Separation of zinc dialkyldithiophosphates in lubricating oil additives by normal-phase high-performance liquid chromatography

N. Lambropoulos[a], T.J. Cardwell[a,*], D. Caridi[a,1], P.J. Marriott[b]

[a]Centre for Scientific Instrumentation, School of Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia
[b]Department of Applied Chemistry, Royal Melbourne Institute of Technology, Melbourne, Australia

Abstract

Eleven zinc dialkyldithiophosphates have been synthesised and their mixtures separated by normal-phase HPLC on a 5-μm silica column. Dichloromethane- or heptane-based eluents containing alkylamine ($\leq 0.4\%$) and acetic acid in a volume ratio of 2:1 and 1% methanol were suitable for separation of mixtures of these metal complexes in commercial lubricating oil additives. In all cases tested, the zinc complexes eluted from the column without decomposition and there was no evidence for ligand-exchange reactions having taken place during synthesis or on the column.

1. Introduction

One group of compounds widely used as multifunctional lubricating oil additives are the zinc dithiophosphates (ZDDPs). They are added to base oils in low concentration (~1%) and act as antioxidants and antiwear agents by maintaining a protective coating on the metal surfaces in internal combustion engines, which prevents rapid degradation of the base oil.

Several reports claim that reversed-phase HPLC on C_{18} columns is suitable for the separation of mixtures of ZDDPs [1–3]. Ohnishi et al. [1] separated ten ZDDPs, with alkyl groups ranging from C_3 to C_{10}, using a methanol–1 mM sodium acetate eluent in a non-linear gradient elution program where the methanol content varied from 10 to 90% in 20 min. Musha et al. [2] employed a linear methanol–water gradient to separate the components of two commercial mixed alkyl ZDDPs. More recently, Shikeguni and Shimizu [3] separated eight ZDDP derivatives on an ODS column using methanol–ethanol–water with linear gradient elution. In our efforts to carry out reversed-phase HPLC of mixtures of ZDDPs, we have encountered several problems; (i) the zinc complexes are not very soluble in aqueous-based eluents; (ii) at flow-rates of around 1 ml/min, high back pressures (ca. 3000 p.s.i.; 1 p.s.i.=6894.76 Pa) develop on 25-cm columns and (iii) testing collected peaks with dithizone indicates that zinc is not present in the eluting peaks, implying that the complexes are not eluted intact under reversed-phase conditions.

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*Corresponding author.
1Present address: Department of Applied Chemistry and Biology, Victoria University of Technology, Ballarat Rd., Footscray, Vic., Australia.

In extensive studies of trivalent metal dithiophosphates, Cardwell et al. [4,5] reported that the dithiophosphates of Cr(III), Co(III) and Rh(III) could be separated in normal-phase HPLC using small amounts (<0.06%, v/v) of an alcoholic polar modifier in a non-polar eluent. However, it was found that divalent metal dithiophosphates could not be eluted from silica columns under these conditions.

Perhaps the most relevant chromatographic studies related to divalent metal dithiophosphates is the separation of divalent metal dithizonates in non-aromatic solvents by Henderson et al. [6]. By addition of small amounts of acetic acid (0.2%, v/v) or mixtures of acetic acid and butylamine (0.2:0.1%) to hexane–dichloromethane eluents, acceptable elution behaviour was observed for lead dithizonate. Solvent systems of hexane–toluene containing 1% isopropanol and 0.15% acetic acid were useful in separating the dithizonates of Cu(II), Zn(II) and Cd(II). It is unclear exactly how acetic acid improves chromatographic elution in the above cases, however, it is suggested that it may serve to either stabilize the metal chelates themselves or to prevent strong adsorption on the support and unfavourable solute interactions [6].

This paper deals with establishing the chromatographic conditions for successful elution and separation of a mixture of ZDDPs by normal-phase HPLC. Eluents containing low concentrations of acetic acid or alkylamine–acetic acid are examined to determine if the zinc complexes are eluted intact and if the eluents can be used without gradient elution to achieve acceptable resolution of components in commercial samples which are claimed to contain ZDDPs.

