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HIGH-TEMPERATURE TG/DSC/QMS APPLICATIONS IN ENVIRONMENTAL PROTECTION

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Abstract

The decomposition reactions of polystyrene, phenolic resin and a protective undercoating material for automobiles which contains PVC were tested using a new type of thermal analysis – mass spectrometry coupling system for measurements to 1500°C or 2000°C, which is based on the principle of a two-step skimmer orifice system. The results will be presented, with particular emphasis on the detection sensitivity of the new system for the products of decomposition.

The capability of this coupling system to detect even heavy metals such as lead and silver in the waste gases from decomposition or after evaporation at high temperatures will also be demonstrated.

Keywords: decomposition gases containing heavy metals, environmental protection, mass spectrometer, thermal analysis, thermal decomposition of plastics products

Introduction

Gas analysis, e.g. with the aid of mass spectrometry, is an interesting method of broadening the information obtained with thermogravimetry and/or simultaneous TG-DSC measurements. Thermal processes play an important role in industry, e.g. in metallurgy and ceramics, as well as in waste disposal and recycling. They are always related to the release of gases which are more or less damaging to the environment. Here, TG/DSC-MS lends itself extremely well for temperature-specific testing for environmentally detrimental emissions.

Methods

Classic solutions for TG-MS couplings are generally based on a heated transfer capillary and an orifice or frit gas inlet on the mass spectrometer. For permanent gases, this solution involving two-step pressure reduction is an optimal system for separation-free detection of the evolved gas. However, such a system cannot completely prevent the condensation of non-permanent gases and is totally incapable of detecting heavy metals.

For these reasons, an improved coupling system, which, to a great extent, eliminates condensation, has been developed using experience gained from

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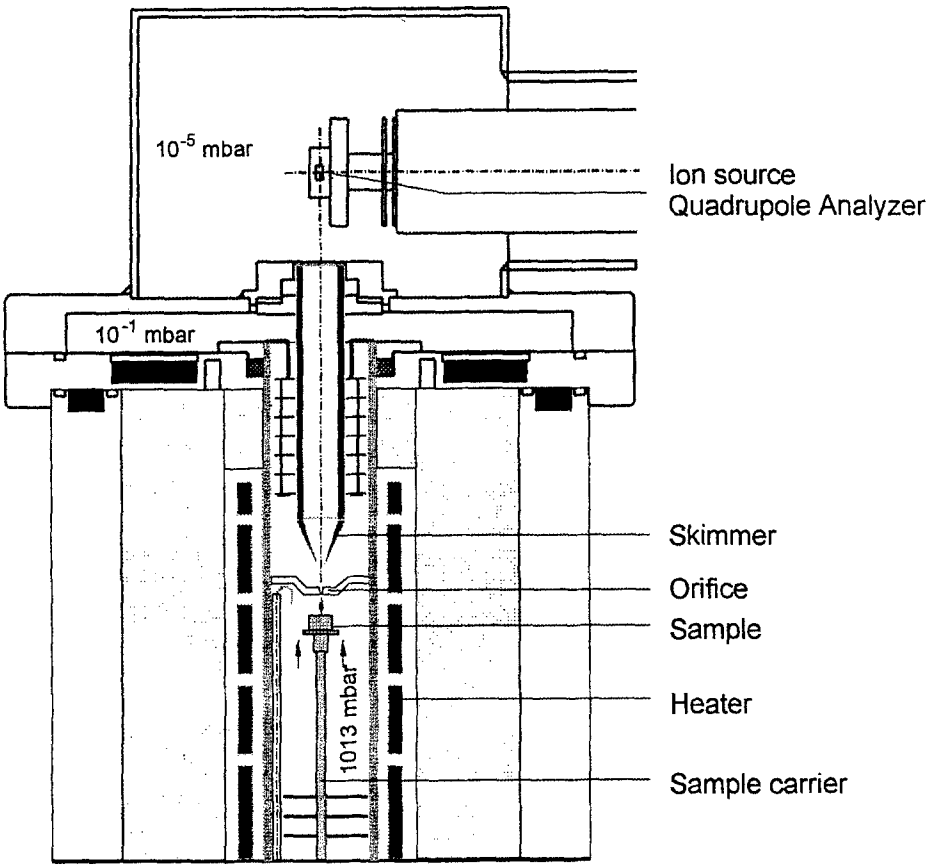

