



THE LIBRARY
FIRE RESEARCH STATION
FOREST WOOD
HETS.
NO. 999FR N1060

Fire Research Note No 1060

LIBRARY REFERENCE ONLY

FORMATION OF A HIGHLY TOXIC ORGANOPHOSPHORUS PRODUCT
(TMPP) DURING THE DECOMPOSITION OF CERTAIN
POLYURETHANE FOAMS UNDER LABORATORY CONDITIONS

by

W D Woolley and P J Fardell
November 1976

54934

LIBRARY REFERENCE ONLY

FIRE
RESEARCH
STATION

Fire Research Station
BOREHAMWOOD
Hertfordshire WD6 2BL
Tel: 01 953 6177

FORMATION OF A HIGHLY TOXIC ORGANOPHOSPHORUS PRODUCT
(TMPP) DURING THE DECOMPOSITION OF CERTAIN
POLYURETHANE FOAMS UNDER LABORATORY CONDITIONS

by

W D Woolley and P J Fardell

SUMMARY

Details are given of a method for the decomposition of small quantities of polyurethane foam and the collection and direct analysis of a highly toxic bicyclic phosphorus compound (termed TMPP) produced from the thermal decomposition of foams containing trimethylol propane polyols in combination with phosphorus-containing additives.

A range of typical commercial flexible and rigid polyurethane foams and polyisocyanurates available in the United Kingdom up to and including the period of 1974 to 1975 when the problem was first identified by bioassay tests, have been tested for potential TMPP release. Flexible and rigid polyurethane foams yield zero to 0.004 and zero to 0.003 weight per cent conversion of foam to TMPP respectively at 500°C. The polyisocyanurate foams show two distinct ranges of zero to 0.003 and 0.1 to 0.15 weight per cent conversion.

A detailed study has been carried out with the polyisocyanurate foams which fall in the high yield range to monitor the temperature dependence of TMPP production in both nitrogen and air atmospheres. The optimum temperature of formation is 600°C in nitrogen and 500°C in air. The maximum temperature at which TMPP is released is about 800°C in nitrogen and 700°C in air which is consistent with the thermal stability of TMPP obtained during direct experiments with TMPP alone.

This work is of a laboratory nature and supplements other work being carried out internationally to evaluate the overall hazard associated with the release of TMPP from foams under fire situations.

© Crown copyright 1976

Department of the Environment and Fire Offices' Committee
Joint Fire Research Organization

FORMATION OF A HIGHLY TOXIC ORGANOPHOSPHORUS PRODUCT
(TMPP) DURING THE DECOMPOSITION OF CERTAIN
POLYURETHANE FOAMS UNDER LABORATORY CONDITIONS

by

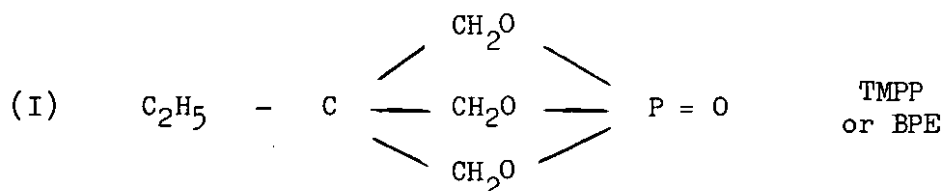
W D Woolley and P J Fardell

INTRODUCTION

In 1975, Professor I N Einhorn and co-workers of the Flammability Research Center of the University of Utah published information¹ related to the release of a highly toxic organophosphorus product during the thermal degradation of certain rigid polyurethane foams. These foams were not commercial products but had been prepared for laboratory use only. This important information came to light during a detailed programme to study the toxicity of the products of a wide range of polymers heated in a modified National Bureau of Standard chamber containing live animals. In the study, the animals (rats) were held in slings within the chamber with appropriate instrumentation for monitoring the blood chemistry (particularly COHb and O₂Hb). Other important factors such as the respiration rate, electrocardiogram and electroencephalogram were monitored in additional experiments.

During the testing of a laboratory-prepared rigid polyurethane foam containing a phosphorus-based flame retardant it was found that the combustion products proved fatal in a very short period of time but with only a moderate uptake of carbon monoxide. Similar experiments with the identical foam but without the flame retardant produced carbon monoxide intoxication but no other sign of a highly toxic material.

