

CHROM. 13,266

SAMPLE COLLECTION AND FIELD ANALYSIS OF TRIS-(2-ETHYLHEXYL) PHOSPHATE USED IN A STUDY OF PESTICIDE SPRAY DRIFT

M. KRZYMIEN

National Research Council of Canada, National Aeronautical Establishment, Unsteady Aerodynamics Laboratory, Montreal Road, Ottawa, Ontario K1A 0R6 (Canada)

SUMMARY

Tris-(2-ethylhexyl) phosphate vapour and aerosol were collected in glass adsorber tubes packed with a plug of fine platinum mesh coated with OV-101 and subsequently thermally released into a gas chromatograph for analysis. The capacity of the adsorber was determined to be *ca.* 700 l of air. Concentrations of $\mu\text{g/l}$ were determined with a precision of better than $\pm 10\%$. The aerosol concentration and its drop-size distribution were determined at a picogram level with $\pm 5\%$ precision using a cascade impactor.

INTRODUCTION

A number of papers have been published describing methods for determination of tris-(2-ethylhexyl) phosphate (TEHP) in plastics. Bloom¹ applied thin-layer and gas-liquid chromatography to the qualitative and quantitative analysis of phosphoric esters. Lerche and March² determined TEHP in poly(vinyl chloride) using gas chromatography (GC) with flame ionization detection. The separation of various plasticizers was achieved with silicone phases, QF-1 and OV-210¹ or OV-1². Armstrong and Yule³ determined TEHP deposited on foliage and twigs using GC (OV-1 column) with flame photometric detection.

However, the chemical literature lacks information on the determination of TEHP in ambient air. The need for such a method arose when it was decided to use TEHP as a non-toxic simulant in a study of the long-range drift of airborne pesticides from aerial spray operations. The method was required to provide information on the concentration of both vapour and aerosol in the atmosphere. The analytical procedures are similar in concept to those used for the determination of fenitrothion in ambient air⁴; however, several important changes in the GC and sampling procedures were made. The methods described here were successfully used for determination of TEHP vapour and aerosol in ambient air during an experimental spraying of New Brunswick forests in July 1979⁶.

EXPERIMENTAL

Preparation of adsorber

Samples of TEHP vapour and aerosol were collected in a 7.5 cm × 6.4 mm O.D. glass tube containing a 1.5-cm plug of tightly packed fine platinum mesh (*ca.* 0.5 g of Pt) coated with a thin layer of OV-101 silicone. The coating was applied by a single dip of the platinum mesh in a 10% chloroform solution of OV-101 and evaporation of the solvent by blowing an air stream over it. The adsorbers were conditioned overnight at 260°C in a nitrogen stream at a flow-rate of 20 cm³/min. A chromatogram was recorded to check the purity of the adsorber. Neither peaks nor baseline drift were observed.

Collection of TEHP vapour and aerosol samples

Air was drawn through the adsorber by two kinds of samplers. The first one was a diaphragm pump ("Air Cadet" from Cole-Palmer Co.) modified to accept a 12 V d.c. automotive fan motor, capable of drawing air at a flow-rate of up to 8 l/min. The outlet of the pump was connected to a built-in flowmeter. The sampler was operated manually and was used to collect large volumes of air over relatively short periods of time, usually 15–40 min, so that the temporal variations of concentration could be determined.

The second type of sampler was operated automatically. Ambient air was drawn through the adsorber by means of a small diaphragm pump (Brailsford Co.) at a flow-rate of *ca.* 2.5 l/min. Designed for unattended operation, the pump could be preset to turn on up to 24 h ahead of time and to turn off after a selected time period by means of an electronic clock. The automatic sampler was powered by a rechargeable battery pack. It was used to monitor dosage of airborne TEHP over long periods when fluctuations of the concentration could be neglected. Automatic samplers were compact and lightweight; up to six could be suspended from a hydrogen-filled "advertising" balloon (4 m diameter) in a vertical array to determine the vertical profile of TEHP concentration.

