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Determination of Trialkyl and Triaryl Phosphates by Narrow-bore Liquid Chromatography with On-line Thermionic Detection[†]

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The potential of a previously reported on-line reversed-phase liquid chromatography–thermionic detector (LC–TID) system has been further evaluated. Several trialkyl (trimethyl to tri-octyl) and triaryl (triphenyl and tri-*o*-cresyl) phosphates were chosen as model compounds. LC was done on an alkyl-bonded silica column with methanol–water (80:20) at a flow-rate of 35–70 $\mu\text{l}/\text{min}$ as eluent. The band broadening in the interface-TID unit increased with decreasing volatility of the compounds and for the relatively non-volatile compounds, the band broadening decreased with increasing eluent flow-rate.

For most of the test compounds, detection limits of 40–100 pg were obtained. As an illustration of the high selectivity of the LC–TID system, the trace-level determination of two aryl phosphates in sediment samples is reported.

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INTRODUCTION

Miniaturization in column liquid chromatography (LC) has eliminated many of the difficulties associated with direct introduction of LC eluents into gas chromatographic detectors. The utilization of detectors such as the electron-capture detector,^{1,2} the mass spectrometer,^{3,4} the flame emission⁵ and thermionic detector⁶ for narrow-bore LC has already been described. We recently published^{7,8} our first results about the coupling of a narrow-bore LC system with a thermionic detector (TID). The possibility of handling mobile phase flow-rates of up to 40 $\mu\text{l}/\text{min}$ of methanol-water was shown, and the organophosphorus pesticides coumaphos, azinphos-ethyl and trichlorfon were determined in cabbage and tomato samples. Detection limits of 30 to 100 pg of injected compound or 0.2–0.5 pg/s of phosphorus were obtained.

In the present study, a series of thermally stable trialkyl and triaryl phosphates was selected as model compounds, to test the applicability of the LC-TID interface performance for compounds of decreasing volatility.

Most of the selected phosphates are of environmental interest. Major uses of trialkyl and triaryl phosphates are as fire retardant plasticizers in the manufacture of PVC plastics and as industrial hydraulic fluids to replace polychlorinated biphenyls. The estimated production of the phosphates is approximately 77×10^6 kg for 1986. This large volume results in substantial release to the environment either from losses during manufacturing or use.^{9,10} Residues of triphenyl phosphate (TPhP) and tri-*o*-cresyl phosphate (TOCP) have been found in several environmental samples such as fish, sediment and water.^{11–13} Recently, the highly toxic TOCP was also found in contaminated edible oils.¹⁴ In the present paper, the determination of TPhP and TOCP in sediment by LC-TID is reported.

EXPERIMENTAL

Materials

All solvents were of HPLC-grade quality (Baker, Deventer, The Netherlands) and were passed through a filter of 0.45 μm pore diameter before use. Analytical reagent grade trimethyl phosphate

(TMP), triethyl phosphate (TEP), tripropyl phosphate (TPP), tributyl phosphate (TBP), tri-octyl phosphate (TOP), triphenyl phosphate and tri-o-cresyl phosphate were obtained as gifts from A. Verweij (TNO, Rijswijk, The Netherlands).

Sample preparation

Sample pre-treatment was carried out using a simple procedure described in the literature¹¹ for the extraction of triaryl phosphates from sediment samples. The procedure is as follows: 25 g of sediment (wet weight) spiked with 2 ppm of TPhP and TOCP were placed in a soxhlet and 150 ml of methanol-water (9:1) were used as extraction solvent for a period of 4 hours. Afterwards, the aqueous methanol was evaporated in a rotary evaporator to a volume of 2 ml.

Chromatographic system

Glass-lined stainless-steel columns (GLT; 200 × 0.7 or 1 mm I.D., SGE, Melbourne, Australia), laboratory packed with 5 μm Spherisorb ODS 2 (Merck, Darmstadt, F.R.G.) were used. Band-broadening studies were carried out using a flow injection system with the injection valve directly coupled to the evaporation interface. A Gilson (Villiers-le-Bel, France) Model 302 high-pressure pump coupled with a laboratory-made membrane pulse damper, or a μLC-500 high pressure syringe pump from ISCO (Lincoln, NE, U.S.A.) provided stable eluent delivery. Samples were introduced via a laboratory-made injection valve having a 0.05 and a 0.5 μl internal loop or a Valco (Houston, TX, U.S.A.) C214W micro valve with a 0.1 μl internal volume rotor. In flow injection analysis, the test compounds were dissolved in the mobile phase.