Subsequently, the high toxicity material was shown to be an organophosphorus compound termed trimethylol propane phosphate (I), and sometimes referred to as BPE or TMPP, produced by the interaction of phosphorus compounds with propoxylated trimethylol propane polyols. Phosphorus compounds are



commonly used in polyurethane foams as flame retardants but small amounts can also be present to enhance the general physical properties.

Compound (I), termed TMPP in the remainder of this report was known to Casida (see Ref.1) and in common with certain other bicyclic phosphates can induce seizure activity at very low concentrations.

Following the publication of this information, a study was carried out at the Fire Research Station, Borehamwood, as a matter of urgency to examine the general production of TMPP from the wide range of polyurethane and polyisocyanurate foams in use within the United Kingdom.

The report outlines the development of a microdecomposition system for the thermal decomposition of small amounts of foam and details are given of a collection system for the direct trapping and gas chromatographic analysis of released TMPP.

Information is given about the general collection efficiency of the apparatus and the temperature stability of TMPP. Results are presented of the TMPP released from a range of flexible and rigid polyurethane and polyisocyanurate foams of commercial origin at the time of these experiments (1974/5).

This information relates to the general decomposition behaviour of foams under carefully controlled laboratory conditions in the absence of flame. The results are required to assist the general understanding of the behaviour of materials in real fires.

It must be emphasised strongly that the results relate only to foams available at the time of these tests. It is understood that the basic polyol ingredients which are necessary for TMPP production are no longer available for commercial use in rigid foams in the United Kingdom.

2. EXPERIMENTAL

2.1. The microdecomposition and TMPP collection systems

The microdecomposition and TMPP collection systems are shown diagrammatically in Fig.1. The decomposition part consists of a silica tube (7 mm ID) held in a standard tube furnace controlled over the working length with a proportional electronic controller to better than $\pm 1^\circ\text{C}$ at 500°C , with a maximum working temperature of 1000°C . The sample of foam (1 to 2 mg) is placed into a small ceramic boat attached to the steel plug (with a length of nichrome wire) which is moved towards the furnace with an external magnet to 'inject' the sample into the hot zone for a 15 minute decomposition period.

The decomposition products including any TMPP are carried by the gas stream (dry air or nitrogen flowing into the system at 50 ml/min at 20°C) from the furnace zone to the collection tube. The collection tube is a 90 mm length of glass tubing (6 mm CD) which is packed with clean silica wool and inserted into the end of the decomposition tube as shown.

2.2. Chromatographic analysis of TMPP

The analyses of TMPP were carried out using a research gas chromatograph fitted with a phosphorus sensitive detector and a modified inlet system to accommodate the collection tubes directly without solvent extraction procedures.

A diagram of the modified injection system is shown in Fig.2. It consists of a length of stainless steel tubing (8 mm ID) connected to the normal injection port of the chromatograph as shown, with the helium supply to the chromatograph redirected through the tube.

The stainless steel tube is 250 mm long and is heated at one end to 300°C with a small furnace. A plunger (6 mm OD) is fitted onto the cold end of the stainless steel tube with a standard neoprene 'O' ring to give a gas tight sliding seal.

In operation the plunger is disconnected at the 'O' ring seal and a TMPP collection tube inserted into the cold part of the inlet system and the plunger reconnected. The TMPP tube is left in the cold section until the chromatographic detector has restabilised (usually less than 30 seconds) and then the plunger is depressed fully to insert the collection tube into the furnace zone. In this way the TMPP in the collection tube is volatilised quickly from the tube in the direct helium supply to the column.

The chromatograph was fitted with stainless steel columns (4.5 mm ID and 0.5 m long) packed with a commercially available FFAP (1 per cent) on chromosorb WAW, temperature programmed from 170 to 230°C at 10°C/min. Peak areas were determined using an electronic integrator.

All experiments were carried out using a phosphorus sensitive flame ionisation detector based on a rubidium chloride crystal, set up and operated in accordance with the manufacturer's instructions.

2.3. Mass spectrometry and NMR spectra

Mass spectrometric analyses of the TMPP solutions were carried out using an AEI/GEC MS20 instrument with an electron impact source operating at 70 eV. Samples were introduced using a standard direct insertion probe. The NMR spectrum of TMPP was obtained using a deuterated dimethyl sulphoxide solvent with tetramethyl silane as reference. A small quantity of deuteriochloroform was added to lower the viscosity.