2. Experimental

Eleven zinc dithiophosphates, $Zn[(RO)_2PS_2]_2$ where R=ethyl (Et), n-propyl (n-Pr), isopropyl (i-Pr), n-Bu, i-Bu, sec-Bu, n-Pent, 2-Pent, 4-Me-2-Pent, i-Oct and n-Dec, were prepared by documented procedures or slight modifications of these methods [7–12]. Solid products (Et, i-Pr and i-Bu) were purified by recrystallisation from chloroform; the remaining derivatives (semi-solids or liquids) were adsorbed on Sep-Pak silica cartridges, washed with

n-heptane to remove impurities and then eluted with methanol. The zinc complexes were characterised by metal analysis using flame atomic absorption spectrometry (AAS) and their identities confirmed by ^{13}C NMR. After purification, complexes derived from lower alcohols ($<C_5$) were ≥95% pure; those derived from n-pentanol and iso-octanol were <90% pure and the iso-octanol derivative was found to be a mixture of isomers by NMR. All complexes were stored in sealed vials in a refrigerator.

The HPLC system consisted of a Knauer 40 pump, a Rheodyne 9725 PEEK injector with a 20-μl PEEK sample loop, a SOMA UV S-310A Model II variable-wavelength detector and a Shimadzu C-R3A integrator. A Spherisorb S5W 5 μm silica (Extech Equipment P/L, Melbourne) 250×4.6 mm column was preceded by a silica guard cartridge (Upchurch Scientific) and all transfer lines were 0.25 mm I.D. PEEK tubing. Extended column equilibration times were necessary when using small quantities of polar modifiers in non-polar HPLC eluents. Furthermore, longer equilibration times were necessary when changing from an eluent with a higher percentage of modifier to one with a lower percentage. In general, after eluent preparation, the flow-rate is set at 2 ml/min for 45 min between eluent changes before a stable baseline is achieved (i.e. retention time does not vary by more than 2%). To overcome significant variations in retention times from one eluent batch preparation to another, large volumes of eluent were prepared, preferably using the same batch and stock numbers for each eluent component. Dichloromethane solutions of the complexes or samples were stored in a refrigerator before use.

A Perkin-Elmer Model 5100 atomic absorption spectrometer was linked in series with the above HPLC system to detect eluting zinc species; the aspiration rate of the burner was adjusted to 2 ml/min to match closely the HPLC eluent flow-rate and additional eluent was drawn through a T-piece, placed ahead of the aspirator, to stabilise the background signal from the flame.

For TLC of the colorless zinc complexes on silica plates, two spraying reagents were used; freshly prepared dithizone solution (1 g/l in chloroform) gave pink spots after drying, indicative of the presence of zinc, and a nickel solution (2 g/l $NiCl_2 \cdot 7H_2O$ in water) yielded purple spots for dithiophos-

phate-containing components. These reagent solutions were also used for spot testing of peak components collected at the outlet of the chromatographic column.

3. Results and discussion

3.1. Preliminary investigations

ZDDPs have been separated successfully by TLC on silica using hydrocarbon-based eluents containing acetic acid. Killer and Amos [13] separated commercial ZDDPs using n-heptane–acetic acid (95:5, v/v). An eluent of toluene–methyl ethyl ketone–acetic acid–pyridine (60:20:10:10, v/v) was used to separate and monitor the degradation of ZDDPs in a lubricating oil during service and to monitor the thermal decomposition of ZDDPs. Similarly, Kawamura et al. [14] monitored the degradation of zinc dithiophosphate to the lead complex in leaded fuels using n-hexane–methyl ethyl ketone–acetic acid (80:15:5, v/v). Coates [15] used the solvent system isooctane–ethyl acetate–acetic acid (60:25:15, v/v) to separate ZDDP components in commercial samples.

In our preliminary investigations, we have tested and confirmed the TLC results achieved previously by Killer and Amos [13] and Coates [15]. Satisfactory separations of the eleven ZDDPs synthesised in this present study have been obtained. Dithizone and nickel chloride sprays revealed zinc and dithiophosphate ligand retained at the same points along the silica surface, leading to the conclusion that the ZDDPs remain intact as they migrate along the TLC plate. Two commercial lubricating oil additives were analysed for the presence of ZDDPs. One sample (sample 1), claimed to be derived from one alkyl alcohol, showed only one spot as expected; the other sample (sample 2), derived from two alkyl alcohols, displayed three spots after spraying; the extra spot is thought to be due to zinc complexed to mixed-alcohol ligand anions, i.e. $(RO)(R'O)PS_2^-$.