Gas chromatographic analysis

TEHP collected on the platinum mesh adsorbers was analysed on a Tracor gas chromatograph which was modified to accommodate the adsorber. The instrument was equipped with a Perkin-Elmer nitrogen-phosphorus detector. A schematic view of the gas chromatograph is presented in Fig. 1. A sample was introduced into the gas chromatograph either by liquid injection through a septum or as a vapour thermally released from an adsorber. The adsorber tube with a sample of air trapped

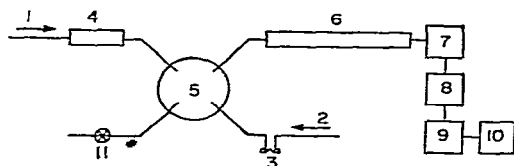


Fig. 1. Schematic view of the gas chromatograph. 1 and 2 = carrier gas (nitrogen) inlets; 3 = septum; 4 = adsorber; 5 = four-port switching valve; 6 = column; 7 = nitrogen-phosphorus detector; 8 = electrometer; 9 = computing integrator with printer; 10 = strip chart recorder; 11 = restriction.

on platinum mesh was reinstalled into the gas chromatograph and purged with a stream of carrier gas. After *ca.* 1 min the stream was redirected by a four-port switching valve (high temperature Valco valve) to a GC column and the adsorber was flash-heated to 250°C by surrounding it with a hot aluminium block. The nitrogen stream carried thermally released vapour to the GC column. The recorded TEHP peak area was compared with that of a TEHP standard solution deposited with a syringe directly on the platinum mesh and analysed in the same manner as an air sample. The concentration of the standard solution was $1.14 \cdot 10^{-10}$ g/ μ l. Usually 5 μ l of the standard solution were injected to obtain *ca.* 50% full scale deflection of the recorder pen.

The chromatographic conditions were as follows: column, 1 m \times 3.2 mm O.D. nickel tube packed with 3% OV-1 on Chromosorb W HP 80–100 mesh; carrier gas, nitrogen at a flow-rate of 40 cm³/min; oven temperature, 240°C; adsorber heater temperature, 250°C; detector temperature, 240°C; detector hydrogen and air flow-rates 3 cm³/min and 100 cm³/min, respectively, rubidium glass bead electrically heated at a setting of 740.

A signal from the detector was amplified by the electrometer and recorded on a Gould-Brush 105 strip chart recorder. Peak areas were integrated by an LDC 304-50 computing integrator and printed out together with retention times. To scale down large peaks the integrator's output attenuator was used.

Collection and analysis of aerosol

Eight-stage Anderson 2000, Inc. impactors were used to collect TEHP aerosol. The aerosol was trapped on consecutive plates according to drop size. Deposited aerosol was washed off each plate with *ca.* 3 cm³ of acetone. The solution was concentrated to a volume of 100 μ l by evaporation of the solvent by blowing a small stream of high purity nitrogen over the surface of the solution while heating to *ca.* 50°C. Then 5- μ l aliquots of the concentrate were injected directly into the gas chromatograph via the septum, *i.e.* without preconcentration on an adsorber. Recorded peaks were integrated and their areas compared with that of a standard injected the same way.

RESULTS AND DISCUSSION

A number of materials were examined as possible adsorbents for trapping TEHP vapour and aerosol. Tenax GC and polar silicones of the OV series supported on Chromosorb required too high a temperature to release trapped TEHP. Moreover, these packings created a significant flow restriction in the adsorber tubes, and therefore it was not possible to achieve the desired sampling rate of 1–1.5 l/min. The adsorbent without these drawbacks was found to be fine platinum mesh coated with OV-101 silicone. Even when packed very tightly to ensure many collisions of vapour and aerosol particles with the adsorbing surface, the adsorber created little restriction to the sample flow. Flow-rates of the order of 2.5 l/min with the automatic sampler and 7.5 l/min with the manual one were easily achieved. The desorption temperature was low enough to deliver a narrow plug of vapour when the heating block temperature was maintained at *ca.* 250°C. Its adsorption capacity was still big enough to trap TEHP from large volumes of air.