Fig. 1 2000°C TA-MS Skimmer Coupling System (NETZSCH STA 409)

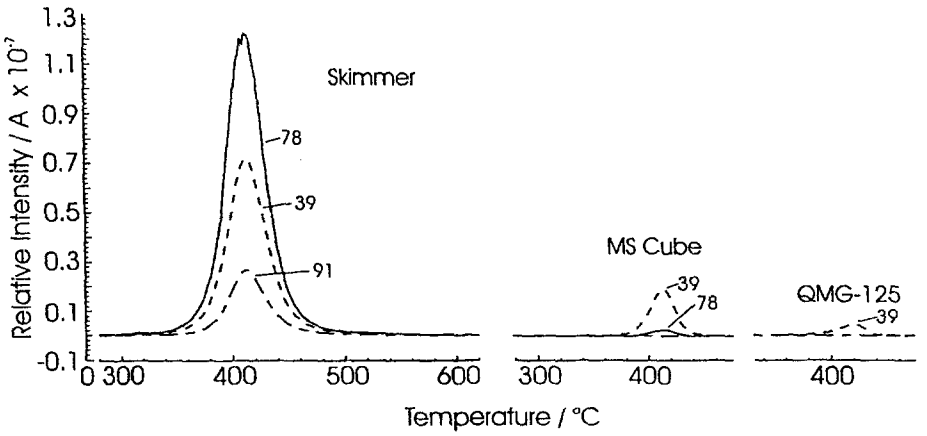

Fig. 2 Intensity comparison of mass numbers 39, 78 and 91 for polystyrene

high-tech applications (Fig. 1). It is based on the principle of a two-step orifice system in which the first pressure reduction step is achieved via a normal orifice and the second via a so-called skimmer orifice. The form and dimensions of the cross-section, the spacing of the pressure reduction steps and the design of the vacuum system lead to the emission of a largely parallel molecular beam through the skimmer directly to the ion source of the MS analyzer. In addition to high sensitivity, the result is that the gases which reach the analyzer are representative of those emitted by the sample. Because this orifice system is integrated directly into the furnace and thus has practically the same temperature as the sample, condensation, especially of larger fragments, is minimized. Depending on the furnace being used and the material of the orifice combination, this TA-MS coupling system can be run with inert gas up to 2000°C, or with oxidizing atmosphere to 1450°C.

Table 1 Comparison of the peak areas for mass numbers 39, 78 and 91 for polystyrene

System	Mass number					
	39		78		91	
	Peak area (A s)/g	Normalized	Peak area (A s)/g	Normalized	Peak area (A s)/g	Normalized
QMG–125 Capillary	6.9×10^{-5}	1	3.9×10^{-6}	1	4.4×10^{-7}	1
MS Cube Capillary	4.5×10^{-4}	7	5.9×10^{-5}	15	1.1×10^{-6}	2.5
Skimmer	2.6×10^{-3}	38	4.4×10^{-3}	1100	9.5×10^{-4}	2100