2.4. Materials

All samples of the foams used in this report were of commercial origin. Some of the foams tested were of known composition. The foams tested are representative of the wide range of materials which were available within the UK at the time of this work, for general use within buildings. For the tests, small samples (1 to 2 mg) of the foams were cut out as core samples using a cork borer.

A small amount of trimethylol propane phosphate (TMPP) was available for the calibration and thermal stability experiments. Details are given of the examination of the TMPP by mass spectrometry, NMR and chromatography for confirmation of its chemical composition and purity. For the majority of the work outlined in this report the TMPP was used as a solution in toluene.

3. RESULTS

3.1. TMPP analysis and calibrations

The mass spectrum of the TMPP obtained by placing a small amount of TMPP (via a toluene solution) on the tip of the direct insertion probe is given in the Appendix. The spectrum shows the molecular ion at 178 with a complex fragmentation pattern which is in very good agreement with the known spectrum of TMPP. No other fragments other than those arising from TMPP and the mass spectrometer background were observed.

The NMR spectrum shows:

- (i) A three proton triplet centred at $\delta = 0.79$ ppm with coupling constant $J = 8$ Hz which is typical of chemically equivalent protons coupled to vicinal methylene protons, arising from the terminal methyl group.

- (ii) A two proton methylene quartet centred at $\delta = 1.29$ ppm.
 $J = 8$ Hz which is typical of chemically equivalent methylene protons coupled to vicinal methyl protons, ie arising from the methylene group attached to the methyl group.
- (iii) A six proton doublet centred at $\delta = 4.56$ ppm $J = 6$ Hz, due to the six bicyclic protons. The down field chemical shift is indicative of the presence of nearby oxygen atoms.

A chromatographic analysis of $1\mu\text{l}$ of a 0.1 per cent (w/v) solution of TMPP in toluene injected directly into the chromatograph with a syringe gave the distinct toluene 'solvent' peak followed by a single TMPP peak eluted at 4.5 min. The amount of TMPP eluted from the chromatograph was too low for mass spectrometric confirmation because of loss in the interface system, but the phosphorus content of the eluted component was very clear because of the marked sensitivity change with crystal position which is a characteristic of this type of chromatographic detector. Under optimum operating conditions the sensitivity of the detector to TMPP and toluene was approximately 10,000 to 1.

The work with mass spectrometry, NMR and gas chromatography confirmed the chemical nature and purity of the calibration material and enabled experience to be gained about the operation of the chromatographic detector for quantitative determinations.

For the quantitative calibrations, $1\mu\text{l}$ samples of TMPP solutions of .0001, .001 and .01 and .1 per cent (w/v) in toluene (containing 1, 10, 100 and 1000 nanograms respectively of TMPP) were injected into the calibration tubes with subsequent analysis to obtain the calibration response shown in Fig.3. This gave a calibration over a dynamic range of 10^3 and was checked regularly because of the tendency of the detector to drift from the optimum response. It was found that there was little difference between the analysis of samples by direct injection (ie by syringe into the conventional septum inlet) or via the collection tube except that in the latter case there was a tendency for peak tailing during analysis.

A chromatogram of a typical calibration run is shown in Fig.4(a).

3.2. TMPP recoveries and thermal stability

Before any foam decomposition experiments were carried out, samples of TMPP ($1\mu\text{l}$ of 0.01 per cent w/v) solution were placed into the ceramic

boat and injected into the furnace at temperatures between 200 and 900°C in nitrogen and air atmospheres and the TMPP collected in the glass collection tubes and analysed by chromatography.

The collections obtained in this way are shown in Fig.5 and are recorded as percentages of the yield obtained by direct analysis of the sample in a collection tube without passage through the furnace. In nitrogen, the low temperature collection efficiency is approximately 90 per cent. At temperatures of about 700°C thermal decomposition becomes important and at 800°C only a small percentage of the injected TMPP survives passage through the furnace. In air, the collection efficiency at low temperatures is somewhat lower than that observed in nitrogen but the reason for this is not clear. The TMPP is less stable in air than in nitrogen at the higher temperatures and only about 10 per cent of the injected TMPP survived at 700°C.

