Thermochimica Acta, 166 (1990) 41–52
Elsevier Science Publishers B.V., Amsterdam

THERMAL ANALYSIS–MASS SPECTROMETRY AND THERMOGRAVIMETRIC ADSORPTION ON FIRE RETARDANTS *

A. KETTRUP [1,2], K.-H. OHRBACH [1], G. MATUSCHEK [2] and A. JOACHIM [1]

[1] *University GH Paderborn, FB 13, Applied Chemistry, P.O. Box 1621, D-4790 Paderborn (F.R.G.)*

[2] *Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-8042 Neuherberg (F.R.G.)*

ABSTRACT

Simultaneous thermal analysis mass spectrometry and an off-line combustion technique were applied to different fire retardants. The samples were commercial products (phosphorus ester compounds containing chlorine substituents). A thermogravimetric adsorption device was developed to adsorb the degradation products of the samples depending on the temperature. Identification of the adsorbed compounds was carried out using gas chromatography–mass spectrometry.

INTRODUCTION

Fire disasters have always been an enormous danger, but it is only now that changes in the ecosystems effected by fires have gained increasing significance. For this reason and with respect to fire protection, newly developed materials (especially those used in buildings of all kinds) must be flame- or fire-protected. To achieve a sufficient level of fire protection, suitable fire or flame retardants are added after or during the polymerization process.

The basic function of fire retardants is to prevent the propagation of flames, i.e. to retard or to inhibit a burning process, and at best to stop it completely. Depending on the type of burning or smouldering material and on the fire conditions additional health risks which result from the composition of the fire effluents may arise.

---

* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

0040-6031/90/$03.50

EXPERIMENTAL

Equipment

Besides the traditional thermal analysis methods such as TG, DTG, DTA and DSC we performed simultaneous thermal analysis–mass spectrometry (TA–MS). The equipment consists of a Netzsche STA 429 thermal analyzer and a Balzers QMG 511 mass spectrometer. The computer hardware is from Digital Equipment Co. The software package, including all graphic options, is self-designed. The DSC instrument is a Perkin–Elmer DSC 7 and for the on-line thermogravimetric adsorption technique we used a Perkin–Elmer TGA 7 thermobalance and a self-constructed adsorption device. For the TA–MS experiments we used, in most cases, a weighed sample of about 20 mg in alumina crucibles with an empty crucible as a reference. The desired atmospheric conditions are adjusted by means of a gas-flow control. The sample gases and the decomposition products are expelled during the linear heating process and pass through a two-stage gas inlet system. This is manufactured from ceramic tubes and the gases pass through orifices of a defined size at the base of the tubes. The internal space between the ceramic tubes is evacuated to about 600 Pa by means of a rotary pump, and the high vacuum of about 10^{-3} Pa in the sample cell of the quadrupole mass spectrometer is produced using a turbomolecular pumping system. The decomposition products are ionized by means of a rhenium ion source. For further information see refs. 1–12.

The mass spectra data are recorded in temperature intervals of 10 K up to the final temperature of each experiment. It is advantageous in some cases to use a mixture of argon and oxygen instead of air, because in this way the superimposition of important sample components by elements and compounds in air is absolutely excluded.

A simple construction was developed for the adsorption of volatile compounds simultaneously with thermogravimetric experiments in defined gas mixtures or an inert gas atmosphere. The quartz tube of the Perkin–Elmer TGA 7 thermobalance was connected to a modified adsorption mechanism. In all cases a flow control and a suitable pumping system permitted a maximum adsorption efficiency from ambient temperature up to the maximum working temperature of the TG instrument without interfering with the TG curves. The adsorbents were XAD-4 resin and NIOSH charcoal tubes. The charcoal tubes were additionally cooled.

Off-line combustions were carried out in a Bayer–ICI–Shell apparatus, a VCI combustion furnace and, if necessary, as an open flame combustion in accordance with a special German legal regulation [13–18].

The methods applied are listed in Table 1.

