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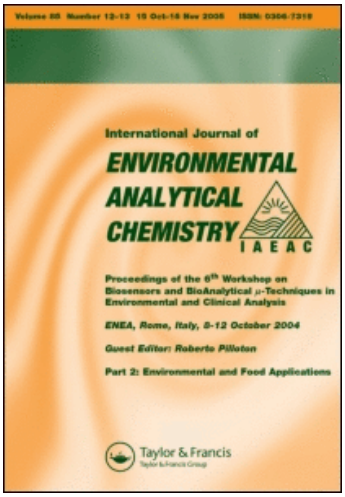


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# Mass Spectrometric Determination of Tris(1,3-dichloro-2-propyl)-phosphate (TDCP) Using NCI-Technique†

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A number of different products suspected to contain flame retardants were analysed. TDCP was found in 11 out of 104 samples. It was most common in polyurethane products such as sound absorbing materials and liners for cars and buses. To get an integrated picture of TDCP exposure the contents of vacuum cleaner bags from two homes were analysed. One of these contained TDCP.

To investigate possible presence in humans, blood samples were analysed. For clean-up, Sep-Pak cartridges with $C_{18}$ phase were used. These cartridges contained TDCP and it was not possible to eliminate this background entirely.

The NCIMS detection sensitivity for TDCP was better when analysing plasma extracts than when analysing pure standard solutions. Thus quantitative determinations of TDCP must be made by standard additions to plasma extracts.

Something in the blood plasma seems to be able to bind or immobilise a certain

†Presented at the Workshop on Chemistry and Fate of Organophosphorus compounds, Amsterdam, June 18–20, 1986.

amount of TDCP. Therefore it was not possible to analyse amounts less than 600 pg/ml whole blood with this method. None of the 37 analysed blood samples exceeded this value.

KEY WORDS: Tris(1,3-dichloro-2-propyl)phosphate, flame retardant, analysis, mass spectrometry, NCIMS.

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## INTRODUCTION

TDCP is used as a flame retardant mainly in polyurethane foam and polyester textiles. Animal experiments have shown that TDCP is readily absorbed from the skin and gastrointestinal tract of rats and rapidly distributed throughout the body. It is subject to rapid and extensive metabolic degradation. Less than 19% of the administered TDCP could be recovered as TDCP 30 min after intra-venous dosing.[1,2] TDCP and some of its metabolites have been reported to be mutagenic.[1-6]

The water solubility of TDCP is approximately 100 ppm, and it is relatively stable in water after 24 hours.[7,8] It is toxic to killifish and goldfish, the $LC_{50,96h}$ values being 3.6 ppm and 5.1 ppm, respectively.[9] In another investigation, 6 out of 6 goldfish were found dead after 24 hours with a concentration of 5 ppm TDCP in the water.[8] In the same work, $LD_{50}$ for rats was found to be 2830 mg TDCP/kg.

TDCP has been found in Canadian drinking water[10,11] and in Japanese water and sediment samples.[12,13] It has also been found in Canadian human adipose tissues. In 5 out of 16 samples the amount of TDCP was between 0.5 to 110 ng/g.[14] In the USA, TDCP was found in human seminal plasma. It was found in 34 of the 123 analysed samples, in the range of 5 to 50 ppb.[15]

This work was performed in order to investigate the present use of TDCP in Sweden and its presence in humans. Mass spectrometry of negative ions from chemical ionisation (NCIMS) shows a good sensitivity for the detection of TDCP. Detection limit was 10 pg.

## EXPERIMENTAL

### Gas Chromatography/Mass Spectrometry (GC/MS)

The GC/MS system consisted of a Finnigan Model 9610 gas

chromatograph interfaced to a Finnigan Model 4021 quadrupole mass spectrometer, equipped with a 4500 ion source (exchangeable ion volumes). It was operated in the chemical ionisation (CI) mode. Data were acquired using an Incos Data System.

