Journal of Thermal Analysis, Vol. 35 (1989) 291–303

THERMAL DEGRADATION OF POLYMERS AND FLAME RETARDANTS

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We have carried out simultaneous Thermal Analysis / Mass Spectrometry by use of a Netzsch STA 429 Thermal Analyzer (TG–DTG–DTA) combined with a Balzers QMG 511 quadrupole Mass Spectrometer.

The combined apparatus is interfaced to a Digital Equipment PDP 11/23+ microcomputer. The complete set of the TA/MS data obtained simultaneously after each run results in detailed information about the thermal degradation of a sample material in general and in addition about the structure–temperature dependent fragmentation. Experiments by use of a Perkin–Elmer DSC 7 Thermal Analysis Station leads to quantitative determination of the characteristic data.

To solve different types of analytical problems the application of different kinds of sensitive analytical methods are needed. From a part of our current studies we have selected some topics to be presented in this paper. The task is to determine the thermal stability of a PVC flooring, hexabromobenzene, dibromopropyldiane and to identify the evolved products in dependence on the temperature. These investigations are conducted especially in connection with the subjected matter.

Experimental

Apparatus: Netzsch STA 429 Thermal Analyzer
Balzers QMG 511 Quadrupole Mass Spectrometer
Digital Equipment PDP 11/23+ Microcomputer
Perkin–Elmer DSC 7, TGA 7 Thermal Analysis Station
Hewlett Packard 5870, 5890 GS/MS Analysis System
Verband der Chemischen Industrie (FRG) Vertical Combustion Furnace

Instrumental Parameters: TA/MS; 5 deg/min heating rate, 0.05 mV DTA measuring range, 12.5 mg TG measuring range, air atmosphere, ambient pressure, alumina oxide crucibles, alumina oxide as reference material, DSC; 20 deg/min heating rate variable measuring ranges, alumina pans, empty pan as reference material, nitrogen atmosphere, ambient pressure.

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Sample material: commercial products of technical grade. All these techniques complement each other to give a significant characterization in dependence on the sample and instrumental parameter like heating rates, particle sizes and the applied atmospheres. In addition we have performed combustion experiments on polyvinylchloride floorings, brominated flame retardants and on chlorinated aromatic compounds by means of a vertical arranged combustion apparatus [1,2].

Results and discussion

The main objective of these tests in connection with the TA/MS experiments has been to investigate the composition of the fire gases with respect to fire scenarios. This intention nowadays is of great interest too with regard to the combustion of polymers in waste incinerating plants and the detection of ecological harmful substances.

The combustion unit consists of a two-zone furnace, capable of being opened. The combustion chamber is preheated and is loaded through a special charging device. The samples are decomposed applying different air flow rates and temperatures of 400, 600, 800 and 1000°. The decomposition e.g. combustion products are adsorbed on suitable resins and charcoal tubes which are connected in series. After desorption they are identified by means of High Resolution Gas Chromatography / Mass Spectrometry (HRGC/MS) followed by quantification using Gas Chromatography (GC). The application of different combustion temperatures as well as different air flow rates influences the kind and the composition of the degradation products. They can be either generated by cleavage of bondings from the sample material or by secondary reactions in the gas phase.

A typical chromatogram of a PVC flooring sample is shown in Fig. 1.

The thermal decomposition of PVC leads to the formation of a great number of different organic compounds. These chromatograms represent the separation of the components which have been adsorbed during an experiment at 400 e.g. 1000°. The indicated peak numbers are corresponding with fire gas components we have identified by use of GC/MS and comparison of the GC retention times after injecting reference materials.

At a combustion temperature of 400° the main decomposition products have been aromatic compounds like benzene, tolouene, styrene, naphthalene and so on. The main peak in the chromatograms at 400 and 600 ° labelled as number thirteen has been detected to be phtalic acid ester anhydride a significant plasticizer degradation component.