3.3. General production of TMPP from polyurethane and polyisocyanurate foams

An initial screening was carried out on a wide range of commercially available foams, by decomposing small samples (1 to 2 mg) of foam and analysing the released TMPP by the collection tube - chromatography method. This screening involved 6 flexible and 20 rigid foams at a temperature of 500°C in a nitrogen atmosphere. (This temperature was chosen by examining TMPP release from selected foams over broad bands of temperature ranges and was shown later to be slightly lower than the optimum).

The results obtained from this screening are given in Table 1.

Table 1. Yields of TMPP from the thermal decomposition of flexible and rigid polyurethane foams

Foam type	Weight per cent conversion to TMPP at 500°C in nitrogen (%)
Flexible	Zero* to 0.004
Rigid	Zero* to 0.003 or 0.1 to 0.15

*Detection limit 0.0005%

In all cases the analysis of TMPP was based on a chromatographic peak with the expected shape and retention time of TMPP. Confirmation by GC/MS was not possible because of the low levels of TMPP involved. For confirmation of the identifications, repeat experiments were carried out with the thermal decomposition 'seeded' with a small amount of TMPP. An increase in peak height without doublet formation confirmed the presence of TMPP.

In Table 1 the general figures obtained for the TMPP yields from flexible polyurethane foams range from the detection limit to .004 weight per cent conversion for a fire retarded foam. With the rigid types of foam, the observed levels of TMPP fell into one of two ranges namely zero to .003 or 0.1 to 0.15 weight per cent conversion. Further examination showed that the 'high' TMPP producers were invariably of polyisocyanurate origin with the 'low' range being predominantly polyurethane.

3.4. Temperature dependence of TMPP production from polyisocyanurate foams

Because of the relatively large amounts of TMPP released from the rigid polyisocyanurate foams, a more detailed study was carried out to examine the TMPP production over a range of temperatures for two typical commercial polyisocyanurate foams termed PI/A and PI/B for the purposes of this report.

The release of TMPP in terms of the weight per cent conversion, at temperatures between 300 and 800°C for foams PI/A and PI/B in a nitrogen atmosphere is shown in Fig.6. Also shown is the equivalent TMPP production curve for foam PI/A in air.

A typical chromatographic trace obtained during this work with foam PI/A is shown in Fig.4(b).

As can be seen in Fig.6, there is an optimum temperature for the production of TMPP of about 600°C in nitrogen and 500°C in air. In general, the two polyisocyanurate foams show similar TMPP production curves except that the PI/A maximum of 0.2 weight per cent conversion is somewhat larger than the value of 0.145 for PI/B. The presence of air reduces the maximum TMPP level but enhances the production of TMPP at lower temperatures. TMPP is detected at temperatures above about 200°C and only relatively small amounts are present at temperatures above 800°C in nitrogen and 700°C in air as expected due to the known thermal instability of the product at high temperatures (see Section 3.2 and Fig.5).

4. DISCUSSION AND CONCLUSIONS

4.1. General discussion

As part of this project a considerable amount of effort was directed, of necessity, towards establishing a means of the collection, handling and analysis of small amounts of TMPP. The use of the small glass collection tubes packed with glass wool has proved to be an effective and simple means of trapping airborne TMPP for the direct analysis of TMPP without a solvent extraction procedure with its inevitable difficulties of sample enrichment and loss.

It is not always possible to analyse TMPP near to the normal detection limit during actual thermal decomposition experiments involving foam because of interference from other peaks eluted with retention times similar to that of TMPP. The lowest level of TMPP which has been monitored in any experiment involving 2 mg of foam is 0.00005 weight per cent conversion. This corresponds to the analysis of one nanogram (10^{-9} g) of TMPP, and based on a nitrogen flow through the apparatus of 50 ml/min for 15 minutes is equivalent to an average concentration of approximately 1.33 ng/litre (1.8×10^{-4} ppm).

As yet, the collection tube analysis system has not been used to monitor TMPP during real fire tests but a limited number of experiments with airborne TMPP indicate the potential of the method for atmospheric monitoring work of this kind. TMPP stored in glass tubes with the ends sealed with silicone rubber tubing has sufficient life to allow the delayed analysis of samples.

4.2. TMPP production from rigid polyurethane and polyisocyanurate foams

The initial screening experiments were carried out with flexible and rigid polyurethane foams at a temperature of 500°C which was later shown to be slightly lower than the optimum temperature for formation, but nevertheless, gave valuable information about potential release. In this way it has been shown that certain polyisocyanurate foams are potential producers of TMPP giving yields of TMPP of about 40 times the maximum recorded levels for all the other flexible and rigid foams monitored in this project.