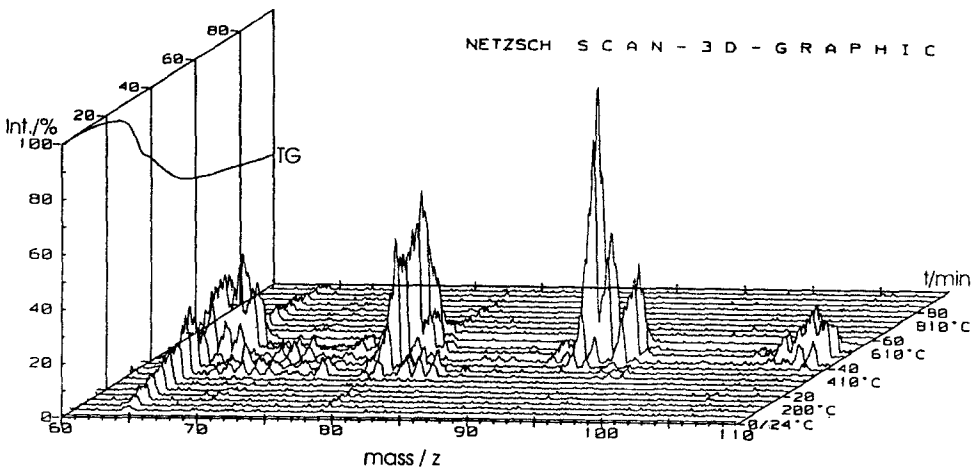

Fig. 3 Mass loss and evolved gases for a phenolic resin (STA 409-MS cube capillary coupling)

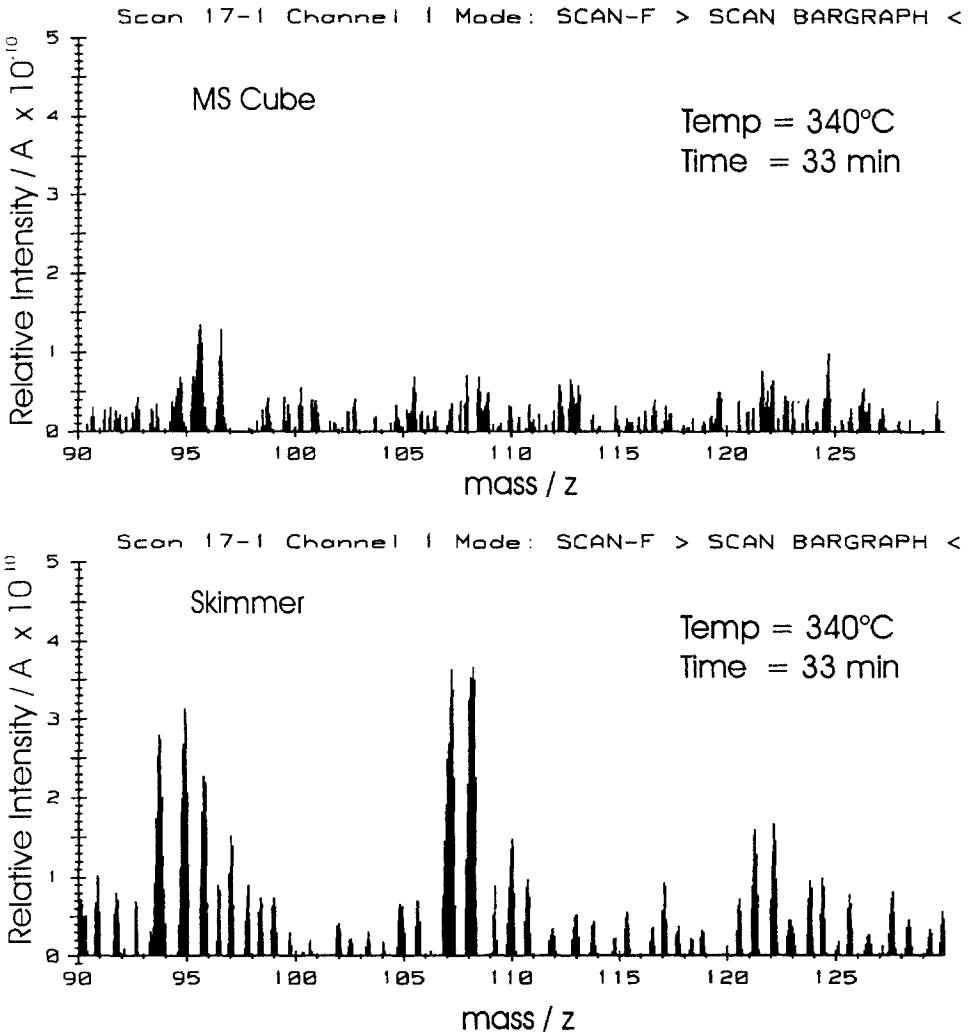

Fig. 4 Intensity comparison of mass numbers 90 to 130 for phenolic resin

Pyrolysis of polystyrene

Comparison of methods

Measurements were carried out on polystyrene in order to compare the detection sensitivity of different capillary coupling systems with that of the newly-developed skimmer coupling system. Figure 2 is a comparison of the intensities of fragments with mass numbers 39, 78 and 91 as a function of temperature. The original capillary coupling system with a Balzers QMG 125