The GC was equipped with a DB-5 (0.25 $\mu$m) fused silica capillary column (25 m × 0.32 mm i.d.) directly fitted into the CI source. Transfer line temperature was 200°C and ion source temperature was 80°C.

Vaporisation injection in the splitless mode was used for sample introduction. Injector temperature was 210°C. Injections were made at a column temperature of 80°C when keeper was added, otherwise at 60°C. This temperature was maintained for 1 min and was followed by a 10°C/min linear temperature program to a maximum of 280°C, which was held for 10 min.

High purity helium (AGA, Stockholm) was used as carrier gas. Methane (99.95%, AGA, Stockholm) was used as reagent gas at a pressure of 0.40 torr. Emission current was 0.2 mA, electron multiplier voltage was 1300 V, and electron energy was 70 eV.

The only ion of importance for TDCP was the $(M-111)^-$ ion, corresponding to loss of a dichloropropyl group from the molecular ion. Measured ions in the mass fragmentogram analyses are shown in Table I. The ions m/z $319^-$, $263^-$, and $292^-$ were used for the quantitative analysis.

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## Gas Chromatography/Electron Capture Detection (GC/ECD)

A Varian Model 3700 gas chromatograph equipped with a $^{63}Ni$ detector and a DB-5 (0.25 $\mu$m) fused silica capillary column

**Table I** Ions used for mass fragmentographic analysis of TDCP

| Compound | *m/z* |
|---|---|
| TDCP | $317^-$, $319^-$, $321^-$, $323^-$ |
| Methylparathion (Internal standard) | $141^-$, $154^-$, $263^-$ |
| 2,2',5,6',-tetrachlorobiphenyl (Injection standard) | $290^-$, $292^-$, $294^-$, $296^-$ |

(5 m × 0.32 mm i.d.) was used. Splitless injections were made at an injector temperature of 210°C and a column temperature of 60°C. The column temperature was maintained for 1 minute, followed by a 6°C/min linear temperature program to a maximum of 280°C, which was held for 5 min. Detector temperature was 300°C. High purity nitrogen (AGA, Stockholm) was used as carrier gas.

## Materials

TDCP (Franzén & Fried). Methylparathion (US EPA). Methanol (Merck, p.a.). Sep-Pak $C_{18}$ (Waters Associated Millipore Ltd.). 2,2′,5,6′-tetrachlorobiphenyl (CA Wachtmeister, University of Stockholm). Bloodtainer, vacuum blood collecting system, 10 ml tubes (testab laboratorieprodukter AB, Huskvarna, Sweden). *n*-Hexane and *n*-undecane were redistilled in our laboratory.

## Products

Most products were bought in shops and supermarkets in or near Stockholm. Products suspected for containing flame retardants were chosen (Table II).

The contents of vacuum cleaner bags from two homes were analysed in order to get an integrated picture of TDCP exposure. One house was recently built and the other one was about 15 years old.

## Blood samples

Most blood donors were employees at the National Environmental Protection Board working in the office, but some worked in our laboratory where TDCP containing materials are used for sound absorbing.

Blood samples (20 ml) in two bloodtainer tubes from each of totally 37 donors were collected. The samples were centrifuged the same day and the plasma was transferred to sample tubes with teflon-lined screwcaps. Samples that were subject to clean-up the following day were placed in a refrigerator overnight, whereas storage for longer periods was done in a freezer. All samples were cleaned-up within one week. Methylparathion was added immediately before clean-up.