A more detailed study of the polyisocyanurate foams has shown that there is a marked temperature dependence of TMPP production with the optimum temperature being about 600°C in an inert atmosphere (500°C in air). It is likely that this maximum is formed as a result of production competing with destruction.

No attempts have been made in the work of this report to correlate TMPP production with either the phosphorus content or other physical and chemical composition details of the foams. It must be emphasised that this work was carried out to obtain direct information about the possible yields of TMPP from the wide range of commercial polyurethane foams in use in the United Kingdom up to and including the 1974/75 period when this concern was expressed.

The work is of a basic laboratory nature and supplements other detailed studies to assess the overall hazard of TMPP producing foams in fire situations. This additional work which involves both analytical and animal testing procedures is being carried out internationally, particularly in Europe and North America.

It must be emphasised that this work was carried out with foams available in the UK up to 1974/75. It is understood that the trimethylol propane polyols which combine in some way with the phosphorus additive during decomposition to produce the highly toxic TMPP, are no longer used in the manufacture of rigid polyurethane and polyisocyanurate foams.

5. ACKNOWLEDGEMENTS

The authors wish to thank the International Isocyanate Institute for many helpful discussions during the course of this work, particularly in relation to the chromatographic analysis of TMPP.

6. REFERENCES

1. EINHORN, I N et al. Extreme toxicity from combustion products of a fire retarded polyurethane foam. Science, Vol 197, 1975 p.742.

APPENDIX

Mass spectrum of TMPP at 70 eV by direct insertion probe (100-150°C).

The ten largest peaks are given.

<u>m/e</u>	<u>Intensity</u>
68	100
67	81
41	56
79	59
151	19
178	11
39	52
80	22
150	44
47	22