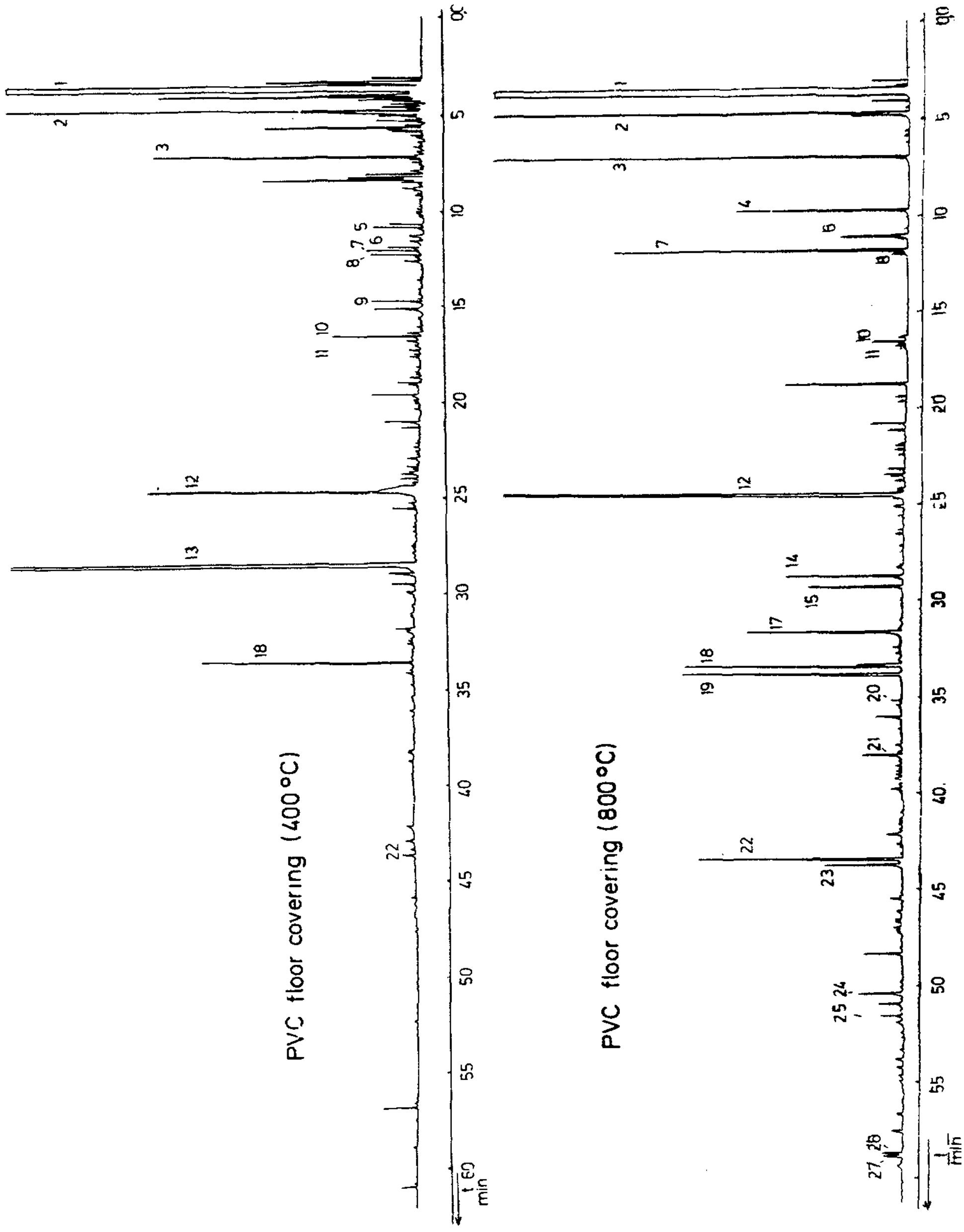


Fig. 1 Chromatograms of a PVC flooring material

Without discussing further details from our results it can be drawn that the composition and concentration of the combustion products changes drastically dependent on the temperature increase up to 1000° and on the residence time of the sample.

Our instrumental TA/MS equipment now works since seven years as a laboratory routine method mainly to solve problems resulting from industrial manufacturing of a broad variety of sample material [2–36].

In view of the fact that mass spectra only can be recorded under high vacuum conditions a pressure reduction system is required. For this purpose the 1600 K furnace is connected with the recipient of the MS apparatus via a special interface to realize a pressure drop from ambient pressure to a constant value of 10^{-3} Pa.

This interface is available either manufactured of quartz glass or of high temperature stable ceramic tubes depending on the desired upper working temperature limit.