Thermionic detector

A Packard (United Technologies, Delft, The Netherlands) Model 427 gas chromatograph was used, which contained a Packard Model 905 TID, the rubidium bead of which was electrically heated by a Packard Model 612 detector controller. The evaporation interface was located in the detector block, which was maintained at 300°C. The termination of the LC column was directly connected to the

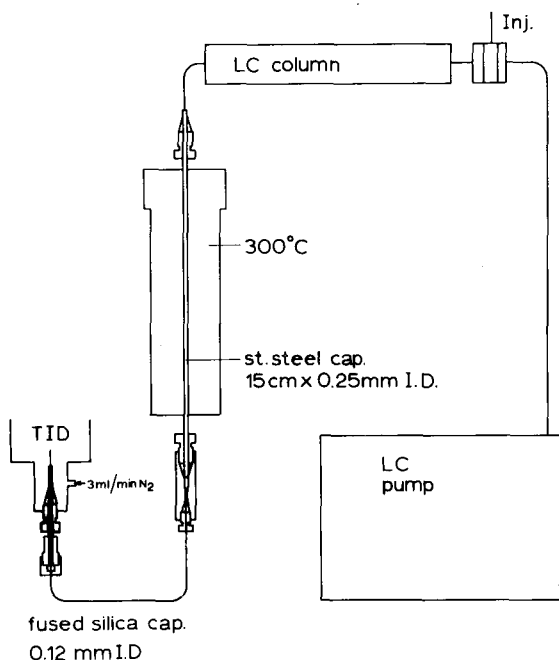


Figure 1 Schematic design of the LC-TID system, also showing the detailed construction of the interface.

15 cm \times 0.25 mm I.D. stainless-steel interface and the vaporized eluent from the interface was introduced into the flame jet via a 15 cm \times 0.12 mm I.D. fused silica capillary; a nitrogen flow of 3 ml/min was added via a T-piece just below the detector body. This gas flow was pre-heated in the GC oven, in order to minimize its cooling effect. A schematic diagram of the LC-TID system used in the present study with the detailed construction of the interface is shown in Figure 1 (see also Reference 8).

RESULTS AND DISCUSSION

Band broadening in the interface

An important criterion for the performance of the LC-TID interface is the contribution to the band broadening of the analytes. A flow

injection system is suitable to measure the band broadening in the interface and detector. It is well known that with this method tailing peaks are often obtained; therefore, band broadening was calculated by means of the Foley-Dorsey¹⁵ experimental approximation of the second moment (M_2).

In a previous study,⁸ M_2 was found to be $0.66 \mu\text{l}^2$ and $1.78 \mu\text{l}^2$ at a flow-rate of $20 \mu\text{l}/\text{min}$ for paraoxon-ethyl and coumaphos, respectively. These numbers demonstrate that the band broadening increases with decreasing volatility of the analytes. Table I, in which M_2 is expressed in both μl^2 and s^2 , shows the same phenomenon for the trialkyl and triaryl phosphates studied in this paper. Table I also shows that an increase of the flow-rate causes an increase of $M_2(\mu\text{l}^2)$ for the relatively volatile test compounds, while a decrease of M_2 is observed for the less volatile compounds such as coumaphos, TPhP, TOCP and TOP. The band broadening $M_2(\text{s}^2)$ decreases for all compounds at higher flow-rates because of the decrease of the residence time in the interface and the detector.

