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Liquid chromatography of organotin compounds on cyanopropyl silica gel

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SUMMARY

Several stationary phases were evaluated for the liquid chromatography of organotin compounds. Cyanopropyl-derivatized silica gels are the most versatile phases for this type of analysis. In order to reduce stationary phase activity, an iodine chloride "on-column" pretreatment was developed. This leads to very fast quantitative and qualitative separations, as was demonstrated by the analysis of organotin standards, organotin-containing tungsten carbonyl complexes and organotin halides for reaction kinetic studies.

INTRODUCTION

Despite the enormous industrial and environmental interest in organotin compounds, good analytical methodology is still lacking. A few liquid chromatographic (LC) methods have been developed for specific tasks[1-4], the main research work being focused on the detection aspects for trace analysis[5-13]. At present, however, there are still problems with LC phase systems for this type of analysis and reproducing published LC methods is often very tedious.

Organotin compounds have a high reactivity towards oxygen-, nitrogen- and sulphur-containing matrices[1]. Reversed-phase LC used relatively inert stationary phases but polar reactive mobile phases. Normal-phase LC uses non-reactive mobile phases. The stationary phases however, owing to the presence of unreacted silanol groups or other reactive moieties, are not sufficiently inert towards reactive organotin halides. This results in irreversible adsorption and peak tailing in both the reversed-phase and normal-phase modes.

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Several phase systems have been described. Silica gel is not sufficiently inert against the reactive organotin halides[1]. Silanized silica gel, C_8 and C_{18} were tried with both normal[1,2] and reversed[14] mobile phases. Pyrocarbon–silica[1], poly(styrene–divinylbenzene) copolymers[1] and silica-based cation exchangers[3] have also been evaluated. One of the most succesful phases is cyanopropyl silica gel[4,8,15]. However, all these studies used either morin complexes or high concentrations of acetic acid in order to mask hydrogen bonding with remaining silanol groups[4].

In this study, different stationary phases for the analysis of organotin compounds were re-examined. New methods, based on a cyanopropyl phase, in which the addition of acid or modifier to the mobile phase is avoided, are proposed.

EXPERIMENTAL

A Varian 5020 liquid chromatograph equipped with a Varian Vista data system (CDS 401) (Varian, Walnut Creek, CA, U.S.A.) was used as a solvent-delivery system. Injections were made with a Rheodyne 7125 RV valve equipped with a 10-μl loop. The detector was a Varian 2050 variable-wavelength UV detector, a Waters refractive index detector or an LKB diode-array rapid spectral detector (LKB, Bromma, Sweden). The columns were 15 or 25 × 0.46 cm I.D. stainless-steel tubes with Valco fittings. RoSiL and RSiL (RSL, Eke, Belgium), Spherisorb (Phase Separations, Queensferry, U.K.) and Nucleosil (Machery, Nagel & Co., Düren, F.R.G.) packing materials were evaluated. The solvents used were of high-performance liquid chromatography (HPLC)grade (Alltech, Deerfield, IL, U.S.A.). Organotin compounds were purchased from Merck (Darmstadt, F.R.G.) or synthesized in the laboratory[16].

The procedure for "on-column" treatment with iodine chloride (ICl) is as follows. An empty LC column (15 × 0.46 cm I.D.) was filled with 0.5% ICl solution in hexane–tetrahydrofuran (THF) (90:10) and installed between the injector and the analytical column. This solution was pumped into the column at 1 ml/min. During this pretreatment the detector was removed from the column. Subsequently the column was rinsed with about 30 ml of solvent until a stable baseline was obtained. Sometimes a second treatment was necessary.

RESULTS AND DISCUSSION

During this study, different stationary phases were evaluated for the analysis of organotin compounds, including some phases examined previously and some completely new. As the results in the literature are contradictory and difficult to reproduce, our results are summarized as follows.

Octadecyl silica gel: owing to the polarity and reactivity of the methanol– or acetonitrile–water mixtures, reversed-phase LC is unsuitable for the analysis of organotin halides. The applicability is restricted to the analysis of tetraalkyltin compounds. Tetramethyl-, -ethyl-, -propyl-, -butyl- and -phenyltin can easily be separated in the isocratic mode.

Poly(styrene–divinylbenzene): these packing materials, being silanol-free, offer good prospects for organotin separations. Used in the reversed-phase mode, again only the analysis of the tetraalkyltin compounds is possible. In the normal-phase mode with hexane–THF mixtures fairly good separations of the organotin halides

can be achieved. Even the monoalkyltin compounds elute from the column. A disadvantage, however, is the low efficiency of the columns.