The capacity of an adsorber is described as a maximum sample volume, *i.e.*, the volume of sampled air at which trapped material begins to elute. This parameter, fundamental to the accuracy of the method, was determined by a direct measurement. Validity of the direct measurement relies on the ability to deliver a continuous stream of TEHP vapour at constant concentration. This can be easily achieved with a continuous-flow trace vapour source⁵.

A continuous stream of air containing a constant concentration of TEHP vapour, say $3 \cdot 10^{-12}$ g/l, was generated by a continuous-flow vapour source. The air was sampled on a platinum mesh adsorber at a constant flow-rate of *ca.* 1–1.5 l/min which was similar to that used during ambient air analysis. Samples were collected for various periods, ranging from 7.5 min to 16 h, to obtain sample volumes from 12 to 1200 l. Each sample was analysed as described above, and TEHP peak areas were plotted *versus* sample volume (Fig. 2).

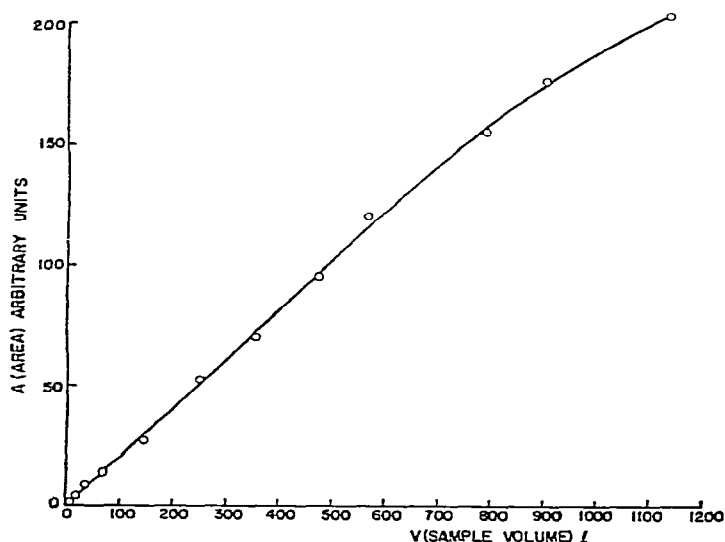


Fig. 2. Maximum sample volume.

Since the concentration of TEHP vapour in sampled air remained constant, the peak area should be directly proportional to the sample volume; if so, a plot of peak area *vs.* volume should be a straight line starting at the origin. The plot (Fig. 2) actually remained a straight line to *ca.* 650–700-l sample volume, and curved slightly for sample volumes over 700 l to 1200 l, owing to elution of TEHP from the adsorber. Therefore, the maximum sample volume can be estimated as being *ca.* 700 l at ambient temperature. The critical point on the curve, 700-l sample volume, was also determined using 8 l/min sampling rate. The obtained peak area agreed with that for 1.5 l/min sampling rate to within $\pm 10\%$.

Efficiency of the adsorbers in trapping the TEHP aerosol was determined in another laboratory test. The TEHP aerosol was released from a large annular jet at a rate of *ca.* 1 mg/min into "still" laboratory air. Eight adsorbers, including manual and automatic samplers, symmetrically positioned over a plume cross-section and a cascade impactor on the plume axis, were used to measure the cross-sectional con-

centration distribution. The concentration determined with the adsorbers and the impactor were the same to within 5%, confirming that the adsorbers trapped aerosol as efficiently as the cascade impactor. Mass budget calculations revealed that more than 80% of the released TEHP could be accounted for. Most of the remaining 20% represents the turbulent flux of aerosol, which could not be measured. The TEHP "far-downwind" concentration fluctuations in the actual field trials are believed to have been lower than in the jet, so that the trapping efficiency of the adsorbers may reasonably be expected to have been at least 90%.