Using the Killer–Amos eluent, n-heptane–acetic acid (95:5, v/v), in normal-phase HPLC on a silica column, $Zn[(iPrO)_2PS_2]_2$ was eluted as a single peak near the dead volume. This peak was found to contain zinc and the dithiophosphate ligand by spot testing with dithizone and nickel(II) chloride solutions. The peak eluted with extreme tailing and very low efficiency. Lowering the solvent strength to n-heptane–acetic acid (99:1, v/v) produced a peak with $k'=2.30$, but again with extreme tailing and poor efficiency. Similar results were obtained for other hydrocarbon–acetic acid and chloroform–methanol–acetic acid eluent mixtures.

A significant improvement in peak shape and hence in column efficiency was achieved by addition of an alkylamine (n-butylamine or isopropylamine) to the hydrocarbon–acetic acid or chloroform–acetic acid mobile phase. Mobile phases containing chloroform or dichloromethane are preferred because of solubility problems (of the amine–acetate salt) in hydrocarbons. Concentrations of amine $>0.4\%$ (v/v) should be avoided in the eluent because of inferior chromatography.

3.2. Optimisation of mobile phase composition for normal phase HPLC

In order to improve the chromatography of ZDDPs based on the preliminary results, the volume ratio of isopropylamine–acetic acid was varied and the peak efficiencies for $Zn[(iPrO)_2PS_2]_2$ were determined. By holding isopropylamine at 0.1% (v/v), the volume of acetic acid was varied in the volume ratio range from 1:4 to 4:1 isopropylamine–acetic acid in chloroform. The results showed that a volume ratio of 2:1 isopropylamine–acetic acid (Fig. 1) gave optimum peak efficiency. Furthermore, when the volume ratio was maintained at 2:1 and the amounts of amine and acetic acid were varied, optimum peak efficiency was achieved at 0.2:0.1 (v/v) isopropylamine–acetic acid in chloroform, but efficiencies were high in the region of 0.1–0.4% isopropylamine. The volume ratio of 2:1 isopropylamine ($d=0.694$)–acetic acid ($d=1.049$) corresponds to a molar ratio of 1.34:1 isopropylamine–acetic acid.

Further improvement in the chromatographic behaviour of ZDDPs was obtained by addition of small amounts of methanol to isopropylamine–acetic acid (0.2:0.1%) in chloroform. Measurements of column efficiency and the resolution of two closely eluting ZDDPs (isopropyl and isobutyl derivatives) indicate that optimum performance occurs at 1% (v/v)
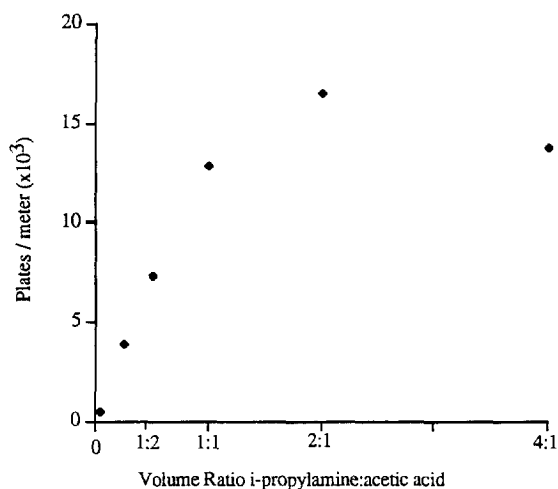
Fig. 1. Effect of volume ratio of isopropylamine–acetic acid mixtures in chloroform on peak efficiency of $Zn[(iPrO)_2PS_2]_2$. Column, 5 μm silica, 250×4.6 mm; flow-rate, 1.0 ml/min; detector, UV at 254 nm; injection volume, 20 μl.

methanol in this mobile phase. Below 1% methanol, k' values decrease with increasing methanol content but with a dramatic increase in peak efficiencies (almost 100% increase on going from zero to 1% methanol). Above 1% methanol, there is a slight decrease in peak efficiencies of the two solutes with increasing methanol content in the eluent. Eluents which contain methanol but no alkylamine and acetic acid give poor chromatography for the zinc dithiophosphates.