A probable explanation for the influence of the flow-rate on the band broadening ($M_2; \mu\text{l}^2$) of the relatively non-volatile test solutes is via the vaporization efficiency of the interface. Generally speaking,

Table I Dependence of second moments (M_2) of several phosphates on mobile-phase flow-rate. Conditions: Carrier stream, methanol-water (80:20). Interface temperature, 300°C . Experiments: $n=4$, rel. S.D. = 3.5–4.5%. M_2 measured for TID interface plus detector

Compound	Boiling point ($^\circ\text{C}$)	$M_2(\text{s}^2)$ at flow-rate ($\mu\text{l}/\text{min}$)				$M_2(\mu\text{l}^2)$ at flow-rate ($\mu\text{l}/\text{min}$)			
		20	30	40	60	20	30	40	60
Paraoxon-ethyl		5.9	3.5 ^a			0.66	1.19 ^a		
Coumaphos		16.1	4.1 ^a			1.78	1.38 ^a		
TMP	197	5.3		2.1		0.58		0.93	
TEP	216	5.4		2.2		0.60		0.97	
TBP	289	5.6		2.4		0.62		1.06	
TPhP	390		39	17	6.5		9.8	7.4	6.5
TOCP	410		40	18	6.5		10	7.8	6.5
TOP	216		101	52	21		25	23	21

^aFlow-rate, $35 \mu\text{l}/\text{min}$.

an increase of the flow-rate may be expected to detract from an efficient evaporation. However, heat from the interface can easily radiate towards the separation column, creating a temperature gradient in the connecting capillary. Therefore, compounds leaving the column experience a gradual warming up, instead of a sharp temperature increase, and are vaporized over a broad zone. This problem will be especially severe with high-boiling substances, which may be incompletely vaporized in the low-temperature region of the capillary. Increasing the effluent velocity reduces this effect by moving the solutes more rapidly through the thermal gradient into the hot interface. This apparently reduces the band broadening in the connecting capillary and the interface.

Finally, it is important to know the maximum band broadening in the interface and the detector that can be tolerated compared to the band broadening in the column. This is demonstrated by an example. A column with a plate number of 10,000 will give a variance of 36 s^2 for an analyte with a retention time of 10 min. If an external band broadening of 10% (or $\sigma = 0.6 \text{ s}$) is considered to be acceptable, $M_2(\text{s}^2)$ has to be lower than 7.6 s^2 . As is shown in Table I, this is true for all relatively volatile compounds, and for TPhP and TOCP at a flow-rate of $60 \mu\text{l}/\text{min}$.

Analytical data

A mixture of TMP, TPP, TBP, TOP, TPhP and TOCP was chromatographed on a C18-bonded phase with methanol-water (80:20) as the eluent. Initially, TEP was also included in the mixture; however, this solute co-eluted with TMP. A typical chromatogram obtained for injected amounts of 50–70 ng of each of the test solutes is shown in Figure 2. The separation was carried out on a 1 mm I.D. column at an eluent flow-rate of $70 \mu\text{l}/\text{min}$, which is about the highest flow-rate that can be handled by the detector without baseline stability problems. Previously, TEP has been shown⁸ to have a detection limit of 40 pg of injected compound at an eluent flow-rate of $40 \mu\text{l}/\text{min}$. In this study, comparable detection limits (signal-to-noise ratio, 3:1) were found for most other phosphates, viz. 40–50 pg for TMP, TPP and TBP and 80–100 pg for TPhP and TOCP. The detection limit of TOP was much higher, i.e., about 1 ng. This is at least partly due to the rather high retention of TOP (cf.

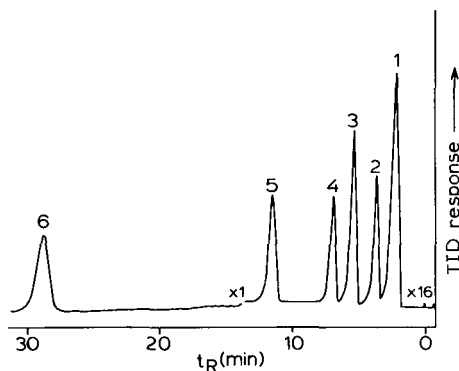


Figure 2 LC-TID chromatogram of 6 alkyl and aryl phosphates. Column, glass-lined stainless steel (20 cm \times 1 mm I.D.) packed with 5 μ m Spherisorb ODS 2. Eluent, methanol-water (80:20) at a flow-rate of 70 μ l/min. Solutes: 1, TMP; 2, TPP; 3, TPhP; 4, TBP; 5, TOCP and 6, TOP. Injected amounts, 50–70 ng.

Figure 2; $k' = 14$) and the relatively low weight percentage of phosphorus of this analyte.