uses a stainless steel capillary with a frit-type MS gas inlet system. In the meantime, an optimized capillary coupling system is available with the Balzers MS Cube. This uses a stainless steel encased quartz capillary, an orifice inlet system and a closed ion source. Figure 2 clearly shows that the intensities for the fragments resulting from the pyrolysis of polystyrene are considerably lower with the capillary systems than with the skimmer coupling system. In addition, the relationship of the mass numbers 39 and 78 is reversed between the capillary coupling and the skimmer. The suspected reason for this phenomenon is that thermal decomposition processes are still occurring in the capillary which falsify the composition of pyrolysis gases detected through thermal analysis.

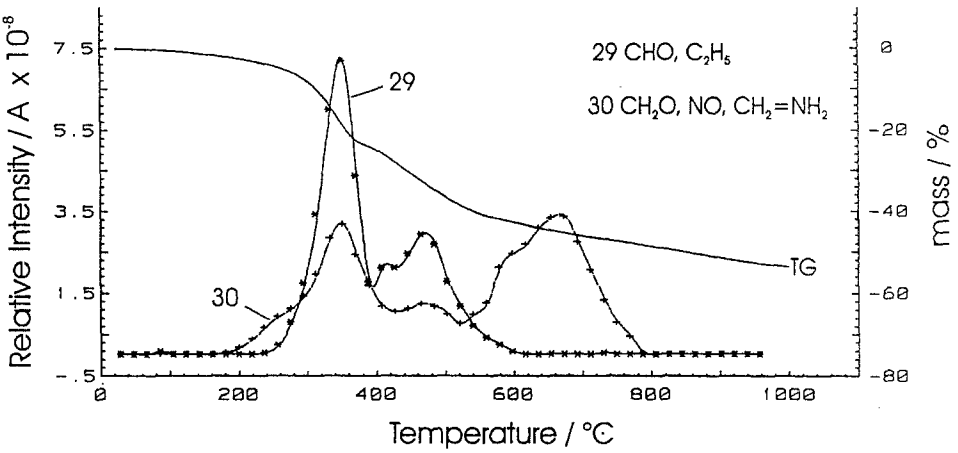

Fig. 5 TG curve and intensities for mass numbers 29 and 30 for phenolic resin

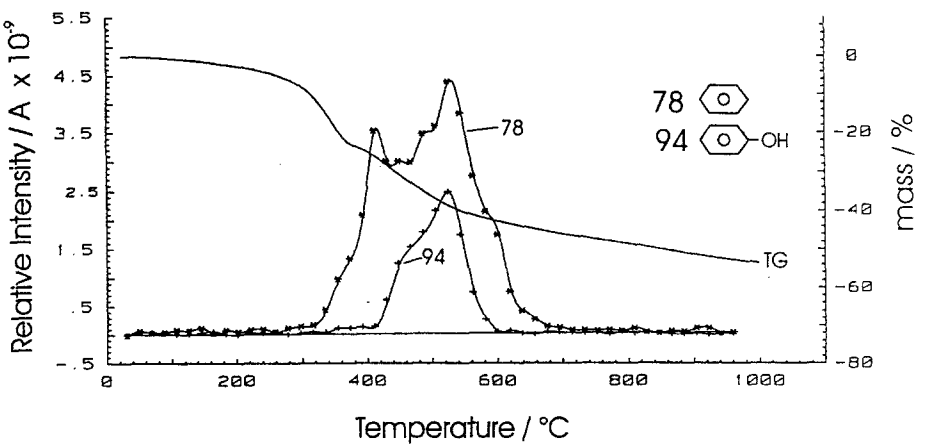

Fig. 6 TG curve and intensities for aromatic fragments 78 and 94 for phenolic resin