Two methods of characterisation were used to establish that the zinc dithiophosphate was eluted intact from the chromatographic column. Fractions of the eluting peaks were collected and treatment with dithizone and nickel(II) chloride solutions confirmed that zinc and dithiophosphate ligand were present in the collected peaks. Additional confirmation of the presence of zinc in each of the chromatographic peaks was obtained from the atomic absorption spectrometer incorporated in the HPLC system, where the AA response coincided with the retention time of each peak observed on the UV detector.

3.3. Normal-phase HPLC of zinc dialkyldithiophosphates

An eluent of the composition isopropylamine–acetic acid–methanol (0.2:0.1:1%) in dichlorome-

thane (rather than chloroform) was applied to the separation of the eleven synthesised ZDDPs as shown in Fig. 2. In general, the complexes are eluted in order of decreasing molecular mass, with the exception of the C_6 (4-methyl-2-pentyl) derivative which elutes prior to the C_8 complex. The octyl and 2-pentyl derivatives elute within 12 s of each other under these conditions, so that the peak for the octyl complex appears as a shoulder on the front of the eluting 2-pentyl peak. The isobutyl and n-butyl derivatives were observed to co-elute. Since the resolution is insufficient to reveal trace impurities arising from impure alcohols or isomers of the same alcohol used in the syntheses, these would lead to apparent peak broadening and lower peak efficiencies of some complexes as in the case of the C_8 derivative. The apparent "crowding" that occurs with the higher carbon numbered alkyl substituted ZDDPs creates inherent difficulties in resolving these high-molecular-mass alkyl derivatives.
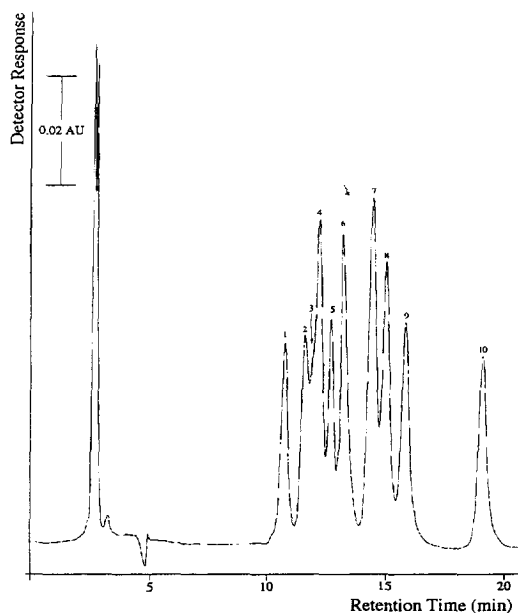

Fig. 2. Separation of eleven ZDDPs on a silica column (250×4.6 mm). Conditions: eluent A consisting of isopropylamine–acetic acid–methanol (0.2:0.1:1%, v/v) in dichloromethane; flow-rate, 1 ml/min; UV detection, 246 nm. Solute concentrations 9.1×10^{-5} M in dichloromethane. Components: 1, $Zn[(nDecO)_2PS_2]_2$; 2, $Zn[(4-Me-2-PentO)_2PS_2]_2$; 3, $Zn[(iOctO)_2PS_2]_2$; 4, $Zn[(2-PentO)_2PS_2]_2$; 5, $Zn[(nPentO)_2PS_2]_2$; 6, $Zn[(sec.BuO)_2PS_2]_2$; 7, $Zn[(iBuO)_2PS_2]_2 + Zn[(nBuO)_2PS_2]_2$; 8, $Zn[(iPrO)_2PS_2]_2$; 9, $Zn[(nPrO)_2PS_2]_2$; 10, $Zn[(EtO)_2PS_2]_2$

In an attempt to improve chromatographic res-
olution of a mixture of the ZDDPs, an eluent of
slightly different composition consisting of iso-
propylamine–acetic acid–methanol (0.4:0.2:1%) (v/
v) in n-heptane–dichloromethane (60:40, v/v) was
prepared and the chromatogram is shown in Fig. 3.
In this case, based on the capacity factors of in-
dividual complexes, the order of elution of the
complexes is strictly in the order of decreasing
molecular mass although the chromatogram of the
mixture suggests co-elution of the C_6 and C_8 deriva-
tives. Only eight peaks were prominent in Fig. 3
because of co-elution of three pairs of complexes,
viz. the octyl and 4-Me-2-pentyl, the 2-pentyl and
n-pentyl, and the isobutyl and n-butyl derivatives.