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**Table II** Type of samples analysed for content of TDCP

| Classes of products | Number | Positive response | |
|---|---|---|---|
| | | GC/ECD | GC/NCIMS |
| Sound absorbing materials | 7 | 6 | 6 |
| Shock absorbing materials | 8 | 1 | 1 |
| Mattresses | 12 | 1 | 1 |
| Wall papers | 3 | – | – |
| Curtains | 1 | – | – |
| Bedding materials | 5 | – | – |
| Carpets | 4 | – | – |
| Furnishing fabrics | 21 | – | – |
| Bus liners | 11 | 2 | 2 |
| Car liners | 6 | 1 | 1 |
| Aircraft fabrics | 1 | – | – |
| Childrens clothes | 4 | – | – |
| Childrens toys | 6 | – | – |
| Ironing board covers | 1 | – | – |
| Lamp-shades | 1 | – | – |
| Kettle-holders | 2 | – | – |
| Diffusor filters (vacuum cleaners) | 1 | – | – |
| Working clothes | 3 | – | – |
| Buildings materials | 5 | – | – |
| Ear plugs | 1 | – | – |
| Commercial flame retardants | 1 | – | – |
| | 104 | 11 | 11 |

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## Analyses of products

The products were extracted with *n*-hexane and analysed qualitatively by GC/ECD. Confirmation of the presence of TDCP was made by GC/NCIMS.

## Analyses of blood samples

A scheme of the method is shown in Figure 1. The blood (20 ml) was centrifuged and 1.14 ng of methylparathion (internal standard) in 100 $\mu$l of *n*-hexane was added to the plasma. The hexane was evaporated with nitrogen. For the clean-up procedure Sep-Pak $C_{18}$

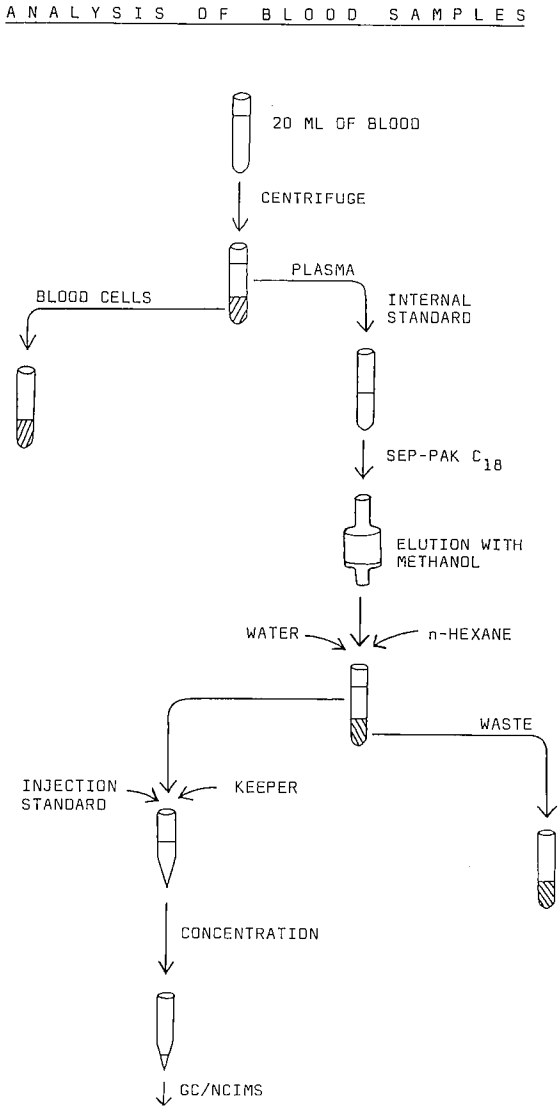


**Figure 1** Schematic of the clean-up method for blood samples.

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cartridges were used. These were Soxhlet extracted for 24 hours with methanol. Immediately before use they were washed with 8 ml of methanol, followed by 5 ml of water. Then the plasma was slowly pumped through the cartridge with a syringe. Following this, 3 ml of water was pumped through the cartridge which was then eluted with 2.5 ml of methanol. To the methanol 0.5 ml of water and $2 \times 1.5$ ml of *n*-hexane were added. To the *n*-hexane phase 25 $\mu$l of *n*-undecane (keeper) and 1.25 $\mu$g of 2,2',5,6'-tetrachlorobiphenyl (injection standard) in 100 $\mu$l of *n*-hexane were added. The volume was reduced to approximately 25 $\mu$l by blowing with nitrogen and then analysed by GC/NCIMS.