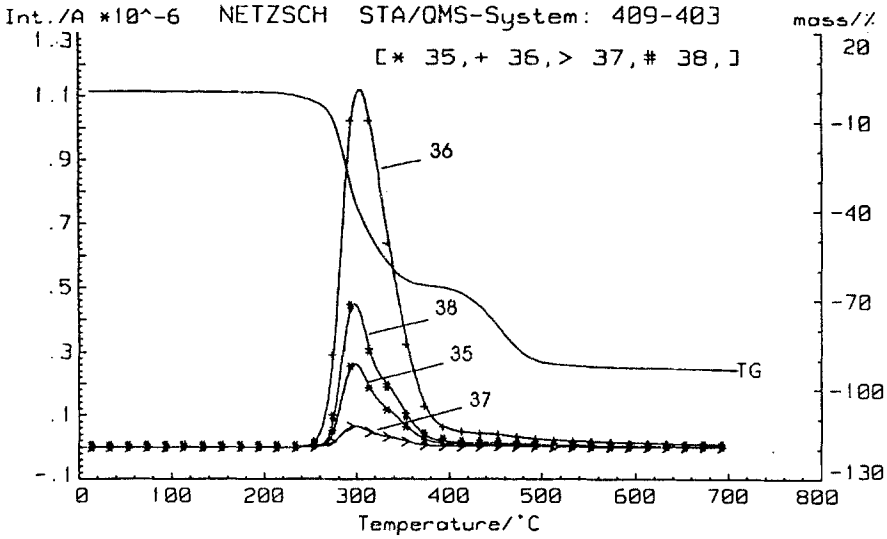

Fig. 7 TG-MS measurements on PVC TG curve and intensities for mass numbers 35, 36, 37 and 38

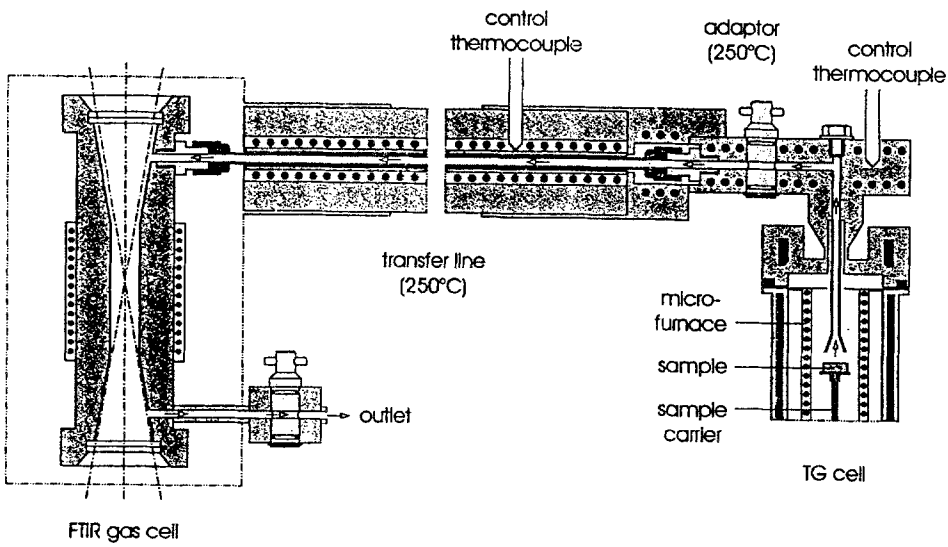

Fig. 8 TG-FTIR coupling system (NETZSCH TG 209-BRUKER FTIR)

Effects from condensation of fragments with higher molecular weights is another possibility. The tropylium with mass number 91 can be detected in the capillary coupling system only with a very low intensity. Table 1 shows the intensity data from Fig. 2 normalized to the QMG 125 capillary system. For example, for mass number 91, the skimmer system is approximately 2100 times more sensitive than the QMG 125 capillary system.