Aminopropyl silica gel: this is unsuitable for this analysis. Owing to the free electron pairs on the nitrogen, the compounds are irreversibly adsorbed on the column.

Diol- or polyol-silica gel: these phases seem to be unsuitable for organotin compound analysis. The alcohol group tends to form strong hydrogen bonds and this results in irreversible adsorption or band broadening.

Cyanopropyl silica gel: in our experience and from literature data[4,8,15], cyanopropyl-bonded phases are the best for this type of analysis owing to the good selectivity and efficiency. This phase was chosen for the separation of all the organotin compounds here.

The retention and selectivity were optimized, a new deactivation procedure is proposed and the applicability is demonstrated by the analysis of a variety of organotin compounds.

Retention and selectivity on cyanopropyl-bonded silica gels

Cyano phases, used in the normal-phase mode, separate molecules according to their polarity. Consequently, the phase is less suitable for the separation of tetraalkyltin compounds. However, a separation can be obtained with the elution order (k'): $(C_4H_9)_4Sn < (C_3H_7)_4Sn < (C_2H_5)_4Sn < (CH_3)_4Sn < (C_6H_5)_4Sn$. The system is very selective for the number of R groups in the organotin compound. The elution order (k') is then $R_4Sn < R_3SnX < R_2SnX_2 < RSnX_3$. No separation can be obtained between tin compounds with the same alkyltin group and with different $X = Cl$, Br, I, acetate, oxide, etc.

Up to now the use of cyanopropyl phases has two major background: the silanol activity and brand-to-brand differences. These points were studied in detail.

Literature data[4] and our own experience show that silanol groups have a negative influence on the chromatographic behaviour or organotin compounds. Different methods for the removal of this silanol activity have been evaluated in our laboratory, *e.g.*, end-capping, dynamic modification with amines. None of the methods proved to be effective or reproducible. The addition of high concentrations of acetic acid (5% in the mobile phase) to mask hydrogen bonding with silanol groups has been proposed[4], but this method is not advisable in, for instance, preparative work.

During the analysis of ICl-containing solutions, a spectacular improvement in the peak shape was observed. Consequently, "on-column" treatment with ICl was optimized as a deactivation method for stationary phases for the analysis of organotin compounds. ICl is considered to form a strong hydrogen bond with the silanol groups. ESCA measurents[17] on ICl-treated silica gels and cyanopropyl silica gels showed a 1:1 ratio of Cl and I, which suggests adsorption and no chemical reaction. This treatment is effective for several weeks of continuous work. The optimized procedure is given under Experimental.

Fig. 1 shows the effect of the ICl treatment on the analysis of tributyltin naphthenate (TBTN) in a commercially available biocide. This treatment always results in a reduction in the retention time and an improvement in the peak shape.