These tubes permit on the one hand the necessary pressure reduction from ambient pressure in the furnace of the thermal analyzer up to 10^{-3} Pa in the mass spectrometer. On the other hand they serve as a gas inlet system into the recipient of the MS. The tubes are concentrically mounted one above each other on stainless steel flanges and then connected with the recipient. They are equipped with defined orifices at their bottoms. A ceramic protective tube surrounds the gas inlet system.

But it has to be mentioned that the similar constructed low cost quartz glass gas inlet system has been proved to be very suitable in more than eighty percent of our applications depending on the thermal stability of the sample material.

The following Fig. 2 represents schematically the scheme of the TA/MS instrument. The experiments can be carried out under ambient pressure in air, inert gas atmosphere as well as in defined reaction gas mixtures. The flow rates of the applied gases always have to be adjusted to the same values as the leaking rates of the gas inlet systems which are differing in some cases.

During the experimental procedure the heating of a polymer may effect an evolution of volatiles. These volatiles pass the outer orifice of the gas inlet due to the first pressure drop from ambient pressure up to a mean value of 600 Pa in the space between the outer and the inner tube of the gas inlet. The evacuation of the recipient by use of a turbo-molecular-pumping unit causes the second pressure reduction. In this way the compounds released reach the electron impact rhenium ion source for ionization.

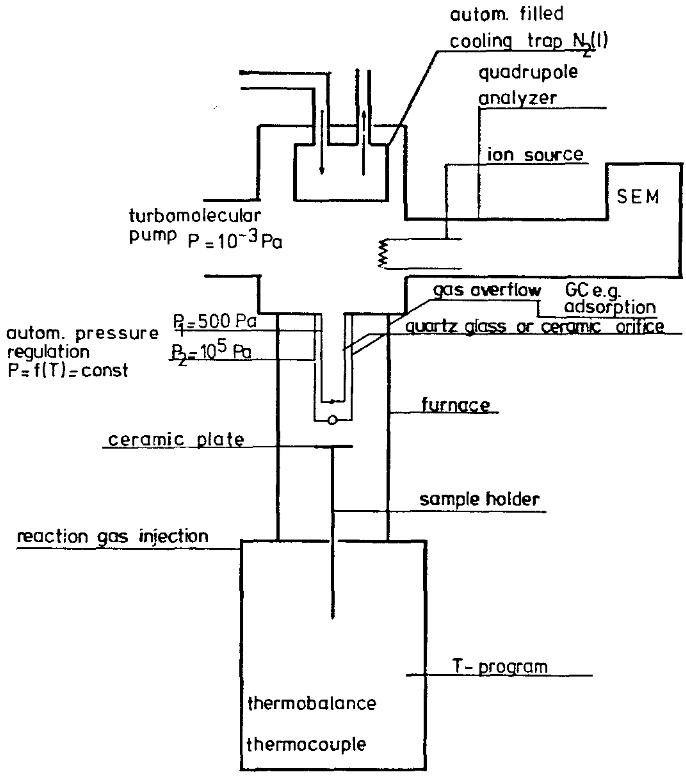


Fig. 2 2 Scheme of the TA/MS instrument

In order to avoid great pollutions of the ion source and the quadrupole system we don't perform high vacuum experiments in the thermal analyzer.

It is very important to note that the working pressure in the MS has to be constant. A variation dependent on the temperature of the furnace leads to uncomparable and unreliable MS data.

The thermal degradation of the PVC material in air atmosphere at ambient pressure which occurs via a five step mass loss of nearly 80% in the temperature range from 200 to 780°. The maximum reaction rates have been determined at 300, 440, 525, 628 and 782°, see Fig. 3.

The residue of 20% mass is due to the presence of undecomposed inorganic matter like fillers, stabilizers, other additives and to the formation of char. The decomposition behaviour of PCV in air atmosphere is expectedly of strong exothermic nature. PVC products burn at high temperatures always accompanied by formation of carbonization products.