Blanks were made in the same way using 20 ml of water which had been allowed to stand for a few days in the same type of bloodtainer tubes as were used for blood sampling. The methylparathion, however, was added after the clean-up.

The clean-up efficiency was evaluated by spiking a number of plasma samples (from 20 ml blood) from the same person with 500 pg, 1 ng, 2 ng and 5 ng TDCP, respectively, before clean-up. For comparison, other plasma samples were spiked with the same amounts after clean-up. One sample in each series was left unspiked.

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## RESULTS AND DISCUSSION

Due to the presence of TDCP containing materials in the laboratory, the air was checked as follows. An open vessel with 100 ml of isooctane was allowed to stand in the laboratory for about 40 hours. The volume was reduced to approximately 1 ml by blowing with nitrogen and then 2 $\mu$l was injected on the GC/ECD. No TDCP was found.

### Product analysis

Qualitative product analyses were made after extracting the different samples with *n*-hexane. The extracts were then injected on GC/ECD and confirmation of the presence of TDCP was made by GC/NCIMS (Table II). TDCP was found only in different kinds of polyurethane foam, such as sound absorbing materials and liners for cars and buses. In Figure 2 are shown chromatograms and mass

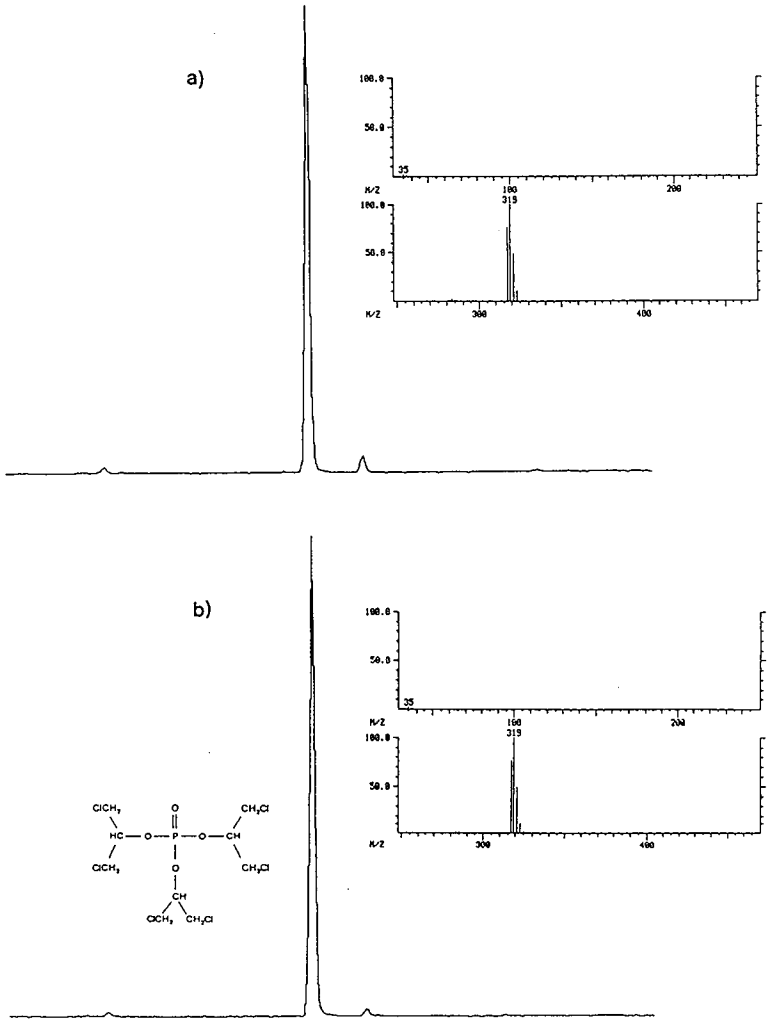


**Figure 2** Chromatograms of (a) an extract of a shock absorbing material (polyurethane) and (b) a TDCP standard, and mass spectra of the major peaks. Chromatographic and mass spectrometric conditions are given in the text.