Silica-based cyanopropyl phases can be synthesized by a number of different procedures. This results in brand-to-brand differences and hence different retentions
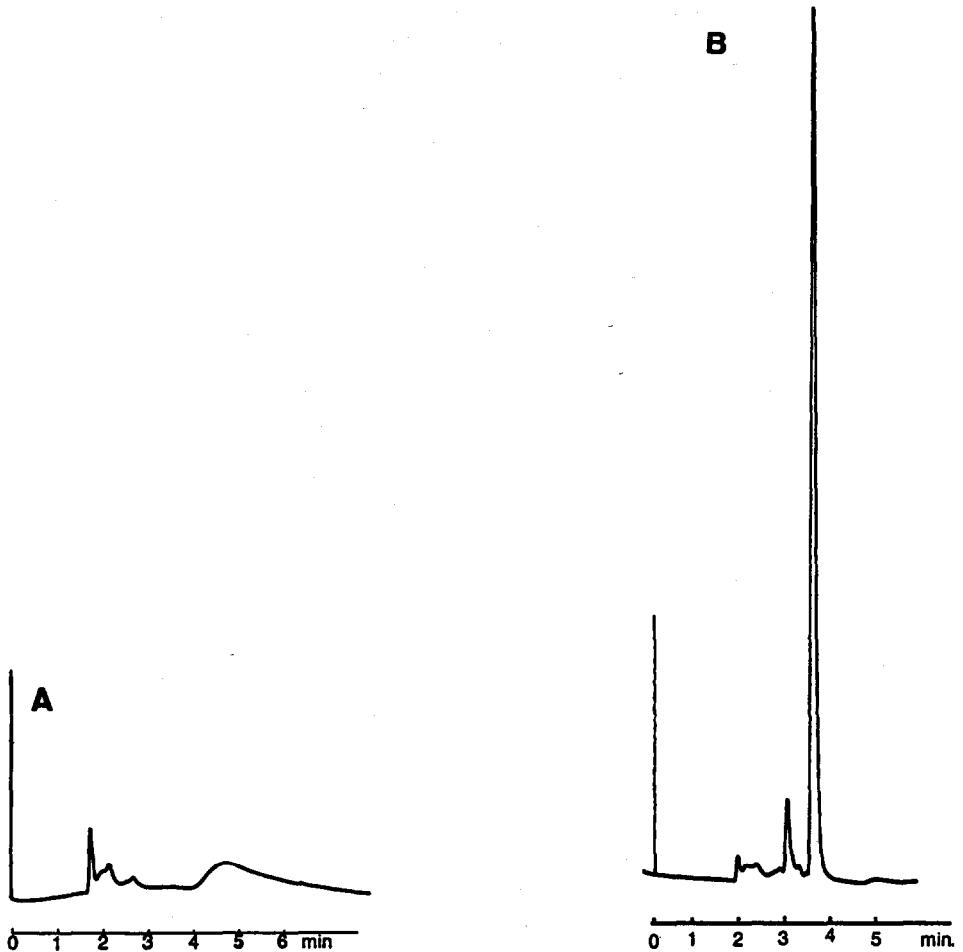
Fig. 1. Effect of ICl preteatment on the analysis of TBTN. Column, 3-μm RoSiL CN (15 × 0.46 cm I.D.); mobile phase, hexane; flow-rate, 1 ml/min; injection volume, 10 μl; detection, UV (220 nm). Sample: commercially available biocide containing TBTN dissolved in mobile phase. (A) Before; (B) after ICl treatment.

and selectivities for organotin compounds. Different laboratory-made and commercially available phases were tested.

In Table I, the capacity factors of some representative organotin halides on different types of cyano phases are shown. As silanol groups are extremely important, cyano phases produced with different silanization procedures on the same base silica gel were compared. The data in Table I were taken after ICl treatment. The following types were used: RoSiL CN prepared with cyanopropyltrichlorosilane and RoSiL $(CH_3)_2CN$ prepared with cyanopropyldimethylchlorosilane. A silica gel prepared with cyanopropyltrichlorosilane (non-end-capped) is expected theoretically to have a 1:2 cyano-to-silanol ratio whereas the cyanopropyldimethylchlorosilane derivative has a 1:0 cyano-to-silanol ratio. The first two RoSiL phases show that the retention

TABLE I

COMPARISON OF DIFFERENT TYPES OF CYANO PHASES FOR THE ANALYSIS OF ORGANOTIN COMPOUNDS

Experimental conditions: columns: 15 × 0.46 cm I.D. or 25 × 0.46 cm I.D. for Nucleosil CN and Spherisorb CN, pretreated with ICl; mobile phase, hexane–THF (90:10); flow-rate 1 ml/min; detection, UV at 220 nm; injection volume, 10 μl.

Compound	k'				
	RoSiL CN	RoSiL (CH$_3$)$_2$ CN	Spherisorb CN	Nucleosil CN	Deltabond CN[a]
(C$_4$H$_9$)$_3$SnCl	0.17	0.41	0.17	0.26	∞; 0.05[c]
(C$_2$H$_5$)$_3$SnCl	0.43	1.24; 0.35[b]	0.40	0.60	∞; 0.18[c]
(CH$_3$)$_3$SnCl	0.81	2.06	0.73	–	∞; 0.21[c]
(C$_6$H$_5$)$_3$SnCl	0.90	2.67; 0.50[b]	0.87	1.13	∞; 0.16[c]
(C$_4$H$_9$)$_2$SnCl$_2$	0.95	1.59[b]	–	2.19	∞; 0.32[c]
(C$_6$H$_5$)$_2$SnCl$_2$	1.83	7.41[b]	1.47	–	∞; 1.37[c]
(C$_2$H$_5$)$_2$SnCl$_2$	2.11	3.11[b]	2.23	∞	∞; 0.66[c]
(CH$_3$)$_2$SnCl$_2$	2.76	2.47[b]	2.33	∞	∞; 1.21[c]

[a] No pretreatment with ICl.
[b] Mobile phase: hexane–THF (50:50).
[c] Mobile phase: hexane–THF (75:25).

seems to be governed by the cyano-to-silanol ratio. The highest retention is obtained on the cyanopropyldimethylsilane-derivatized silica gel. Also, the peak shape is better for phases with a high concentration of cyano groups.