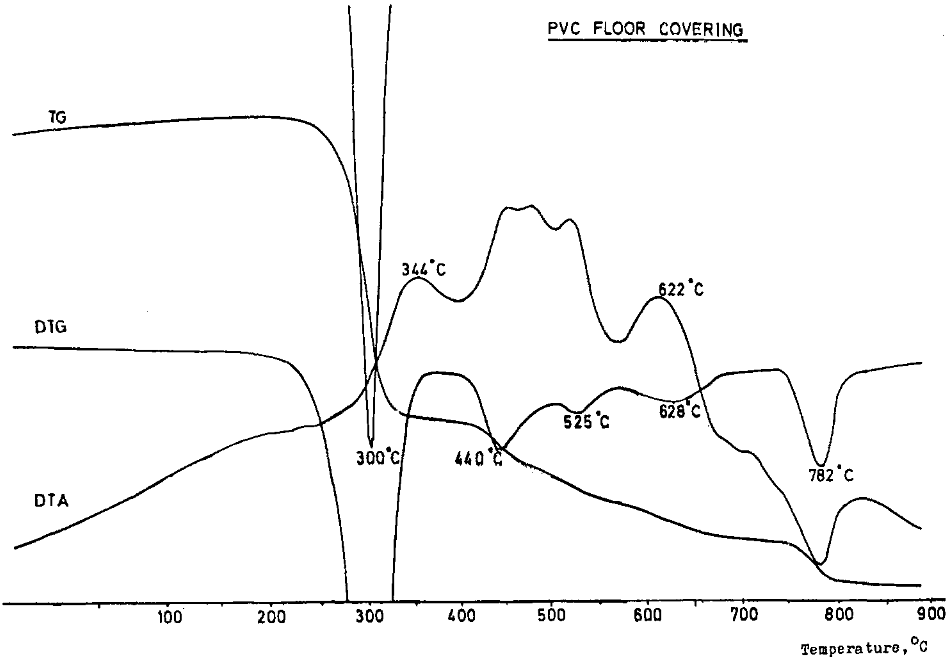


Fig. 3 TA curves of a PVC flooring material

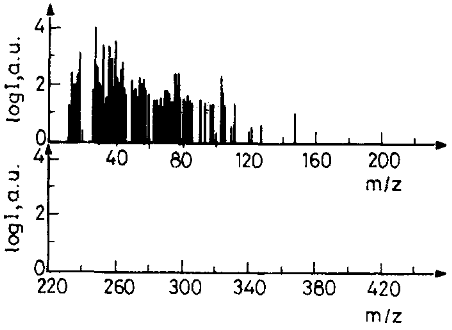


Fig. 4 Mass spectrum of PVC floor covering at 570K/290°C

The composition of the released compounds is given by a mass spectrum recorded at 300° which is shown in Fig. 4.

The thermal properties of platicized PVC depend greatly on the amounts and chemical types of plasticizers added. The mass fragment with the greatest *m/z* value has been recorded at 148 amu corresponding with the degradation of the plasticizer dioctylphthalate into phatlic acid anhydride.

The anhydride decomposes into carbon monoxide, benzene, the phenyl cation and produces obviously great portions of tropylium cations.

Monomeric vinyl chloride could not be detected. It is important to note that the MS counts of residual gaseous compounds in the recipient e.g. resulting from the air are automatically subtracted by software operations.

Besides the fast availability of the MS fragmentation patterns our software package includes an evaluation routine permitting the graphic representation of all ion current intensities which appear as peaks in the overall taken mass spectra. It is well known that the thermal decomposition of PVC products yields high concentration of hydrogen chloride as well as chlorine. The Fig. 5 exactly shows the temperature dependent course of the ion current intensities of chlorine in the ratio of 3:1 corresponding with the natural abundance of the chlorine atoms. The chlorine formation occurs in the temperature range from 250° to 600° with a maximum evolution rate at circa 300°.

To confirm the results of our combustion experiments as mentioned before see Fig. 6.

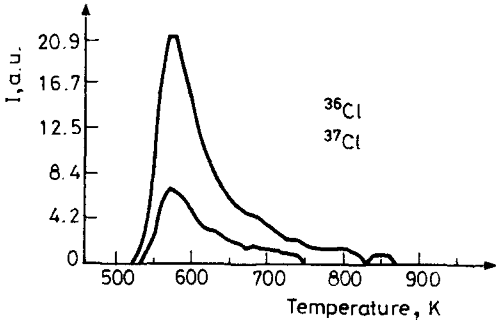


Fig. 5 Ion current of chlorine isotopes, PVC floor covering

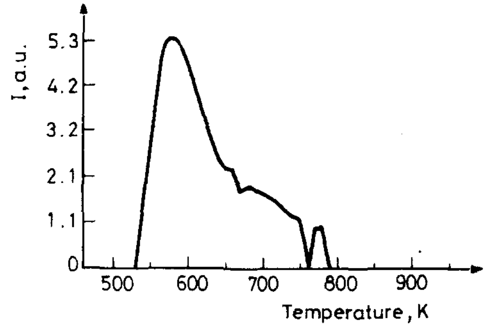


Fig. 6 Ion current of phthalic acid anhydride m/z = 148

Phthalic acid anhydride can be detected in the range from 260° to 520°. The maximum temperature of the ion current intensity has been estimated at 300°.