Aerosol samples were collected on the plates of cascade impactors. The material trapped on a metal plate was exposed to a large volume of air flowing over it at high flow-rate. This could cause a significant loss of material by evaporation and/or decomposition, as was the case with fenitrothion⁴. However, the loss of TEHP was, as proved in the experiment, negligible because of its low vapour pressure and chemical stability. TEHP formulation (5% solution of TEHP in fuel oil No. 585) was diluted with hexane to a concentration of 0.63 ng/ μ l. Then 20 μ l of the solution (12.6 ng TEHP) were deposited by syringe on each plate of a cascade impactor in the smallest possible drops and air was drawn through the impactor for 5 h at a flow-rate of *ca.* 30 l/min. The plates were then analysed by the method described above. The results are presented in Table I. Relative standard deviation of eight measurements was less than $\pm 5\%$. The results are scattered more or less symmetrically around the true value, showing that the method was not burdened by systematic error. The very good recovery rate proved that TEHP was not lost either during collection of aerosol or during analysis of the plates. The integrator was programmed not to print out peaks below 100 area units, corresponding to *ca.* 1 pg of TEHP. Since a 5- μ l aliquot injected into the gas chromatograph is only 5% of the total TEHP deposited on the plate, 20 times that, *i.e.* 20 pg, is the minimum amount of TEHP that can be quantitatively determined with a precision of *ca.* $\pm 5\%$ (Table I).

TABLE I
RECOVERY OF TEHP DEPOSITED ON CASCADE IMPACTOR PLATES

<i>Amount deposited (ng)</i>	<i>Amount recovered (ng)</i>	<i>Recovery (%)</i>
12.60	12.5	99.2
12.60	12.2	96.8
12.60	12.3	97.6
12.60	13.3	105.6
12.60	11.7	92.9
12.60	11.9	94.4
12.60	13.2	104.8
12.60	12.0	95.2
	average: 12.4	
	standard deviation: 0.59	
	relative standard deviation: 4.76%	

A typical chromatogram of TEHP preconcentrated on OV-101 coated platinum mesh is presented in Fig. 3. The retention time of TEHP is 111 sec when a sample is introduced as a vapour thermally released from an adsorber, and 94 sec for samples injected as a liquid (Fig. 4). The difference occurs because it takes time to heat the

adsorber to the release temperature, and also because the adsorber acts as a chromatographic column and as such retains TEHP for a noticeable period. The retention time was measured from the moment when a heating block was placed around the adsorber. The short retention time is very advantageous when a great number of samples are to be analysed. During the field experiment as many as 100 samples were analysed daily. In some instances, as presented in Fig. 3, when contaminated air was analysed some overlap of the TEHP peak with background peaks occurred. The peak, however, was well shaped and suitable for quantitative analysis, providing the right integration procedure was applied. The case was treated as a peak above a negative sloping baseline. In this situation as soon as the tail of the peak falls below the microvolt level at which it was first detected, the integrator calculates the peak width AB, doubles it and projects to time C where the integration ends. No peak has been detected before time C, the integrator then draws a baseline from A to D. By doing so, it eliminates the overlapping background peaks, so the integrated area represents only the TEHP peak. This procedure allows keeping analysis time short without sacrificing accuracy.