The fire retardants were dimethylmethylphosphonate (DMMP), diethyl-*N*,*N*-bis(hydroxyethyl)aminomethylphosphonate (DAMP), tris(β-chloroiso-

TABLE 1

Applied methods

No.	Thermal analysis (TA) methods	Combustion methods
1	Thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA)	
2	Thermal analysis–mass spectrometry (TA–MS), differential scanning calorimetry (DSC)	
3	On-line thermogravimetry adsorption technique with subsequent GC or GC–MS analysis	
4	Modified Bayer–ICI–Shell (BIS) apparatus	
5 [a]	Combustion using the VCI (Verband der Chemischen Industrie) apparatus	
6 [a]	Open flame combustion furnace (OFCF)	

[a] Methods 4, 5 and 6 include an adsorption technique followed by desorption and GC, GC–MS, or HRGC–MS analysis.

propyl)phosphate (TCPP), and tris(chloroethyl)phosphate (TCEP). All commercial products are of technical grade with unknown specifications with the exception of their physical properties.

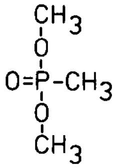
RESULTS AND DISCUSSION

With regard to polymers, a distinction is made between fire retardant additives and reactive fire retardants. Fire retardant additives are not strongly bound in the polymeric structure because they are only added to the polymer material after polymerization. This is in contrast to the reactive compounds which are added during the polymerization process and are strongly bound in their structural elements. In polymers, therefore, the volatility of the reactive products is lower than that of the additive compounds.

Dimethylmethylphosphonate

The structure of the fire retardant DMMP is shown in Fig. 1. DMMP is a colourless liquid having a fluid point of −50 °C, a vapour pressure of 2660 Pa at 65 °C and a phosphorus content of 50%. It is slightly volatile at room temperature. DMMP is a fire retardant additive.

DMMP decomposes in air in a two-stage weight loss of 90% and 9% (see Fig. 2). The second mass loss possibly results from the formation of residual



$$O{=}\overset{\overset{CH_3}{|}{O}}{\underset{\underset{CH_3}{|}{O}}{P}}{-}CH_3$$

Fig. 1. Structure of the fire retardant DMMP.

oxidation products. This assumption can be confirmed because in an argon atmosphere the same experiment only showed a one-stage weight loss of nearly 100%. The undecomposed vaporization of the compound is accompanied by a strong endothermic DTA peak with a maximum at 338 K. To confirm this result we performed simultaneous thermogravimetric adsorption.

The flame ionization gas chromatograph of the adsorbed volatile components of DMMP which are separated on a fused silica column is shown in Fig. 3. The experiment was performed in air flow. An adsorbent XAD-4 resin was used. The adsorbed compounds were desorbed using acetone as a desorption solution. The internal standard was in most cases tetradecane. For the identification of all fire retardants, the pure compounds were used as reference substances. The amount of the undecomposed fire retardant

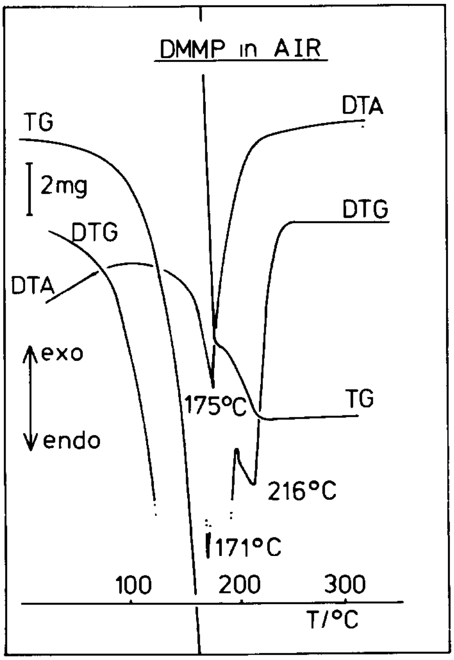


Fig. 2. Thermal analysis curves for DMMP.