The formation of naphthalene occurs in a similar way. The curve shows two maximum temperatures at 300°C and 500°C with a low concentration level at 400°. The temperature values of all ion currents intensities are always in good agreement with the maximum reaction rates taken from the DTG curves. But it depends on structure-stability relationships wether there appear one or more maxima and on the thermal stability of the compounds released during the thermal treatment in the furnace see Fig. 7.

The thermal analysis curves of hexabromobenzene show that the product vaporizes in the temperature range from 215° and 375° without showing any exothermic behaviour.

Hexabromobenzene is commonly used as a flame retardant. A mass spectrum of 98% pure hexabromobenzene is illustrated in the following Fig. 8.

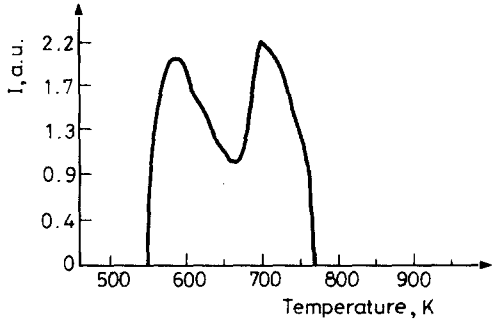


Fig. 7 Ion current intensity of naphthalene

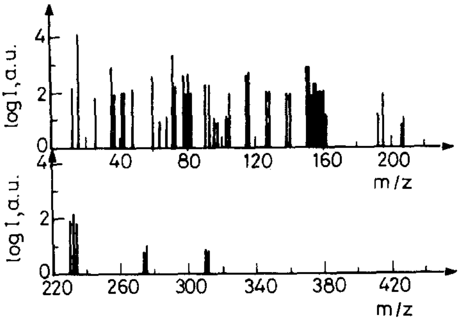
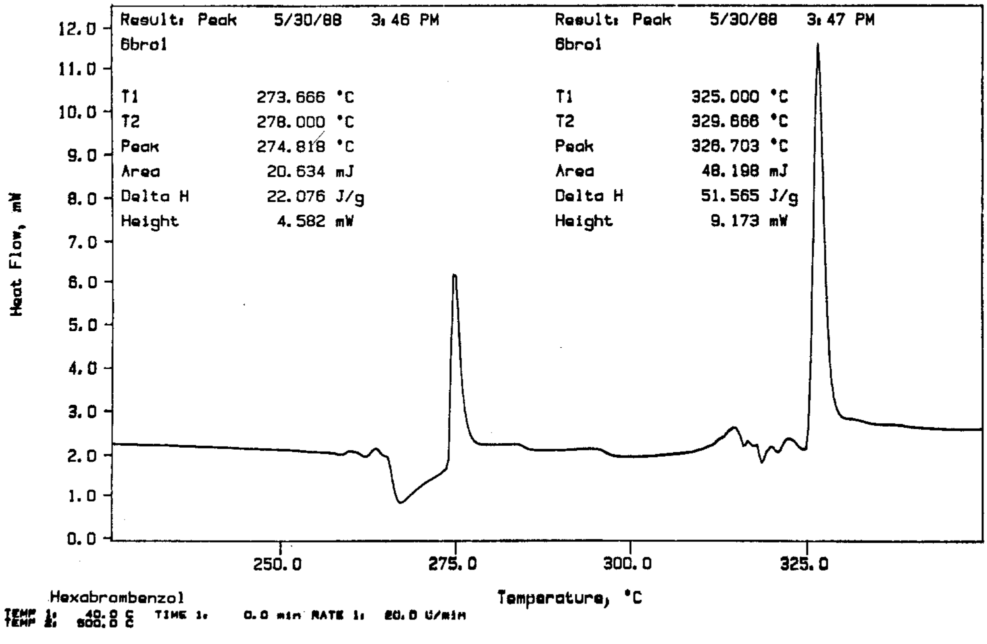