Before the experimental TEHP spray operation began, a number of air samples were collected in the forest area designated for spraying. Analysis of these samples

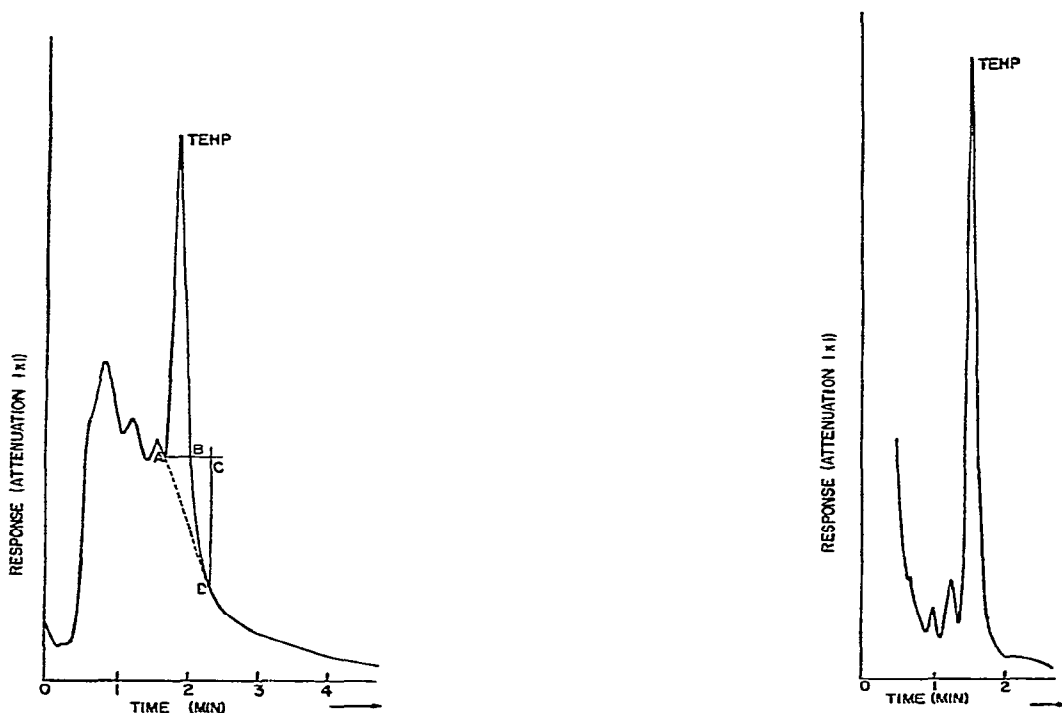


Fig. 3. Chromatogram of an air sample, containing 0.86 ng of TEHP. Sample volume, 165.25 l; TEHP concentration, 5.24 ng/m³; sampling time, 25 min with manual sampler. The TEHP peak is integrated.

Fig. 4. Chromatogram of TEHP solution washed off a cascade impactor plate and containing 1.11 ng of TEHP.

showed that no TEHP was present in the air. Chromatograms of the samples, together with chromatograms of TEHP standard, were used to identify the presence of TEHP in air samples taken during aerial spraying and shortly after.

The analytical method presented here provided the experimental data for evaluation of the effect of atmospheric stability on long-range pesticide drift⁶ and of the mathematical model of long-distance transport of vapour and aerosol generated during aerial spraying of pesticides over forests⁷.

REFERENCES

- 1 P. J. Bloom, *J. Chromatogr.*, 75 (1973) 261–269.
- 2 J. Lerche and J. March, *Arch. Pharm.*, (1973) 25–30.
- 3 J. A. Armstrong and W. N. Yule, *Can. Ent.*, 110 (1978) 1259–1267.
- 4 M. Krzymien, *NRC-NAE-LTR-UA-49*, National Research Council, Ottawa, April 1979.
- 5 M. Krzymien and L. Elias, *J. Phys. (E) Sci. Instrum.*, 9 (1976) 584–586.
- 6 R. Crabbe, L. Elias, M. Krzymien and S. Davie, *NRC-NAE-LTR-UA-52*, National Research Council, Ottawa, February 1980.
- 7 R. Crabbe and J. Reid, *Proc. 2nd Joint Conference on Applications of Air Pollution Meteorology, March 24–27, 1980, New Orleans*, American Meteorological Society, Boston, MA, 1980, p. 285.