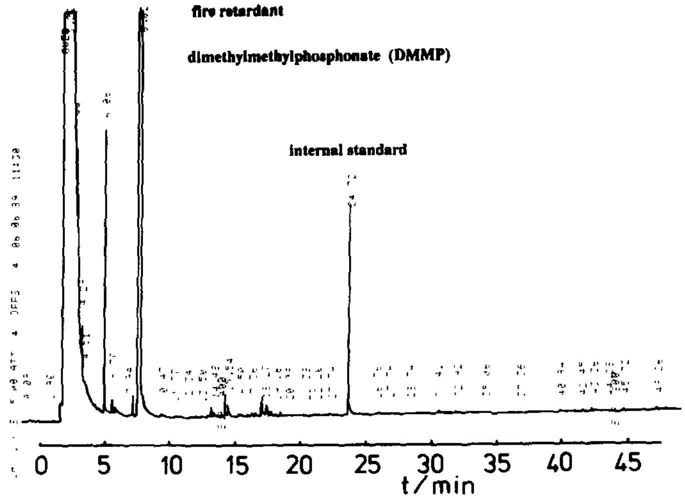


Fig. 3. Gas chromatograph of DMMP.

was 38% in air and 43% in an inert gas atmosphere. The other peaks are as yet unidentified.

The mass spectrum of DMMP in Fig. 4 was recorded in an argon/oxygen mixture at a temperature of 493 K using the Netzsch–Balzers TA–MS coupling system. The spectrum shows a base peak at a mass-to-charge ratio of 79, representing three different structural elements. The molecular ion is detected at 124. The successive cleavage of the three methyl groups resulting in peaks at 109, 94 and 79 on the mass scale is clearly shown by this mass spectrum.

Diethyl-N,N-bis(hydroxyethyl)aminomethylphosphonate

The flame retardant DAMP (see Fig. 5) is a yellowish liquid having a phosphorus content of 25%, a nitrogen content of 5.5% and a vapour pressure of 1800 Pa at 338 K. In contrast to DMMP, DAMP is applied as a reactive phosphonate ester.

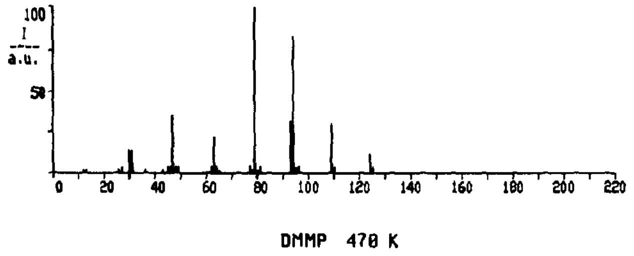
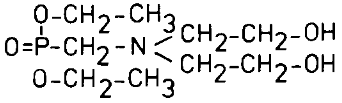


Fig. 4. Mass spectrum of DMMP in an argon/oxygen mixture ($m/z = 0$–220 a.m.u.).



$$O=\overset{\displaystyle O-CH_2-CH_3}{\underset{\displaystyle O-CH_2-CH_3}{P}}-CH_2-N\begin{matrix}\nearrow CH_2-CH_2-OH\\ \searrow CH_2-CH_2-OH\end{matrix}$$

Fig. 5. Structure of the fire retardant DAMP.

The thermal analysis curves of DAMP (see Fig. 6) were recorded in air flow. In all experiments the air-flow rate is adjusted to a value of about 20% above the leaking rate of the gas inlet system. Higher values effect very low detection limits in the mass spectrometer because the volatiles are transported out of the furnace by the air flow through a gas outlet installed as a necessity which avoids an overpressure in the furnace.

The TG/DTG curves show three stages of weight loss. A total weight loss of 88% and 12% residual char were determined. The last weight loss with a maximum reaction temperature of 626 ° C results mainly from the formation of carbon monoxide in equilibrium with carbon dioxide and water. This is a result taken from the mass spectrometric evaluation.

The experiment in argon leads to only two stages of weight loss and a total weight loss of 75%. The third weight loss could not be detected. The temperatures of both DTG peaks are shifted to higher values. The shapes of the DTA curves are very unspecific in both TA–MS runs.