Fig. 8 Mass spectrum of hexabromobenzene at 590K/320°C

Thermal treatment of highly brominated organic compounds yield high concentrations of hydrogen bromide in the gas phase. In the case of open fires HBr serves as an inhibitor for hydrogen- and hydroxyl radicals effecting the rate of burning and the flame spread rate. The smoldering of hexabromobenzene in the TA/MS run yields bromine and hydrogen bromide ions ranging from 79 to 82 amu in remarkable concentrations. The mass range of our quadrupole instrument is limited to 511 amu. For this reason it is no possible to record the molecular ion peak. The highest value for the mass to charge ratio has been determined at 312 amu corresponding with the structural isomers of C_6Br_3. This measurement leads to the result that the degradation of hexabromobenzene occurs by successive cleavage of single bromine atoms as well as single carbon atoms as shown in Fig. 8.

In addition to these investigations we have carried out DSC measurements in nitrogen atmosphere applying a heating rate of 20 deg/min. The melting of the compound at 275° is followed by vaporization in the range of 325° characterized by these two sharp endothermic DSC peaks as shown in Fig. 9.



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Result: Peak    5/30/88   3:46 PM
6brol

T1              273.666 °C
T2              278.000 °C
Peak            274.818 °C
Area             20.634 mJ
Delta H          22.076 J/g
Height            4.582 mW
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Result: Peak    5/30/88   3:47 PM
6brol

T1              325.000 °C
T2              329.666 °C
Peak            326.703 °C
Area             48.198 mJ
Delta H          51.565 J/g
Height            9.173 mW
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Fig. 9 DSC Curve of hexabromobenzene in nitrogen

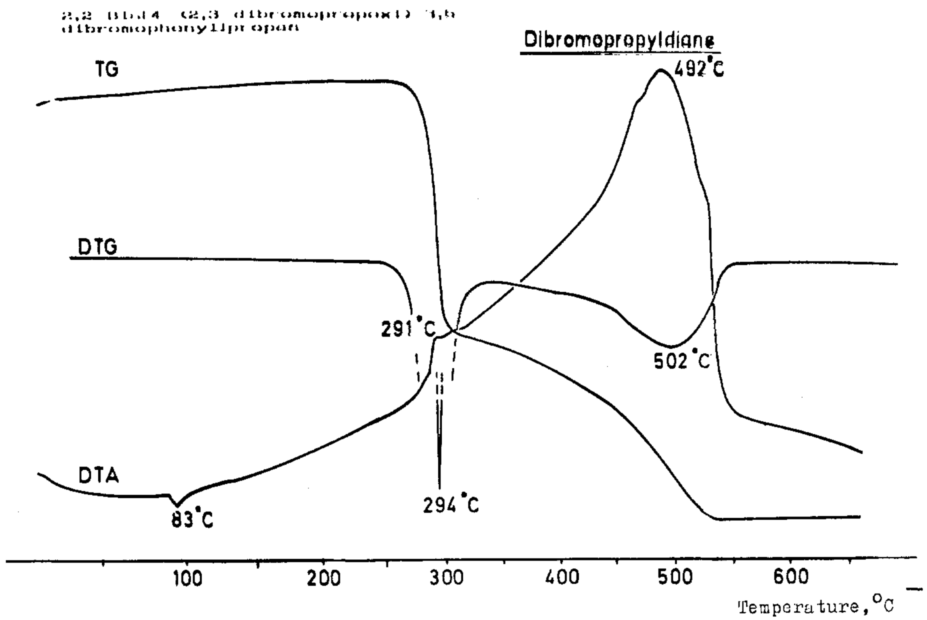

Fig. 10 TA curves of dibromopropyldiane (DPD)

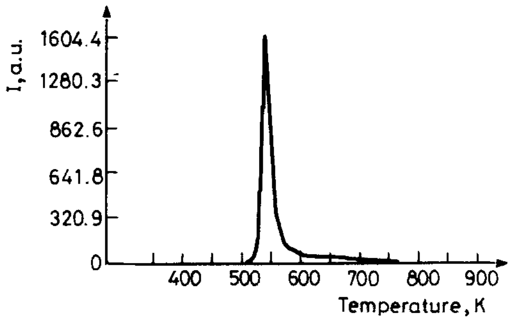

Fig. 11 Total ion current intensity, dibromopropyldiane (DPD)

Another commercially available flame retardant is dibromopropyldian e.g. 2,2-bis(4-(2,3-dibromopropoxi-3,5-dibromophenyl)propane. The thermal analysis curves are shown in Fig. 10.