3.4. Normal-phase HPLC of commercial zinc dithiophosphates

Calibration plots are linear in the zinc concen-
tration range 0.5–20 mg/l with the exception of the
ethyl complex (0.5–10 mg/l). A detection limit of
0.05 mg/l of metal, which corresponds to 1.0 ng of
metal for a 20-μl injection, was attainable for the
ZDDP complexes.

Five commercial ZDDP samples were analysed
using the heptane-based eluent. Some information
concerning the alcohols used in their manufacture
(Table 1) was provided with samples 1–3. The
packaging for sample 5 claimed that it contained
ZDDPs but the chromatogram for this sample re-
vealed no peaks. Fig. 4a–d shows the four samples
giving peaks in the chromatograms. A summary of
analysis of the commercial samples is presented in
Table 1.

Sample 1, prepared from a secondary alcohol (4-
methyl-2-pentanol) produces one peak with a capaci-
ty factor characteristic of the 4-methyl-2-pentyl
derivative. Sample 2 displays three distinct peaks,
two of which correspond to the capacity factors of
$Zn[(iPrO)_2PS_2]_2$ and $Zn[(4-Me-2-PentO)_2PS_2]_2$, as
one might expect from a sample prepared from a
mixture of 4-methyl-2-pentanol and isopropanol
(3:2, v/v). $Zn[(4-Me-2-PentO)_2PS_2]_2$ displays a
lower than average plate count indicative of band
broadening, which suggests that there may be addi-
tional co-eluting peaks derived from impurities in the
original C_6 alcohol. The third peak eluting between
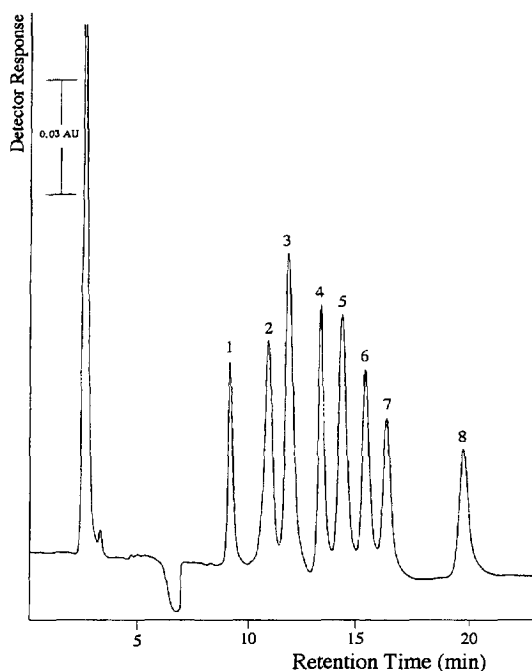the i-propyl and 4-methyl-2-pentyl derivatives is

Fig. 3. Separation of eleven ZDDPs on a silica column (250×4.6
mm). Conditions: eluent B consisting of isopropylamine–acetic
acid–methanol (0.4:0.2:1%, v/v) in n-heptane–dichlorometh-
ane (60: 40, v/v); other conditions, as in Fig. 2. Compon-
ents: 1, $Zn[(nDecO)_2PS_2]_2$; 2, $Zn[(4-Me-2-PentO)_2PS_2]_2$ +
$Zn[(iOctO)_2PS_2]_2$; 3, $Zn[(2-PentO)_2PS_2]_2$+$Zn[(nPentO)_2PS_2]_2$; 4,
$Zn[(sec.BuO)_2PS_2]_2$; 5, $Zn[(iBuO)_2PS_2]_2$+$Zn[(nBuO)_2PS_2]_2$; 6,
$Zn[(iPrO)_2PS_2]_2$; 7, $Zn[(nPrO)_2PS_2]_2$; 8, $Zn[(EtO)_2PS_2]_2$.