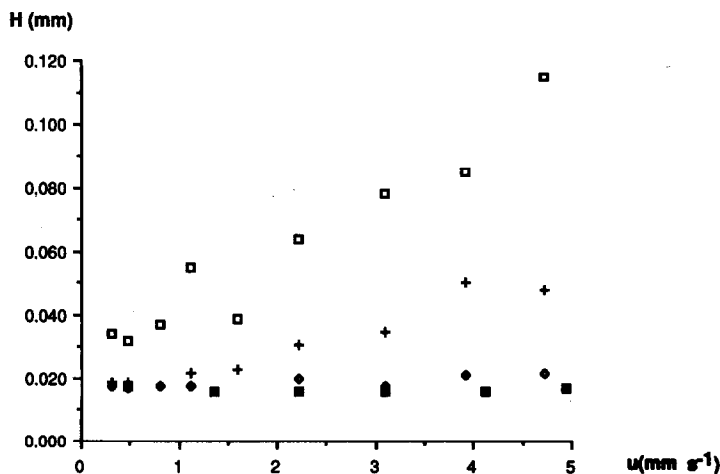Other commercially available cyano phases were tested, such as Spherisorb CN

Fig. 2. H–u curves for organotin compounds on a cyanopropyl phase. Column as in Fig. 1. (a) Without pretreatment; mobile phase, hexane–THF–acetonitrile (75:18:7). (b) Pretreated with ICl; mobile phase, hexane–THF–acetonitrile (85:10:5). Detection, UV (220 nm). Plate number calculated from band width at half-height. $\Diamond$ = (C$_6$H$_5$)$_4$Sn (a); + = (C$_6$H$_5$)$_3$SnCl (a); $\square$ = (C$_6$H$_5$)$_2$SnCl$_2$ (a); $\blacksquare$ = (C$_6$H$_5$)$_2$SnCl$_2$ (b).
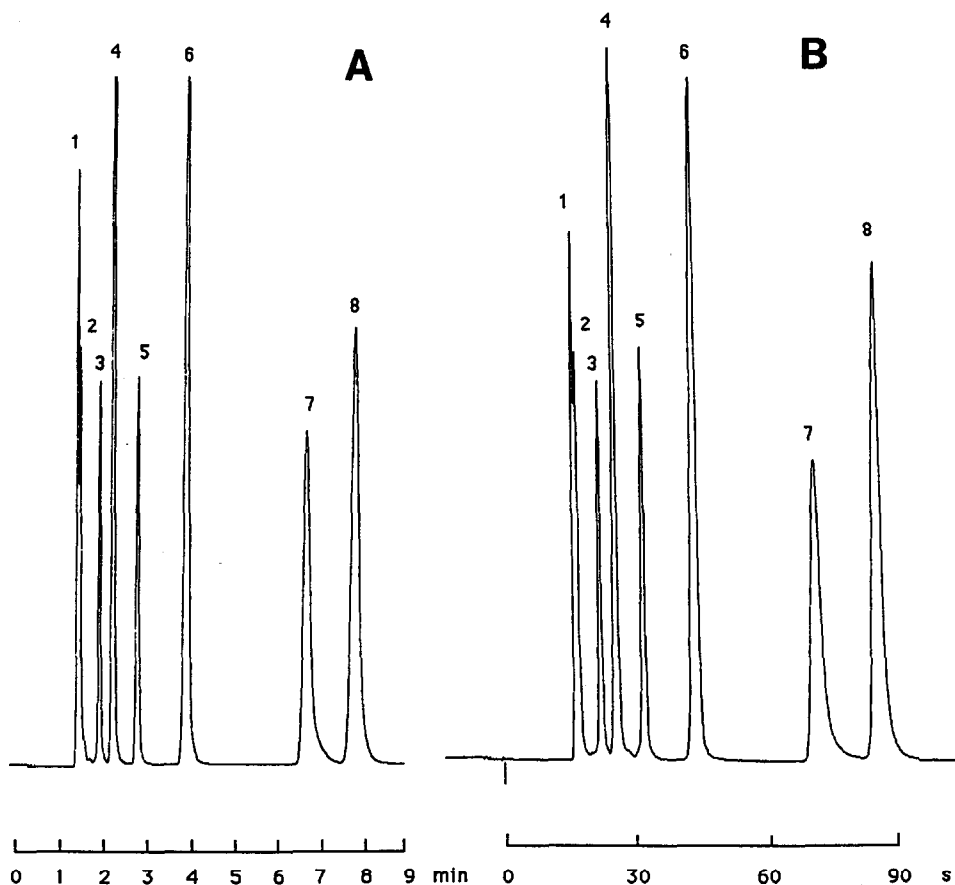
Fig. 3. Fast LC of organotin compounds on a cyanopropyl phase. Column as in Fig. 1. Mobile phase, hexane–acetonitrile–THF (90:4:6). Flow-rate: (A) 1 ml/min; (B) 6 ml/min. Detection, 220 nm (time constant 50 ms). Sample: 1 = $(C_4H_9)_4Sn$; 2 = $(C_2H_5)_4Sn$; 3 = $(C_4H_9)_3SnCl$; 4 = $(C_6H_5)_4Sn$; 5 = $(C_2H_5)_3SnCl$; 6 = $(C_6H_5)_3SnCl$, $(C_4H_9)_2SnCl_2$; 7 = $(C_6H_5)_2SnCl_2$; 8 = $(C_2H_5)_2SnCl_2$.