Two steps of mass loss are indicated with a maximum reaction rate at 294° and 502°. The melting of the flame retardant of technical grade occurs at 83° followed by vaporization and exothermic decomposition.

After baseline correction the first mass loss has been 56% and the second 42%. The following Figs. 11 and 12 represent further results to prove the efficiency of the method applied.

The Fig. 11 shows the temperature dependent course of the total ion current intensity ranging from 250° to 900° with a maximum temperature at 290°.

This evaluation mode can be performed by means of a special option of our menu driven software package. This summarizing mode is very useful because it permits a comparison of the characteristic TG or DTG temperatures with those taken from these plots. This is essential to ensure the reliability of the TA / MS data. Other examples are represented in Fig. 12 and 13.

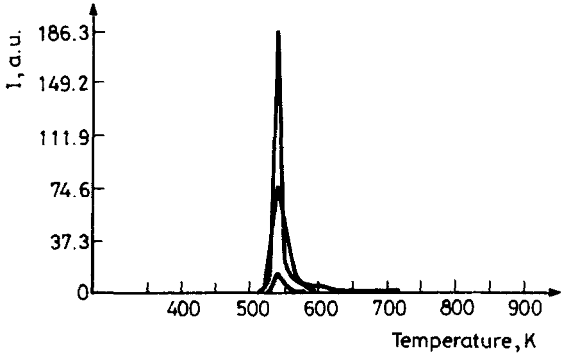

Fig. 12 Ion currents of brominated-aliphatic compounds of DPD

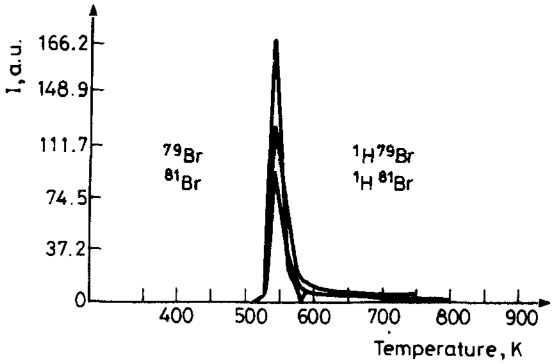

Fig. 13 Ion current intensities of bromine and hydrogen bromide from DPD (isotopic distribution)

The curves exhibit that technical grade DPD decomposes into different aliphatic bromine substituted mass fragments in the lower mass range like methyl-, ethyl- and the isomers of propyl bromide. During the heating the bromine cations and hydrogen bromide are formed simultaneously according to the ratio of the relative natural abundance of their isotopes. The second mass loss of about 40% is due to the oxidation of the partially carbonized residue which produces volatiles like carbon monoxide and -dioxide as well as typical small fragments of aromatic hydrocarbons.

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Zusammenfassung – Es wurden simultane thermoanalytische – massenspektrometrische Untersuchungen mit Hilfe einer Gerätekombination Netzsch STA 429 (Thermowaage) und Balzers QMG 511 (Quadrupol Massenspektrometer) durchgeführt. Dieses Kopplungssystem ist mit einem Digital Equipment PDP 11/23+ Microcomputer verbunden. Der komplette Datensatz, der aus einer TA/MS Messung erhalten wird, charakterisiert in sehr detaillierter Weise das thermische Abbauverhalten von Substanzen und gibt Aufschluß über die temperatur–struktur–abhängige Fragmentierung der Verbindungen.

Резюме – Проведено совмещение термического анализа и масс-спектрометрии, используя термоанализатор Нетщ СТА /ТГ–ДТГ–ДТА/ соединенный с квадрупольным масс-спектрометром Бальцерс КМГ 511. Такая совмещенная аппаратура была соединена с микрокомпьютерной системой ПДП 11/23. Полученный при одном измерении полный набор данных ТА/МС, дал детальную информацию о термическом разложении вещества в целом, а также дополнительную информацию о структурно–температурной фрагментации. Измерения, проведенные с помощью термоаналитической системы Перкин–Эльмер ДСК 7, позволили количественно определить характеристические параметры реакции.