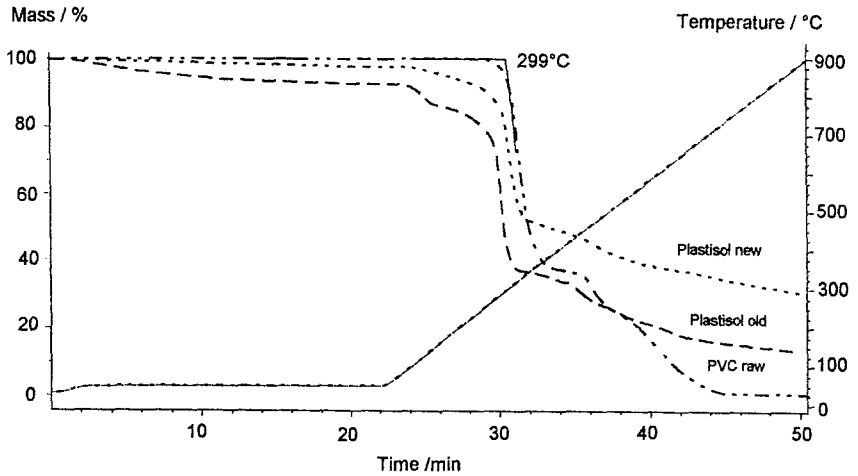

Fig. 9 Comparison of TG curves for two types of automobile protective undercoatings and for pure PVC

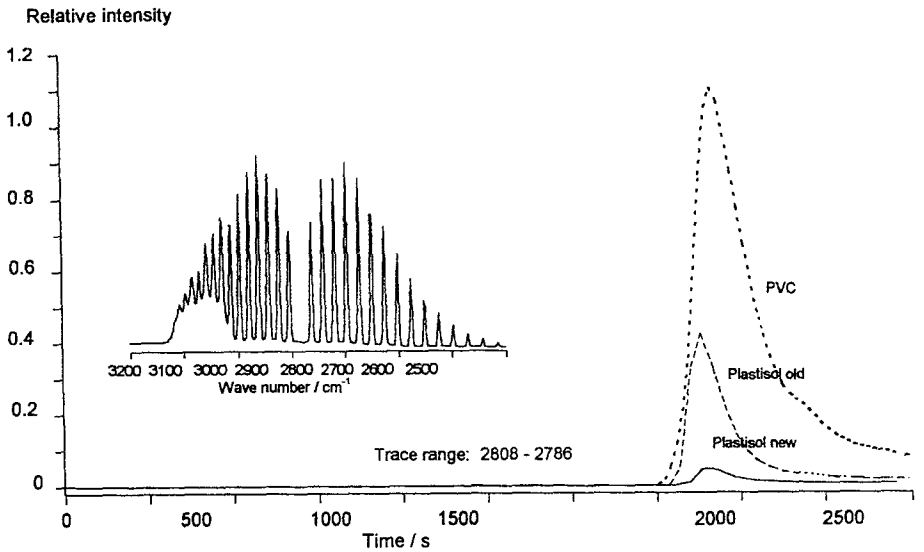

Fig. 10 Comparison of the intensities of HCl microstructure bands at 2808–2786 cm^{-1} from the TG-FTIR measurements of two types of automobile protective undercoatings and of pure PVC

Decomposition of phenolic resin

A comparison of the sensitivity values of the skimmer and the MS Cube was made using TG-MS measurements on a phenolic resin (Fig. 3 – three-dimensional plot). The results of the MS Cube and skimmer system measurements for

the mass number range of 90 to 130 amu at 340°C are shown in Fig. 4. The higher sensitivity of the skimmer system is clearly demonstrated. Figure 5 depicts mass numbers 29 and 30 together with the TG curve. The curve for these two mass numbers indicates that formaldehyde is released even at low temperatures. The aromatic fragments with mass numbers 78 and 94 (Fig. 6) are first released at higher temperatures, with the onset of actual pyrolysis at approximately 300°C, and can be detected in all three stages of decomposition.