The mass spectra of DAMP shown in Fig. 7 are not very representative. The detection of the molecular ion peak for the undecomposed DAMP was not possible in air, argon/oxygen nor in pure argon flow. We found the highest mass fragment at 157. The base peak at 31 a.m.u. results from the cleavage of methylene ions from the ethoxy groups to form a methoxy ion, as well as from the nitrogen-bound hydroxyethyl substituents. In the argon

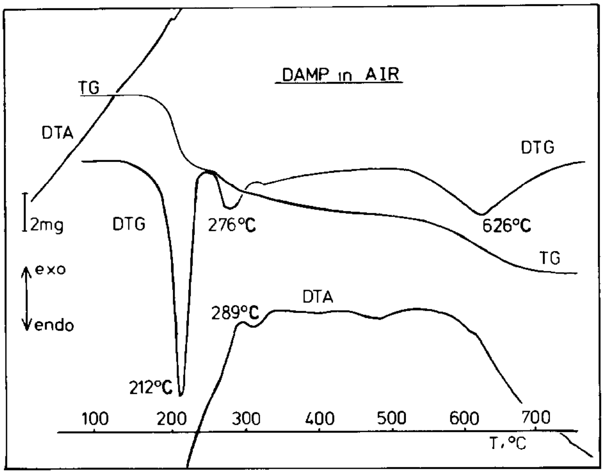


Fig. 6. Thermal analysis curves for DAMP.

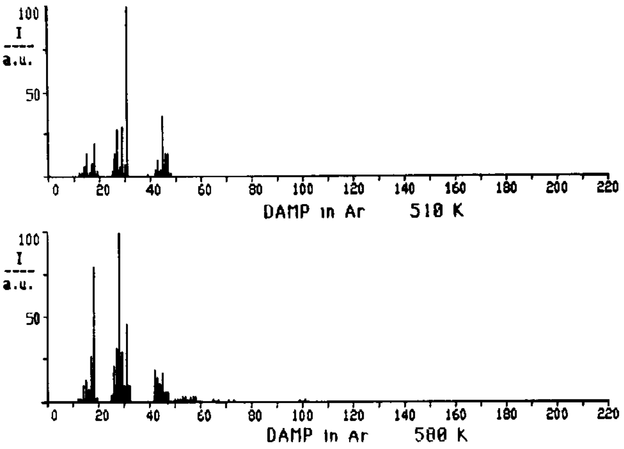


Fig. 7. Mass spectra of DAMP in argon at (top) 510 K and (bottom) 580 K ($m/z = 0$–220 a.m.u.).

spectrum only fragments in the mass range of C_4 units occur. Additionally, the water as well as the hydroxyl and the carboxyl ion concentrations have increased. From the molecular structure, we expected the formation of pyridine-, pyrazoline- and morpholine-related compounds for the thermal degradation of this compound, as reported in the literature. However, the results have shown that these compounds could not be detected. This is possibly an effect of insufficient sensitivity of the quadrupole mass spectrometer and not of the thermal instability of the fire retardant DAMP.

The reproducibility of the DSC curves of DAMP was not satisfactory in wide ranges. Between 200 °C and 250 °C the shapes of the DSC curves show superimposed vaporization and decomposition effects, particularly in the range of the maximum reaction rates.

The gas chromatograph obtained from the adsorption of the volatiles of DAMP (Fig. 8) clearly shows a reduced concentration for the undecomposed fire retardant at a retention time of 32 min (not show in this figure). This is in agreement with the simultaneously recorded TA–MS results. These thermogravimetric fingerprint gas chromatographs show a higher degree of reliability than expected. A disadvantage is the time-consuming identification and quantification of the decomposition components. For these and other series of fire retardant materials, this work is continuing. Only for DAMP have we identified 11 compounds by using the TG adsorption technique. The compounds were identified as pyrimidine (1), pyridine (2), methylmorpholine (3), 3-pyridine amine (4), 2,3- or 4-methylpyridine (5), 4-ethylmorpholine (6), ethylpyrazine (7), 2,3-dimethylpyrazine (8), *N*,*N*-dimethyl-4-pyride amine (9), a pyrolidine derivative (10) and a phosphonic acid ester (11).