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spectra for a polyurethane sample and a TDCP standard, respectively.

The content of one of the vacuum cleaner bags (from the older house) contained TDCP, while the other one did not.

## Blood analysis

The conditions for the chromatography are influenced in a positive way by components in the plasma. The NCIMS detection sensitivity for TDCP and methylparathion was also much better when analysing blood extracts than when analysing pure standard solutions. Because of this effect, quantitations must be made by standard additions of TDCP to plasma extracts.

The plasma samples spiked with 500 pg, 1 ng and 2 ng TDCP, respectively, gave approximately the same response relative to the injection standard as the unspiked sample. The sample spiked with 5 ng TDCP gave a higher value. The samples spiked after the Sep-Pak clean-up gave a fairly good calibration curve. These results indicate that there is something in the blood plasma that is able to bind or immobilise a certain amount of TDCP.

In Figure 3 mass fragmentograms of a blood sample spiked with TDCP, an unspiked blood sample and a blank, are shown. The Sep-Pak cartridges contained TDCP and it was not possible to eliminate this background entirely although they were Soxhlet extracted with methanol for 24 hours. Washing with ethanol and Soxhlet extraction with *n*-hexane did not improve the blanks. After Soxhlet extracting with methanol for 24 hours the background was, however, at a relatively constant level.

Due to the background problems and bad recoveries of spiked TDCP only levels above 600 pg/ml whole blood could be analysed. None of the 37 analysed blood samples exceeded this value.

## CONCLUSIONS

TDCP does not seem to be commonly used in Sweden. Its usage seems to be limited to specific product groups.

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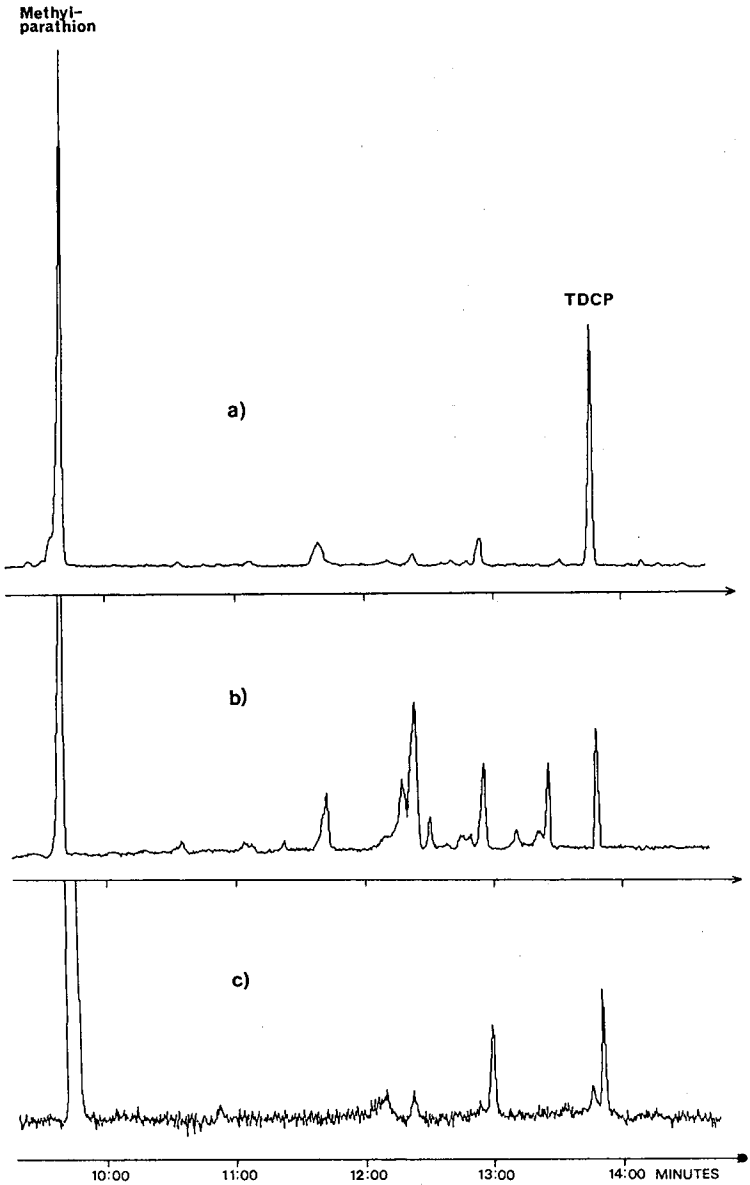