Decomposition of materials containing PVC

With the pyrolysis of PVC, corrosive and poisonous HCl is released, especially in the first stage of the two-stage decomposition. Figure 7 shows typical curves obtained from a TG-MS measurement for the mass numbers 35 to 38 characteristic of chlorine and HCl. In the automobile industry, protective undercoating systems are used which contain considerable amounts of PVC. In order to prevent the release of large amounts of HCl, e.g. during processing of automobile scrap, inorganic additives are employed to bind the chlorine components of the PVC during thermal decomposition. The task was to check whether a newly-developed protective undercoating actually showed a lower emission of HCl during thermal decomposition than an older type of protective undercoating. For this test, the TG-FTIR coupling was used as an alternative, economical coupling method (Fig. 8). Indeed, the TG curve alone (Fig. 9) demonstrates that the newly-developed protective undercoating shows a lower mass loss than the older and, in particular, pure PVC. However, the source of this difference

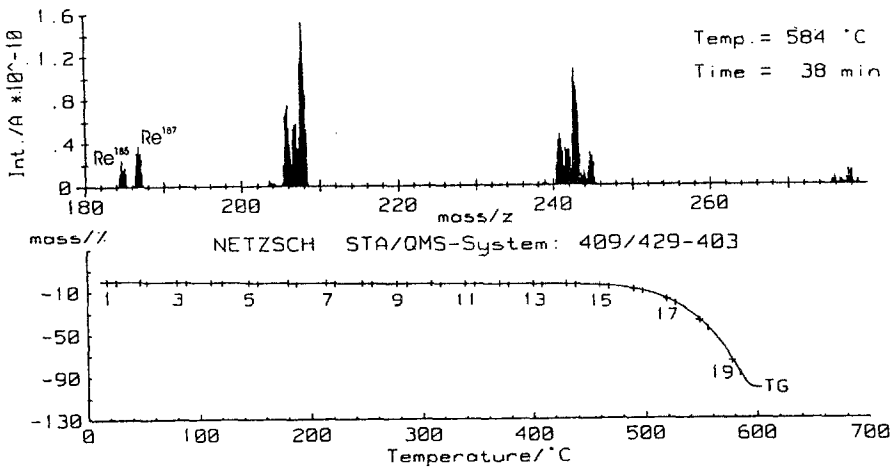

Fig. 11 TG/DSC-MS measurement on lead chloride (STA 409-MS skimmer coupling), TG curve and mass spectrum of scan 19 (584°C)

cannot be detected. Through the coupling of FTIR spectroscopy with thermogravimetry and the plotting of the intensity of a microstructure band of HCl with respect to time, area integration can be used to prove that, in fact, considerably less HCl results with the newly-developed protective undercoating (Fig. 10).