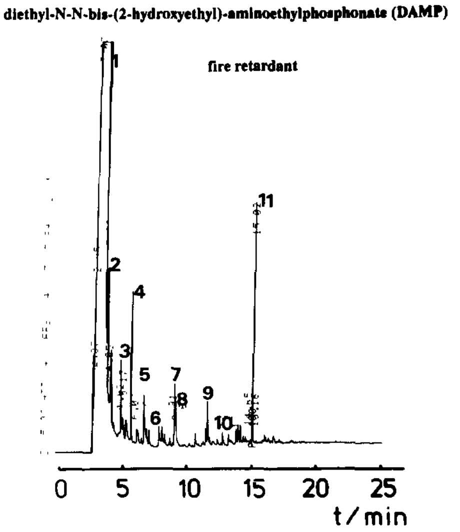


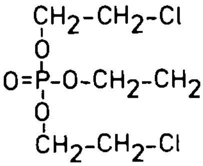
Fig. 8. Gas chromatograph of DAMP.

Tris-(β-chloroethyl)phosphate

The first retardant TCEP (for structure, see Fig. 9) is a phosphorus- and chlorine-containing liquid fire retardant having the additional properties of a plasticizer. The phosphorus content amounts to 11% and the chlorine content to 37%. TCEP has a vapour pressure of about 2500 Pa at 65 °C.

The thermal analysis curves of TCEP are shown in Fig. 10. TCEP vaporizes completely in argon and air atmospheres. In an air atmosphere we determined two stages of weight loss with maximum reaction rates at about 300 °C and 520 °C. The main decomposition products during the small second weight loss are carbon dioxide and water. The degradation in an argon atmosphere occurs only in one step.

From each recorded mass spectrum it is possible to represent each detected peak as a function of the temperature by use of a special software option (see Fig. 11). The curve in Fig. 11 shows the formation of hydrogen chloride from TCEP; only the HCl with ^{35}Cl is shown. The generation of HCl starts at about 430 K and reaches maximum intensity at 570 K. This is



$$\begin{array}{l} CH_2-CH_2-Cl \\ | \\ O \\ | \\ O=P-O-CH_2-CH_2-Cl \\ | \\ O \\ | \\ CH_2-CH_2-Cl \end{array}$$

Fig. 9. Structure of the fire retardant TCEP.

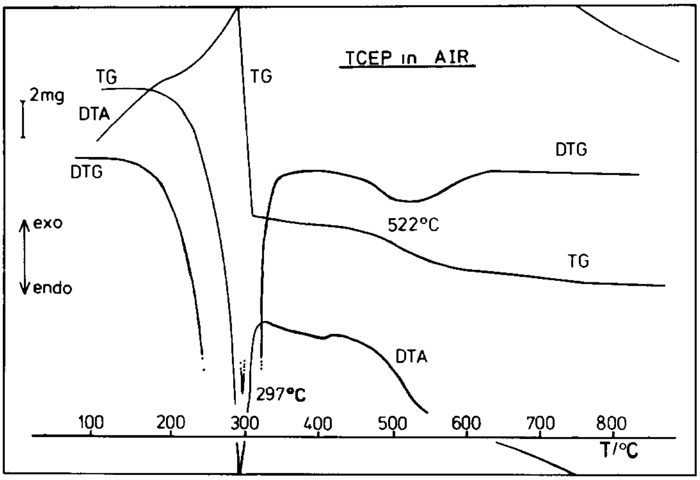


Fig. 10. Thermal analysis curves for TCEP.

exactly the temperature of the DTG maximum. The same evaluation routine permits graphical representation of all ion-current-corresponding mass fragments, sums of selected mass ranges and the total ion current from all stored mass spectrophotometric data.

Tris-(β-chloroisopropyl)phosphate

The structure of TCPP is shown in Fig. 12. TCPP is a colourless liquid having a phosphorus content of 9.5% and a chlorine content of 32.5%. The liquid point is at −40 °C and the vapour pressure at 65 °C is 900 Pa. TCPP is a fire retardant additive. In argon, as well as in air, the substance vaporizes completely.