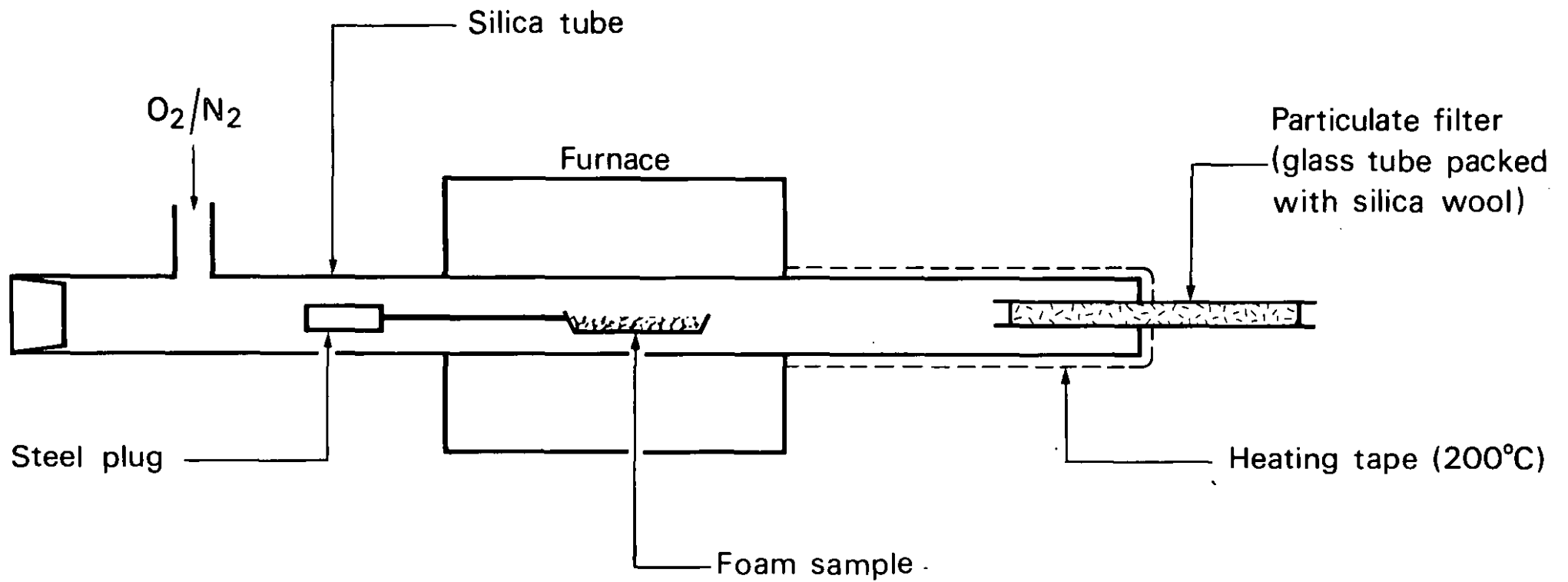


Figure 1 The microdecomposition and TMPP collection system

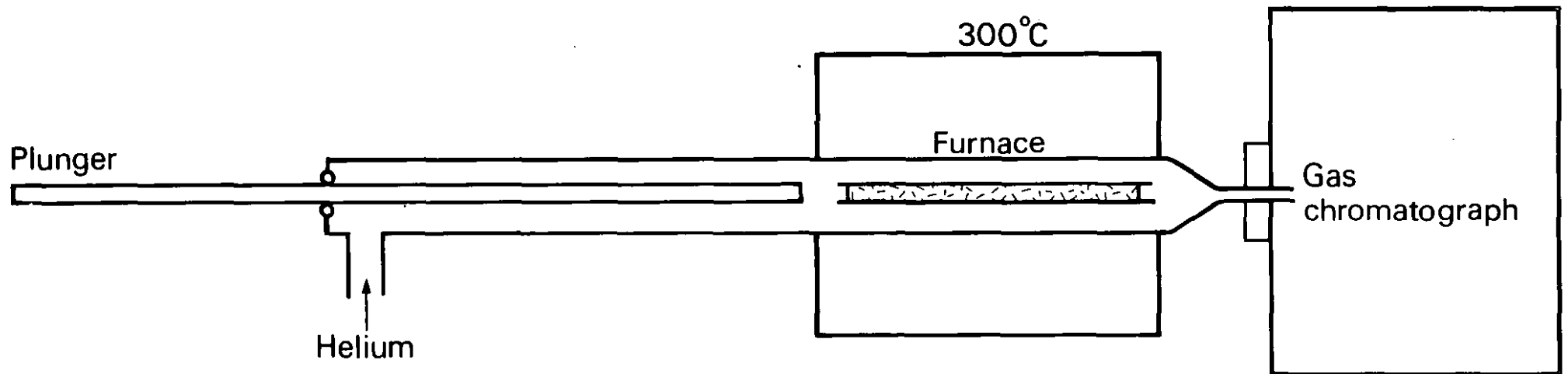


Figure 2 Chromatographic inlet system for TMPP sample tubes

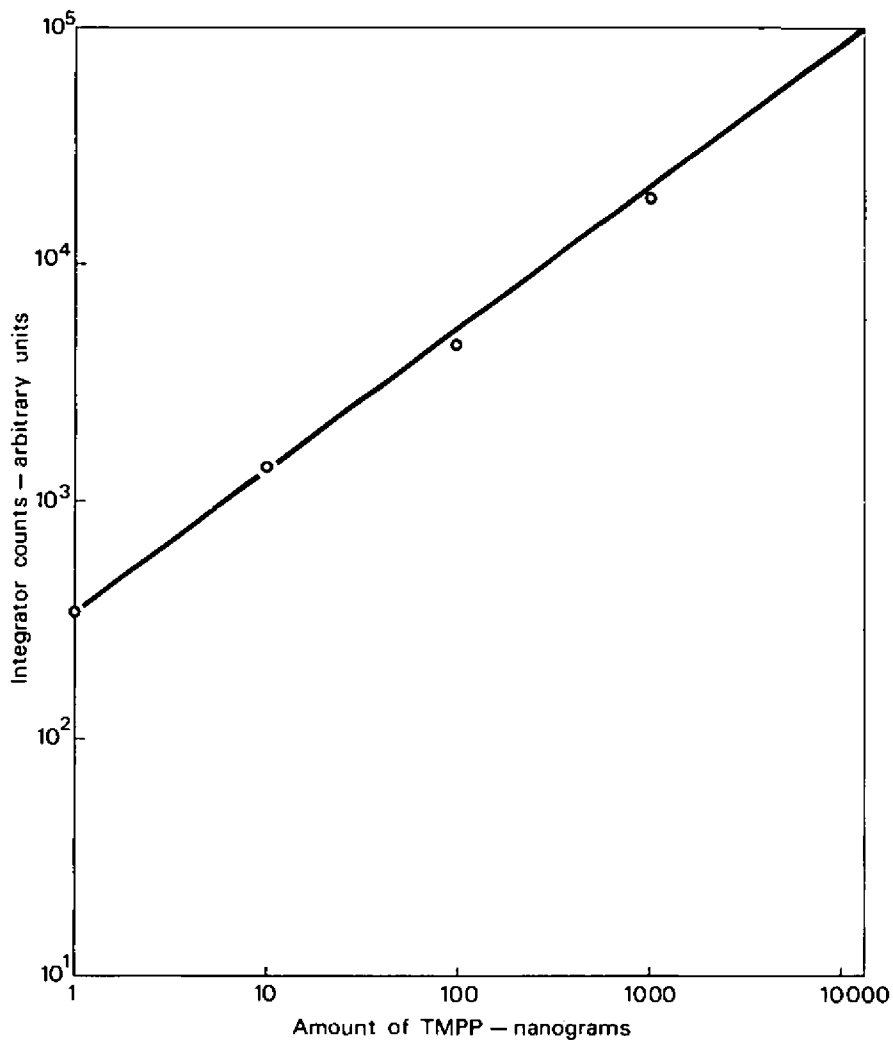