and Nucleosil CN. All these phases can be readily used for organotin analysis after ICl treatment. Nucleosil CN (see Table I) shows one of the highest retention times.

Finally, a Deltabond CN phase was evaluated. This phase, prepared by polymeric polysiloxane chemistry, is mentioned as being silanol-free[18], which offers good prospects for organotin analysis. Table I shows, however, a very high retention behaviour if tested under the same conditions as for the silane-based cyano phases. Peaks elute from the column on increasing the THF concentration but the peaks are very broad. Apparently this polymeric phase swells in normal-phase eluents and this reduces mass tranfer.

Efficiency

H–u curve. The ICl treatment has a great effect on the efficiency and symmetry of the peaks and also on the shape of the plate height *versus* linear velocity (*H–u*)
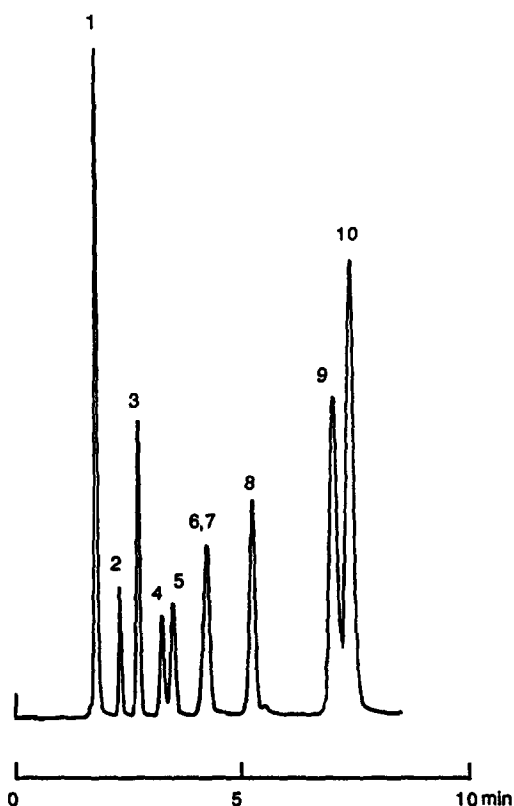
Fig. 4. LC of tungsten carbonyl complexes. Column as in Fig. 1. Mobile phase, hexane–THF (90:10); flow-rate, 1 ml/min; detection, LC–DAD; chromatogram at 220 nm. Sample: 1 = $W(CO)_6$; 2 = (i-$C_4H_9)_3SnW(CO)_3(\pi$-C_5H_5); 3 = $(CH_3)_3SnW(CO)_3(\pi$-C_5H_5); 4 = (i-$C_4H_9)_2ClSnW(CO)_3(\pi$-C_5H_5); 5 = $[W(CO)_3(\pi$-$C_5H_5)]_2$; 6 = (i-$C_4H_9)_2Sn[W(CO)_3(\pi$-$C_5H_5)]_2$; 7 = $(CH_3)_2ClSnW(CO)_3(\pi$-C_5H_5); 8 = $(C_6H_5)_3SnW(CO)_3(\pi$-C_5H_5); 9 = $(C_6H_5)_2ClSnW(CO)_3(\pi$-$C_5H_5$); 10 = $ClW(CO)_3(\pi$-C_5H_5).

curve[19]. Fig. 2 shows the H–u curves for different phenyltin halides before and after this treatment. $(C_6H_5)_4Sn$ is not active towards the stationary phase and shows a relatively low resistance to mass transfer or C term (C = 0.2 ms). The C term for $(C_6H_5)_3SnCl$ and $(C_6H_5)_2SnCl_2$ is calculated to be 8.1 and 20 ms, respectively. After the ICl treatment all components show ideal chromatographic behaviour and the slope and intercept become comparable to the situation for $(C_6H_5)_4Sn$.