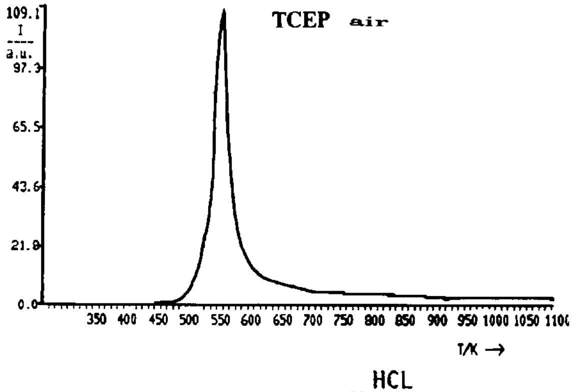


Fig. 11. Ion current intensity of $H^{35}Cl$ from TCEP.

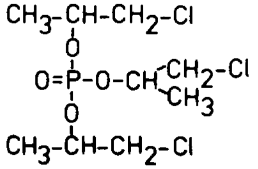


Fig. 12. Structure of the fire retardant TCPP.

In air TCPP decomposes in two stages with maximum decomposition rates at about 260 ° C and 630 ° C (see Fig. 13). The DTA maximum was determined at 270 ° C, from the oxidative degradation of the product which is superimposed by a rapid evaporation. The residual char products are decomposed slightly between 260 ° C and about 700 ° C.

The simultaneously recorded mass spectra show a strong fragmentation in the first DTG maximum in air as well as in an argon atmosphere. The molecular ion peak was not detected. In an argon flow, the highest mass fragments were observed at about 280 a.m.u. In an argon/oxygen mixture only decomposition products up to 78 a.m.u. were formed. Vinyl chloride may be formed by a simple reaction mechanism during the thermal treatment of TCPP.

The determination of the vinyl chloride (*m*/*z* 62, 64) temperature concentration profile is shown in Fig. 14. Both compounds are formed at 450 K and reach a maximum intensity at 510 K in this gas mixture. The ratio of the intensities is 3 : 1, which is in agreement with the relative natural abundance of the chlorine isotopes. We have performed the same experiment in argon atmosphere. The shapes of the ion current intensities, as well as the initial

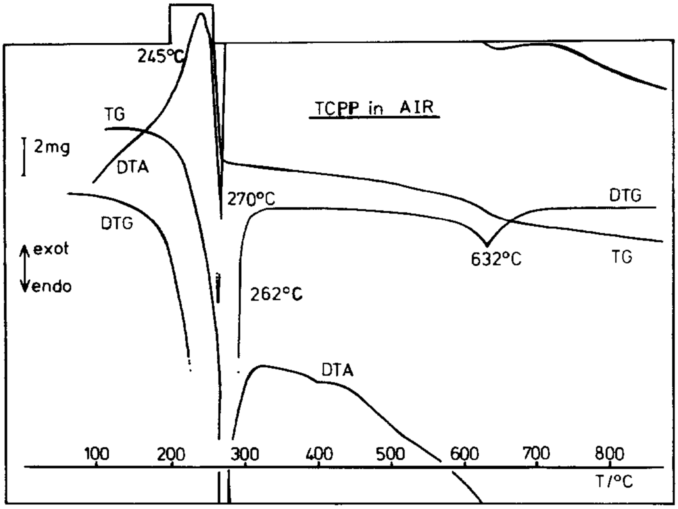


Fig. 13. Thermal analysis curves for TCPP in air.

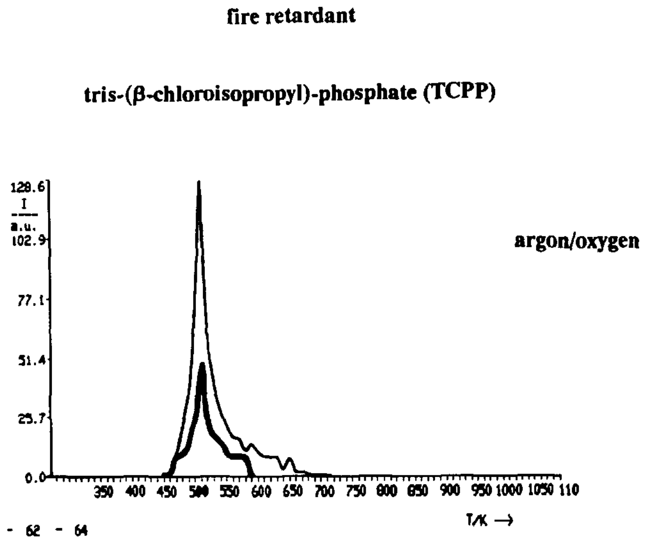


Fig. 14. Ion current intensities of vinyl chloride from TCPP in an argon/oxygen atmosphere.

and final temperatures, are quite similar; only the maximum intensity is shifted to a higher temperature value at 540 K.