**Figure 3** Mass fragmentograms (m/z $319^- + 263^-$) of (a) a blood sample spiked with TDCP; (b) an unspiked blood sample; and (c) a blank. Chromatographic conditions are given in the text.

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TDCP and methylparathion both chromatograph better in blood extracts than in pure solvents. The detection sensitivity using NCIMS is also better in blood extracts.

TDCP in blood plasma is lost to a certain degree. It is therefore not possible to detect levels of TDCP below 600 pg/ml whole blood with this method.

## Acknowledgement

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## References

1. A. A. Nomeir, S. Kato and H. B. Matthews, *Toxicol. Appl. Pharmacol.* **57,** 401 (1981).
2. R. K. Lynn, K. Wong, C. Garvie-Gould and J. M. Kennish, *Drug Metab. Disp.* **9,** 434 (1981).
3. E. J. Söderlund, E. Dybing, J. A. Holme, J. K. Hongslo, E. Rivedal, T. Sanner and S. D. Nelson, *Acta Pharmacol. et Toxicol.* **56,** 20 (1985).
4. A. Nakamura, N. Tateno, S. Kojima, M.-A. Kaniwa and T. Kawamura, *Mutation Res.* **66,** 373 (1979).
5. D. Brusick, D. Matheson, D. R. Jagannath, S. Goode, H. Lebowitz, M. Reed, G. Roy and S. Benson, *J. Environm. Path. Toxicol.* **3,** 207 (1979).
6. M. D. Gold, A. Blum and B. N. Ames, *Science* **200,** 785 (1978).
7. V. D. Ahrens, G. A. Maylin, J. D. Henion, L. E. St. John, Jr and D. J. Lisk, *Bull. Environm. Contam. Toxicol.* **21,** 409 (1979).
8. A. T. Eldefrawi, N. A. Mansour, L. B. Brattsten, V. D. Ahrens and D. J. Lisk, *Bull. Environm. Contam. Toxicol.* **17,** 720 (1977).
9. K. Sasaki, M. Takeda and M. Uchiyama, *Bull. Environm. Contam. Toxicol.* **27,** 775 (1981).
10. D. T. Willams and G. L. LeBel, *Bull. Environm. Contam. Toxicol.* **27,** 450 (1981).
11. G. L. LeBel, D. T. Williams and F. M. Benoit, *J. Assoc. Off. Anal. Chem.* **64,** 991 (1981).
12. S. Ishikawa, T. Taketomi and R. Shinohara, *Water Res.* **19,** 119 (1985).
13. S. Ishikawa, pers. communication, 1986.
14. G. L. LeBel and D. T. Williams, *J. Assoc. Off. Anal. Chem.* **66,** 691 (1983).
15. T. Hudec, J. Thean, D. Kuehl and R. C. Dougherty, *Science* **211,** 951 (1981).