Fast analysis. One of the consequences of the low resistance to mass transfer is the possibility of ultra-fast LC of organotin compounds. This can be useful for routine analysis as the number of analyses per unit time on the same instrument can be increased by a factor of about 5. As can be seen from Fig. 2, the linear velocity can be increased without a decrease in efficiency. This is demonstrated in Fig. 3A and B for a mobile phase velocity of 1 and 6 ml/min. The analysis is completed in about 60 s without a decrease in resolution. Under these conditions, however, it is necessary to reduce the time constant of the detector to its minimum (50 ms).
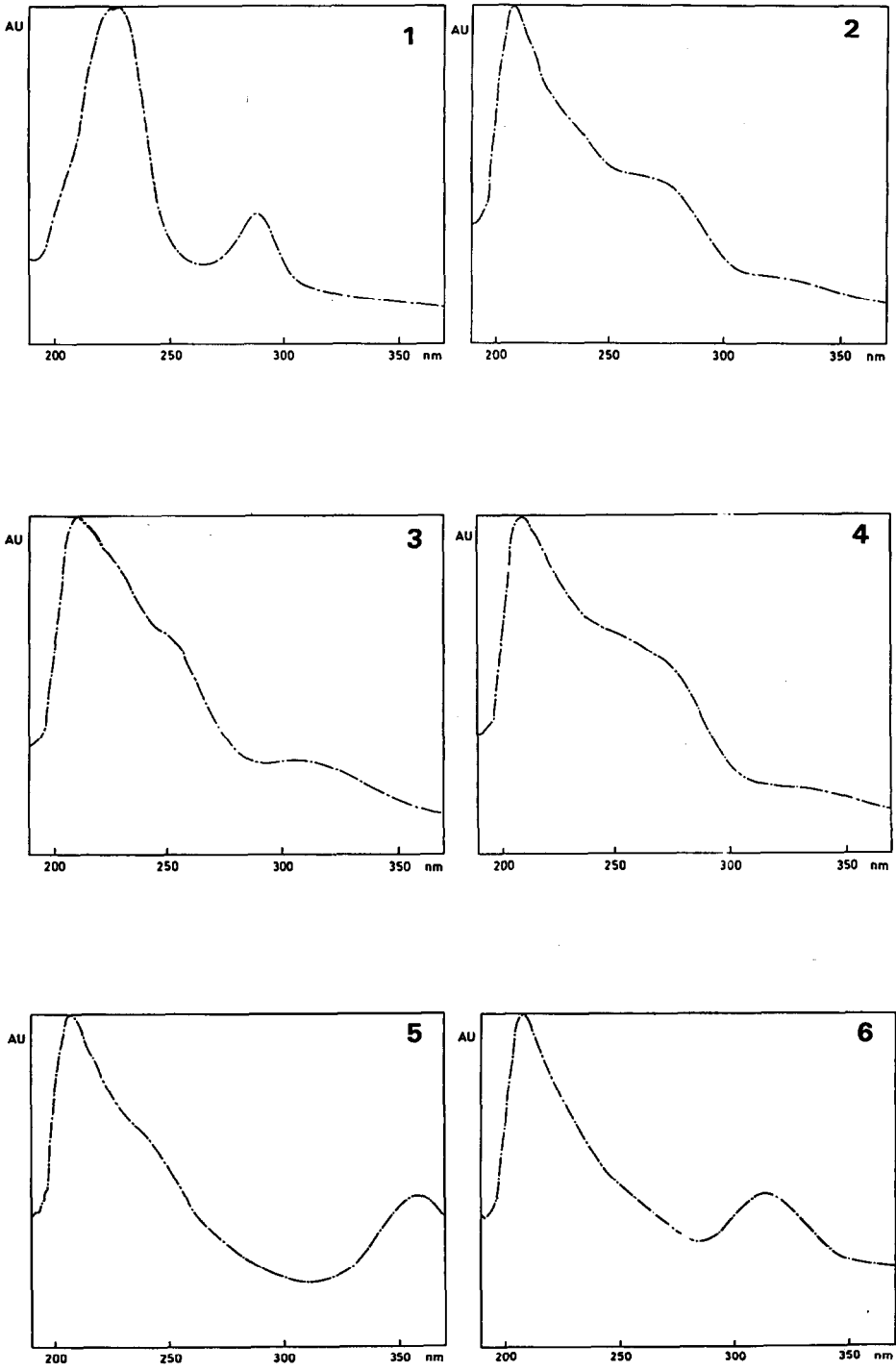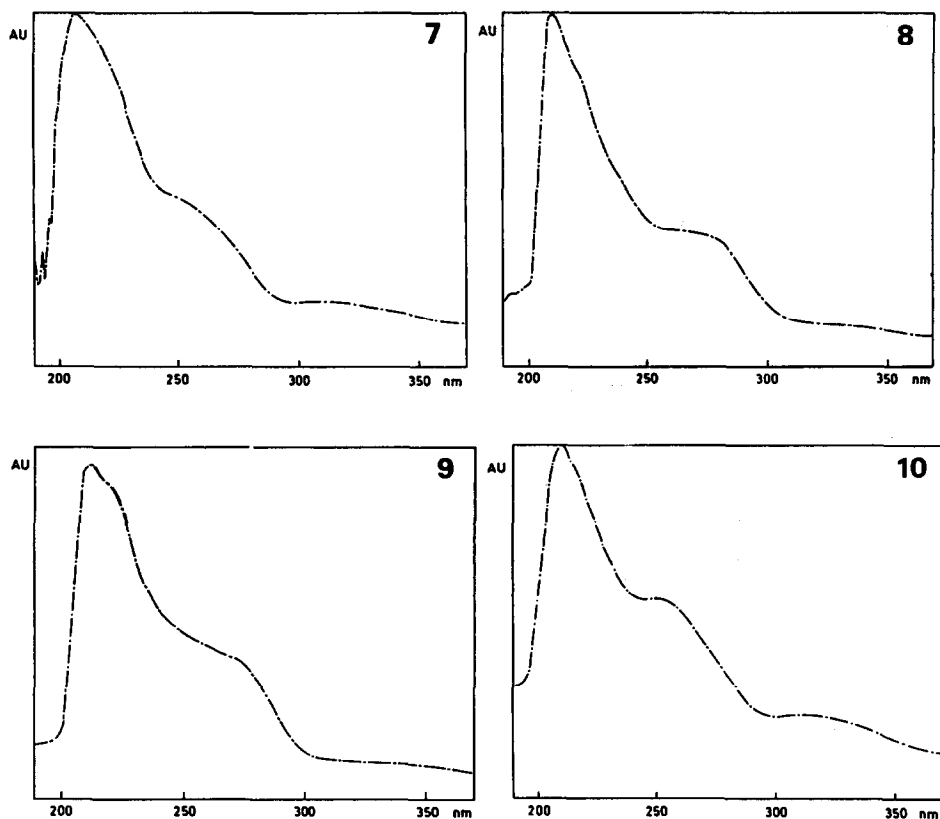
Fig. 5.