CONCLUSION

The task of simulating real burning conditions for a great variety of materials is very difficult. It depends on the residence time of samples in burning chambers, on the air supply and on the temperature. The accompanying problem, the identification of decomposition products, also becomes more difficult with burning a greater number of individual substances or even mixtures.

This contribution describes different thermal analysis methods for the investigation of fire retardants as an approach to an additional suitable tool for supplementing the usually applied fire gas test methods. It was not the objective to discuss ecotoxicologic effects of fire effluents, especially of biological hazards which may be formed in such processes. If required, in addition to the further development of combined thermal analysis techniques this may be the next step. We believe that improvement of the on-line thermal analysis adsorption method followed by subsequent separation is needed for complete characterization of thermally treated substances of all types.

REFERENCES

1 K.-H. Ohrbach and A. Kettrup, Prepr. Pap. Natl. Meet. Div. Fuel Chem., Am. Chem. Soc., 29 (2) (1984) 12.

2 K.-H. Ohrbach, W. Klusmeier and A. Kettrup, Fresenius Z. Anal. Chem., 320 (7) (1985) Appendix.

3 K.-H. Ohrbach, G. Radhoff and A. Kettrup, Thermochim. Acta, 85 (1985) 403.

4 K.-H. Ohrbach and A. Kettrup, J. Polym. Degradation Stability, 13 (1985) 99.

5 A. Kettrup, K.-H. Ohrbach and G. Matuschek, Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie, Hamburg, Forschungsbericht 356, 1985, p. 70.

6 K.-H. Ohrbach, G. Matuschek, A. Kettrup and K. Henning, Thermochim. Acta, 108 (1986) 175.

7 K.-H. Ohrbach, G. Matuschek and A. Kettrup, Thermochim. Acta, 112 (1987) 101.

8 K.-H. Ohrbach, A. Kettrup and G. Matuschek, Office for Official Publications of the European Communities, EUR 11150, Luxembourg, Catalogue No. CD-NA-11150-3A-c, 1987, p. 39.

9 K.-H. Ohrbach, A. Kettrup and G. Matuschek, Proc. 4th Conf. on Indoor Air Quality and Climate, Vol. 3, Oraniendruck, Berlin, 1987, p. 241.

10 K.-H. Ohrbach, G. Matuschek and A. Kettrup, Biomed. Environ. Appl. Mass Spectrom., 16 (1988) 447.

11 K.-H. Ohrbach, G. Matuschek and A. Kettrup, J. Therm. Anal., 35 (1988) 291.

12 A. Kettrup, K.-H. Ohrbach and G. Matuschek, in M. Earnest (Ed.), Proc. 17th North American Thermal Analysis Society Conf., Orlando, FL, Vol. II, 1988, p. 613.

13 W. Klusmeier, A. Kettrup and K.-H. Ohrbach, J. Thermal Anal., 29 (1989) 291.

14 W. Klusmeier, K.-H. Ohrbach and A. Kettrup, Polym. Degradation Stability, 13 (1985) 121.

15 W. Klusmeier, P. Vögler, K.-H. Ohrbach, H. Weber, and A. Kettrup, J. Anal. Appl. Pyrol., 14 (1988) 25.

16 W. Klusmeier, P. Vögler, K.-H. Ohrbach, H. Weber and A. Kettrup, J. Anal. Appl. Pyrol., 13 (1988) 277.

17 W. Klusmeier, K.-H. Ohrbach and A. Kettrup, Thermochim. Acta, 103 (1986) 231.

18 W. Klusmeier, R. Sonnemann, K.-H. Ohrbach and A. Kettrup, Thermochim. Acta, 112 (1987) 75.