thought to be a zinc complex containing mixed-
alcohol ligands originating from the two alcohols.
These results are consistent with the TLC results,
where only three spots are revealed for sample 2.
The normalised peak area ratios for sample 2 were
found to be 37:48:15. A synthetic mixture of ZDDPs
derived from the same quantities of 4-methyl-2-
pentanol:isopropanol (60:40, v/v) reveals almost
identical results to sample 2, with three peaks of area
ratios in good agreement with those expected from
statistical distribution (i.e. 36:48:16 calculated
from a 60:40 (v/v) ratio of the original alcohols).
Two of the peaks were confirmed to contain
$Zn[(iPrO)_2PS_2]_2$ and $Zn[(4-Me-2-PentO)_2PS_2]_2$ by
standard addition. In contrast with the behaviour of
trivalent metal dithiophosphates [4], the presence of
three chromatographic peaks rather than six indicates
that ligand-exchange reactions are not taking place in
mixtures of two or more zinc dithiophosphates.

Table 1
Analysis of commercial samples by normal phase HPLC

Sample number	k'	R-group(s) identified in $Zn[(RO)_2PS_2]_2$	Concentration of ZDDP[a] (mg/g)	Manufacturer's specifications: starting ROH(s)
1	3.34	4-Me-2-Pent	842	4-Me-2-Pent
2	3.34	4-Me-2-Pent	387	60:40 (v/v)
	4.10	unknown[b]		4-Me-2-Pent/i-Pr
	5.04	i-Pr	185	
3	2.90	unknown k' [c]	—	Dodecyl phenol
4	3.33	4-Me-2-Pent	—	Unknown
	4.28	sec.-Bu	—	Label claims
	4.41	unknown[b]		"contains ZDDPs"
	4.63	i-Bu or n-Bu	—	
5	—	none	—	Label states "contains ZDDPs"

Eluent: isopropylamine–acetic acid–methanol (0.4:0.2:1.0%) in n-heptane–dichloromethane (60:40, v/v); Flow-rate, 1 ml/min; UV detection, 246 nm; Column, Spherisorb S5W 5 μm silica 250×4.6 mm column; Sample solutions, approx. 10^{-4} M in dichloromethane.
[a] Determined by spiking the sample with the identified component.
[b] Zn species with mixed-ligand.
[c] Found to contain zinc diaryldithiophosphates by electrospray mass spectrometry (ESMS) [16].

Sample 3 elutes as a single broad peak at $k' = 2.90$, which matches none of the dialkyldithiophosphates investigated in this work. In a previous paper, we have provided good evidence from electrospray mass spectrometry that this sample is a mixture of zinc diaryldithiophosphates, derived predominantly from dodecyl phenol [16]. The low efficiency of this peak is attributed to the presence of isomers in the starting alcohol. Sample 4 produces four main peaks, three of which correlate with C_4 and isomers of C_6 alkyl ZDDP derivatives. The other peak may be attributed to a complex containing a mixed-ligand as it does not match the capacity factors of any of the zinc derivatives synthesised in this work. In samples 1–4, testing of peaks collected from the end of the column indicated that zinc and dithiophosphate ligand were present in all retained components.

4. Conclusions

The following eluents were found to be the most suitable for separation of zinc dialkyl dithiophosphates on a silica column: eluent A, isopropylamine–acetic acid–methanol (0.2:0.1:1) in dichloromethane; eluent B, isopropylamine–acetic acid–methanol (0.4:0.2:1) in n-heptane–dichloromethane (60:40, v/v). The addition of alkyl amines (no greater than 0.4%) and acetic acid in a volume ratio of 2:1 to dichloromethane or n-heptane–dichloromethane overcomes the unfavourable fronting and tailing effects observed when both of these components are absent from the eluent. Small quantities, ca. 1% (v/v), of methanol also improve elution of the complexes, whereas higher concentrations produce marginal decreases in resolution.

Eluent B provides better baseline resolution for ZDDP derivatives of different carbon numbers and elutes the complexes in order of decreasing carbon numbers on the alkyl chain, whereas eluent A leads to elution of the i-octyl derivative slightly ahead of the C_6 derivative. Commercial samples were analysed using eluent B without the need for pretreatment. It is interesting to note that additives originating from two alcohols gave three chromatographic peaks, in agreement with TLC analysis.