Fig. 5. LC–DAD UV spectra of tungsten carbonyl complexes after separation on an RoSiL CN column. Column as in Fig. 1. 1–10 as in Fig. 4.

Applications

Qualitative analysis of tungsten carbonyl complexes by LC with diode-array detection (DAD). Tungsten carbonyl complexes $LW(CO)_3$ (π-C_5H_5) (L = $R_nCl_{3-n}Sn$, Cl) have been studied as catalysts for the metathesis of olefins[16]. These precursors are activated by (i-C_4H_9)$AlCl_2$ in the presence of oxygen. During this activation process, tungsten carbenes are formed. The influence of the $R_nCl_{3-n}Sn$ substituents (R = CH_3, C_6H_5) on the reactivity as a catalyst was measured. This indicated that the purity of the prepared products has to be carefully checked. Further, for the understanding of the activation process an analysis of the reaction mixture is very helpful.

With this aim, a reference test sample was subjected to LC on a cyanopropyl column. The identification and purity control were performed using diode-array detection. The results are shown in Figs. 4 and 5. This method confirmed the formation of $HW(CO)_3(\pi$-$C_5H_5)$ and $ClW(CO)_3(\pi$-$C_5H_5)$ during the activation process, already identified by IR spectroscopy. On the other hand, this method showed that (i-C_4H_9)$_2ClSnW(CO)_3(\pi$-$C_5H_5)$ is always formed, notwithstanding the initial reagent $R_nCl_{3-n}SnW(CO)_3(\pi$-$C_5H_5)$ (R = CH_3, C_6H_5) in the reaction mixture.

conc.(M)
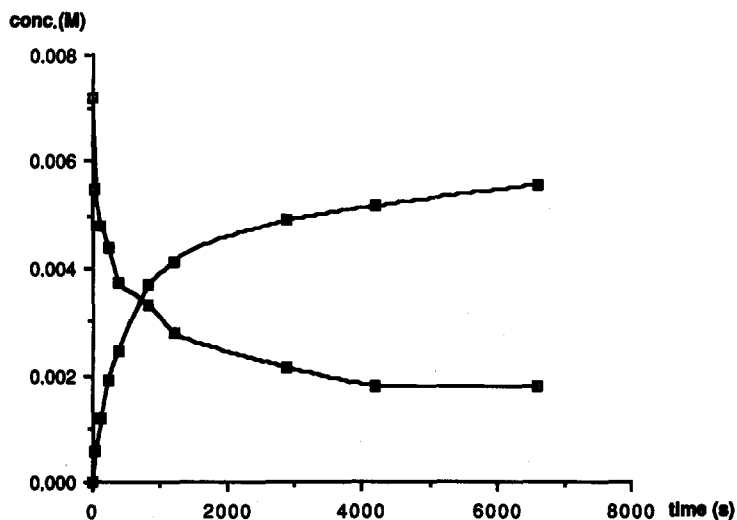
Fig. 6. Concentrations of (□) $(CH_3)_3SnCl$ and (■) $(CH_3)_2SnCl_2$ for the reaction $(CH_3)_3SnCl + ICl \rightarrow$ $(CH_3)_2SnCl_2 + CH_3I$ (solvent, CH_2Cl_2; temperature, 15°C) as a function of time measured by LC.
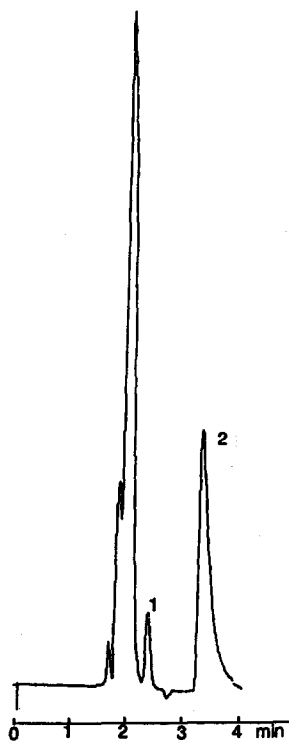

Fig. 7. LC analysis of the reaction mixture 4200 s after mixing the reagents. Column as in Fig. 1. Mobile phase, hexane–THF (75:25); flow-rate; 1 ml/min; injection volume 50 μl; detection, 220 nm. After mixing the reagents, 100-μl samples were taken at different times and dissolved in 1 ml of mobile phase in order to stop the reaction. 1 = $(CH_3)_3SnCl$; 2 = $(CH_3)_2SnCl_2$.

Quantitative analysis of organotin halides for reaction kinetic studies. The influence of solvent and temperature on the reaction rate of the reaction $R_3SnCl + ICl \rightarrow R_2SnCl_2 + RI$ (R = alkyl; solvent = $CHCl_3$, CH_2Cl_2, CCl_4) was evaluated by UV spectrometry, monitoring the ICl band. However, fast LC offers new perspectives for this type of work.

This is illustrated in Fig. 6, where the concentrations of $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$ for the above reaction are shown as a function of time, measured by LC. The LC analysis of the reaction mixture after 4200 s is shown in Fig. 7. It has been verified that under, HPLC conditions, no reaction of ICl with the organotin analytes takes place.

CONCLUSION

Cyanopropyl-derivatized silica gels are the most versatile stationary phases for the LC analysis of organotin compounds. In order to reduce stationary phase activity, an ICl "on-column" pretreatment was developed, which results in very fast quantitative and qualitative separations. The applicability was demonstrated by the analysis of organotin standards, organotin-containing tungsten carbonyl complexes and organotin halides for reaction kinetic studies. Qualitative analysis was performed by DAD.

ACKNOWLEDGEMENT

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