Figure 3 Typical calibration response for TMPP analysis using the specific phosphorus detector

660.

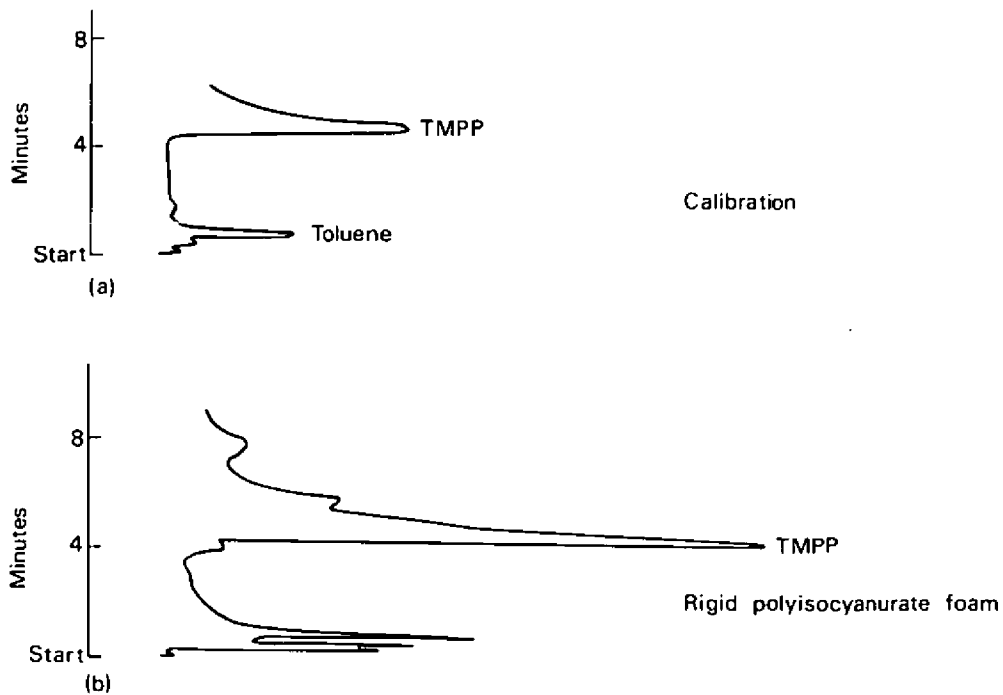


Figure 4 Chromatographic traces obtained during calibration and foam decompositions