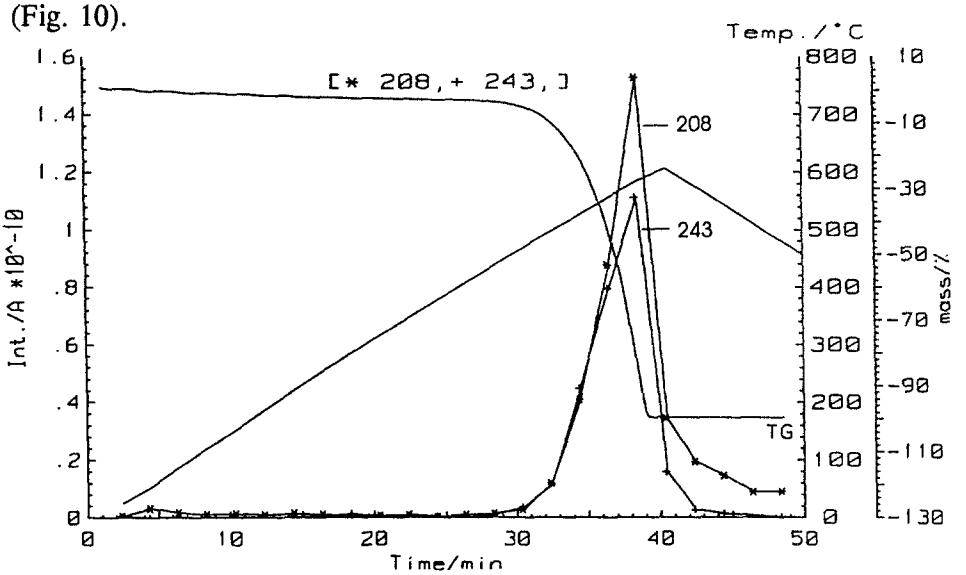

Fig. 12 TG/DSC-MS measurement on lead chloride (STA 409-MS skimmer coupling), TG curve and intensities for mass numbers 208 (lead) and 243 (PbCl)

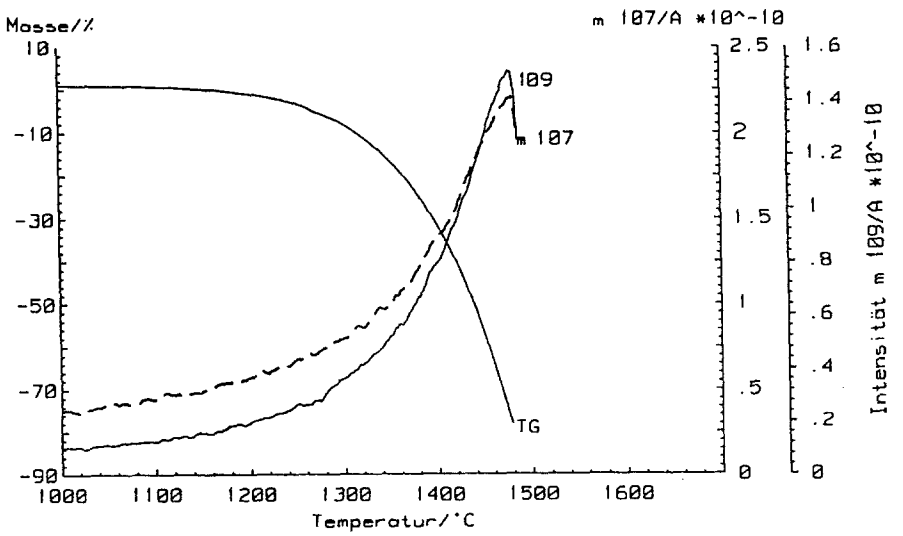

Fig. 13 TG/DSC measurement on silver (STA 409-MS skimmer coupling) TG curve and intensities for mass numbers 107 and 109

Detection of heavy metals

However, the new high-temperature skimmer-MS coupling system not only does a better job of detecting organic decomposition products than is possible with capillary couplings; this highly-developed coupling technique can also successfully detect heavy metals. Figure 11 shows the thermogravimetric curve for lead chloride (sample weight only 4.34 mg) together with the MS scan at 584°C (max. decomposition rate). Here the characteristic mass numbers for lead and PbCl are clearly seen in the intensity probabilities resulting from the natural occurrence of lead and chlorine isotopes (Table 2). The intensity curves for the mass numbers 208 for Pb and 243 for PbCl are shown together with the corresponding TG curve in Fig. 12. Heavy metals such as silver (Fig. 13) can be unmistakeably detected with the TG-MS skimmer coupling system, even at temperatures above 1400°C. For this measurement, the weight of the silver sample was only 3.04 mg.

Table 2 Combinations of Pb and Cl isotopes

	Mass number	Natural occurrence / %
Pb	204	1
	206	24
	207	23
	208	52
Cl	35	75
	37	25
PbCl	241, 242, 243, 244, 245	
$PbCl_2$	276, 277, 278	

Conclusions

The results presented demonstrate marked progress in the development of suitable coupling systems for thermal analysis of decomposition gases. With this progress, paths have been opened for improved investigation of thermal processes from the aspect of environmental protection.

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