Interferences are minimised using a normal-phase system where the base oil and organics elute at the void volume, whereas these components are retained on reversed-phase columns. Furthermore, satisfactory separations can be achieved in normal-phase chroma-
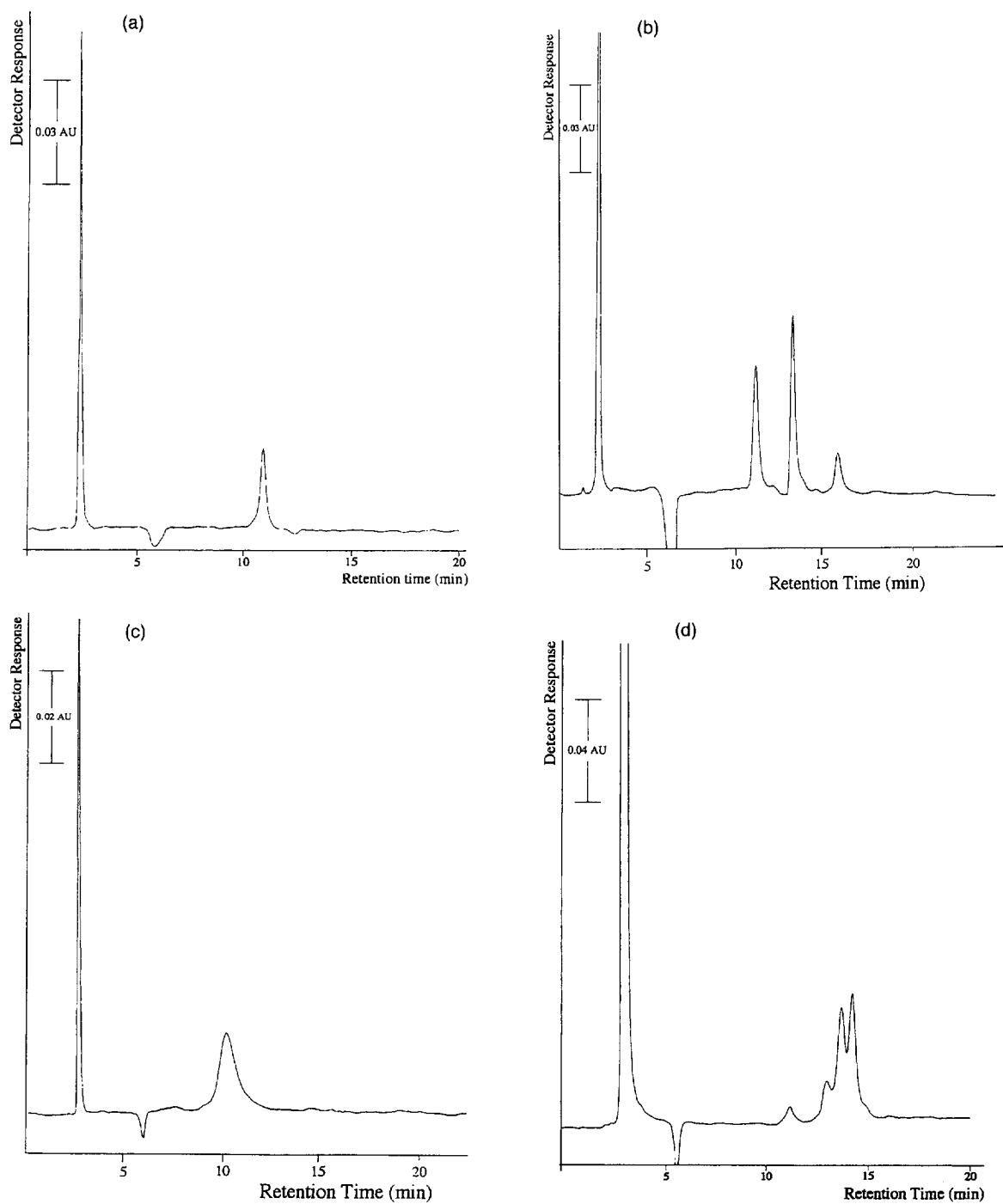
Fig. 4. Normal-phase chromatograms of commercial samples. Conditions, as in Fig. 3. (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4.

tography in acceptable analysis times without the need for gradient elution.

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