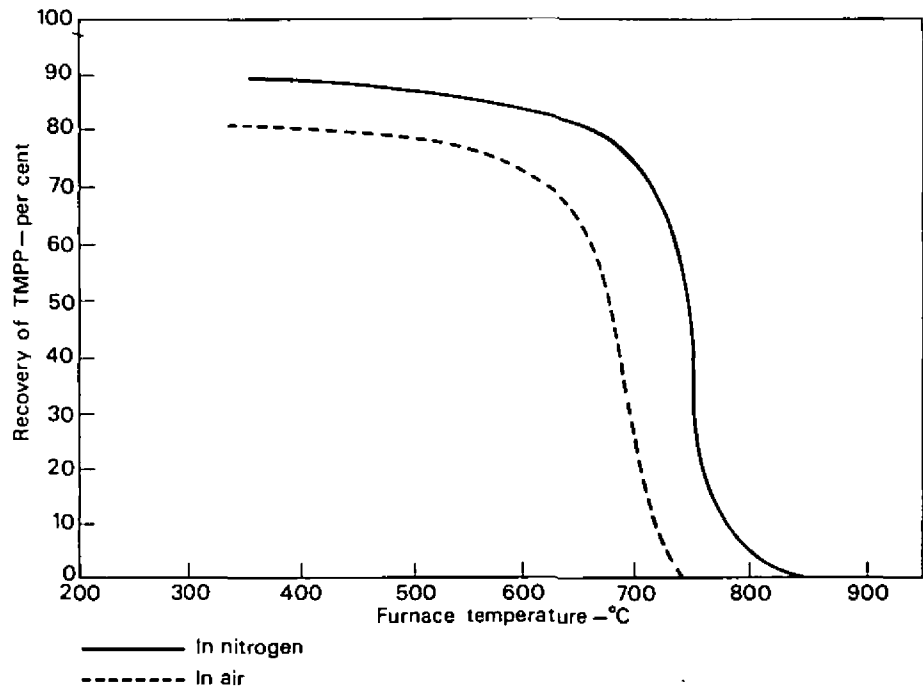


Figure 5 Recovery of TMPP from the furnace

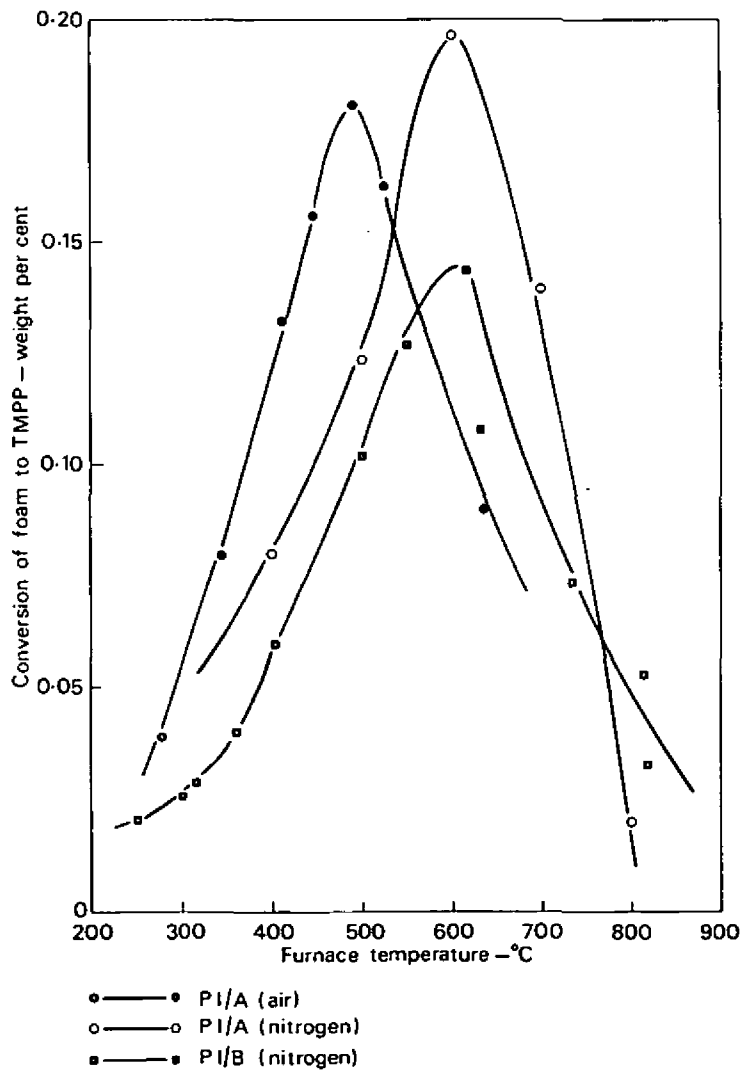


Figure 6 Release of TMPP from foams PI/A and PI/B