The repeatability of the system was determined for injected analyte amounts of 50–70 ng at an LC flow-rate of 35–55 μ l/min. At 35 μ l/min, the rel. S.D. for TMP, TPP and TBP was between 2.5 and 5.0% ($n = 10$), and the rel. S.D. for TPhP and TOCP were 8.5 and 9.5% ($n = 10$), respectively. At 55 μ l/min, the rel. S.D. for TPhP and TOCP improved to 5.5 and 6.0% ($n = 10$), respectively, while the repeatability did not change for the other compounds.

Determination of triaryl phosphates in sediment

Gas chromatography (GC)-TID^{11–13} and GC-mass spectrometry¹³ are the methods of choice for the determination of triaryl phosphates in environmental samples (e.g., sediment, fish, water). LC has been applied to the determination of triaryl phosphates, either using rather non-selective UV detection at 260 nm¹⁶ or highly sophisticated graphite furnace atomic absorption detection.¹⁷ Because of this, the use of the thermionic detector is becoming increasingly important, because it can fill the need for a selective and relatively simple LC detector for such compounds.

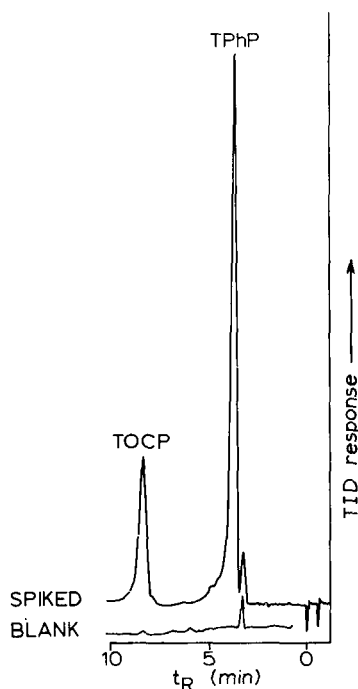


Figure 3 LC-TID chromatogram of the extract of a sediment spiked with 2 ppm of TPhP and TOCP. Column, glass-lined stainless steel (20 cm \times 0.7 mm I.D.) packed with 5 μ m Spherisorb ODS 2. Eluent, methanol-water (80:20) at a flow-rate of 35 μ l/min. Injected amounts, 20 ng TPhP and 10 ng TOCP. For sample preparation, see Experimental.

A sediment sample from the lake Het Nieuwe Meer (Amsterdam, The Netherlands) was spiked with 2 ppm of each TPhP and TOCP. The sample preparation was limited to a 4 h soxhlet extraction with aqueous methanol, which has been shown to be more efficient than less polar solvents.¹¹ Figure 3 shows the LC-TID chromatogram of the spiked sediment. Practically no interferences from the sediment matrix are observed in the chromatogram. The high selectivity of the LC-TID system for the aryl phosphates is similar to that previously observed for phosphorus-containing pesticides in tomato, cabbage and onion samples.^{7,8} In Reference 7, the selectivity of the LC-TID system was calculated to be 1×10^5 g of carbon per g of phosphorus.

CONCLUSIONS

The performance of an interface recently described⁸ for on-line LC-TID has been further evaluated. Generally speaking, band broadening in the interface increases with decreasing volatility of the organophosphorus compounds. For the relatively non-volatile phosphates such as TPhP, TOCP and TOP, the volumetric band broadening considerably decreases when the eluent flow-rate is increased. However, the opposite is true for the more volatile test compounds. Optimization will therefore at least partly be determined by the nature of the sample constituents to be analyzed. For the rest, it is important to note that the highest eluent flow-rate that can be handled by the present LC-TID system is 70 $\mu\text{l}/\text{min}$.

The determination of trialkyl and triaryl phosphates by means of LC-TID is a relevant example, because these compounds lack specific UV absorption and native fluorescence.^{10,16} The simple procedure elaborated for sediment samples containing low-ppm levels of triaryl phosphates illustrates the selectivity and sensitivity of LC-TID in environmental analysis.

The determination of weak organic and inorganic phosphorus-containing acids will be the focus of future work. Preliminary results indicate that acceptable peak profiles can be obtained for, e.g., orthophosphoric acid, provided an eluent having a pH of 2.0–2.8 is used.

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