the copper-modified silicas. In addition, the silver-modified silicas could not be used with a perfluorinated alkane as the mobile phase, because alkenes would not be eluted. Therefore, for light gasolines, the phase system consisted of a bare silica gel of specific surface area about  $500 \text{ m}^2/\text{g}$  and perfluoroalkane FC 72 remains a valuable alternative method, enabling a more sensitive and accurate determination of the lowest hydrocarbons. For heavy and complete gasolines the use of *n*-pentane is advocated for solubility reasons, and the only possible alternative to silver-modified silicas is a bare silica with the largest specific surface area ( $800 \text{ m}^2/\text{g}$ ). The resolution afforded was satisfactory thanks to exclusion phenomena occurring over and above

adsorption. Consequently, the peaks of each family were slightly gathered together. However, the water content of the mobile phase was no longer a critical parameter with silver-modified silicas, and a sufficient resolution was maintained with up to 20 ppm of water in *n*-pentane. Lastly, for heavy petroleum samples, such as distillates, cracked distillates and residues, only the silver-modified silica gels could provide a full separation between the alkane and alkene groups, the aromatic compounds being eluted from the single column by back-flushing. These silica gels, superficially modified with silver silica, are easily prepared with reproducible silver loadings and then conditioned under well standardized conditions.

## REFERENCES

- 1 J. C. Suatoni, H. R. Garber and R. R. Davis, *J. Chromatogr. Sci.*, 13 (1975) 367.
- 2 J. C. Suatoni and R. E. Swab, *J. Chromatogr. Sci.*, 18 (1980) 375.
- 3 R. L. Miller, L. S. Ettre and N. G. Johansen, *J. Chromatogr.*, 259 (1983) 393.
- 4 J. M. Colin and G. Vion, *J. Chromatogr.*, 280 (1983) 152.
- 5 P. Chartier, P. Gareil, M. Caude, R. Rosset, B. Neff, H. Bourgoignon and J. F. Husson, *J. Chromatogr.*, 357 (1986) 381.
- 6 J. F. McKay and D. R. Latham, *Anal. Chem.*, 52 (1980) 1618.
- 7 S. Matsushita, Y. Tada and T. Ikushige, *J. Chromatogr.*, 208 (1981) 429.
- 8 F. R. Hartley, *Chem. Rev.*, 73 (1973) 163.
- 9 T. A. Norris and M. G. Rawdon, *Anal. Chem.*, 56 (1984) 1767.
- 10 E. Heftmann, G. A. Saunders and W. F. Haddon, *J. Chromatogr.*, 156 (1978) 71.
- 11 R. R. Heath and P. E. Sonnet, *J. Liq. Chromatogr.*, 3 (1980) 1129.
- 12 R. Vivilecchia, M. Thiebaud and R. W. Frei, *J. Chromatogr. Sci.*, 10 (1972) 411.
- 13 R. R. Heath, J. H. Tumlinson, R. E. Doolittle and A. T. Proveaux, *J. Chromatogr. Sci.*, 13 (1975) 380.
- 14 R. Aigner, H. Spitzzy and R. W. Frei, *Anal. Chem.*, 48 (1976) 2.
- 15 R. Aigner, H. Spitzzy and R. W. Frei, *J. Chromatogr. Sci.*, 14 (1976) 381.
- 16 A. M. Siouffi, J. C. Traynard and G. Guiochon, *J. Chromatogr. Sci.*, 15 (1977) 469.
- 17 W. A. Patrick and E. H. Barclay, *J. Phys. Chem.*, 29 (1925) 1400.
- 18 M. Caude and A. Foucault, *Anal. Chem.*, 51 (1979) 459.
- 19 A. Foucault, M. Caude and L. Oliveros, *J. Chromatogr.*, 185 (1979) 345.
- 20 F. Guyon, A. Foucault and M. Caude, *J. Chromatogr.*, 186 (1979) 677.
- 21 F. Vydra and V. Markova, *J. Inorg. Nucl. Chem.*, 26 (1964) 1319.
- 22 T. Ichikawa, H. Yoshida and L. Kevan, *J. Chem. Phys.*, 75 (1981) 248.
- 23 K. K. Unger, *Porous Silica (Journal of Chromatography Library, Vol. 16)*, Elsevier, Amsterdam, 1979.
- 24 P. Chartier and P. Gareil, unpublished results, 1984.
- 25 F. T. Weiss, *Determination of Organic Compounds, Methods and Procedures*, Wiley-Interscience, New York, 1970.