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SAFETY TESTS FOR PRODUCTION PROCESSES IN THE CHEMICAL INDUSTRY USING DIFFERENTIAL THERMAL ANALYSIS

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To be able to responsibly evaluate chemical production processes according to aspects of safety, it is essential to carry out experiments to determine the fundamental properties of the materials involved.

These basic data include the physical material constants, such as specific heat, glass transition temperature, melt temperature, melt heat, evaporation heat (under normal pressure) etc.

As far as safety is concerned, however, the most important properties of the substances and mixtures are based on their chemical composition: they involve the desirable and particularly the undesirable reactions. The majority of the latter can be grouped together under the term decomposition, but also include undesirable oxidations, polymerizations etc. For identifying the undesirable reactions, a large variety of different instruments is available. They are usually very simple, not very sensitive and require large amounts of substance to increase the sensitivity.

In 1968 I began carrying out safety tests with the aid of DTA. At that time, DTA was regarded as being completely unsuitable for dealing with questions of safety because of the small amount of sample and the dynamic working procedure. To a certain extent this was true. The DTA apparatus and measuring methods available at that time were not particularly suitable for carrying out safety tests. This made me especially keen to become active in this field.

First of all, DTA apparatus had to be developed to enable tests to be carried out on mixtures of substances in a highly inert atmosphere and container, if necessary in the presence of strong

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acids and under high pressures. An additional requirement was that, should the substances boil over or the sample vessels explode, the damage to the apparatus would not be such that it would put it out of operation for a prolonged period of time. The simplest solution was achieved with a DTA heater made of aluminium and sample holders made of glass (Fig. 1).

The temperature and the temperature difference are measured by metal clips that are attached to the glass vessels and to which thermocouples are fixed. Technical solutions were also found for measuring substances containing HF or strongly alkaline substances.

The next illustration (Fig. 2)[+] shows the DTA measurement on the p-nitroaniline in an open glass vessel. The heating rate here was 20 K min^{-1}.

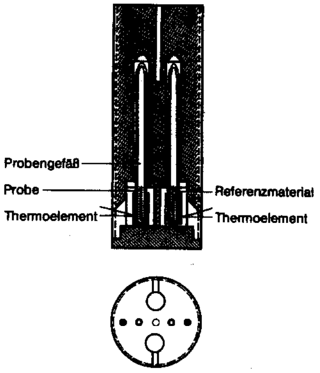
Above the melting range, the substance begins an exothermal transformation, which is in fact the start of decomposition. At somewhat higher temperatures, the endothermal heat of evaporation dominates. At even higher temperatures, at which the decomposition would take place very rapidly and would release a large amount of decomposition heat, the substance has already evaporated. This measuring method was thus unsuitable for investigating decomposition processes.

If, on the other hand, the sample under examination is measured in a closed vessel, e.g. in a sealed glass ampoule, troublesome evaporation processes can be largely avoided since the vapour pressure in the sealed sample vessel is always that of the enclosed samples and corresponds to the temperature.

This is to be illustrated taking water as an example (Fig. 3). No significant heat of evaporation is found, although under critical conditions at the critial temperature, the familiar inconsistency of the specific heat is found.

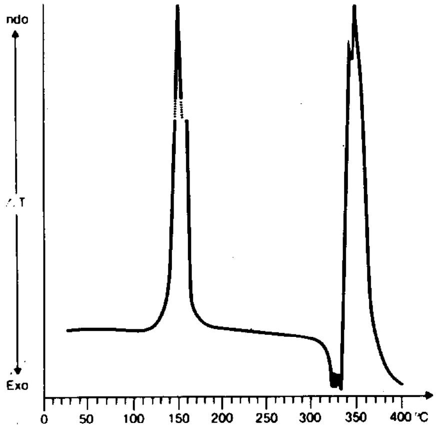
This can be measured very well during heating up and cooling down.

[+] The diagrams are printed in the new German standardization: DIN 51 005



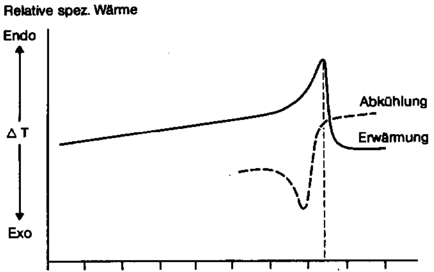
DTA-Ofen für Glasampullen
p: 300 bar T: -150 °C bis 500 °C

1



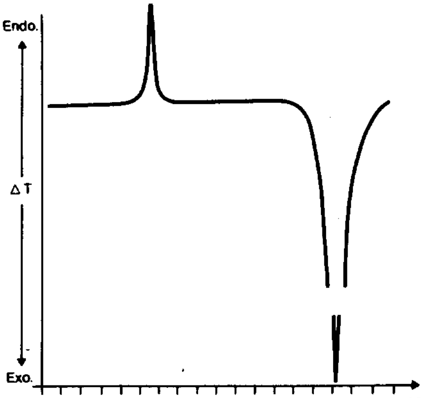
p-Nitranilin
HR 20K min^{-1} Luft 1 bar 20 mg

2



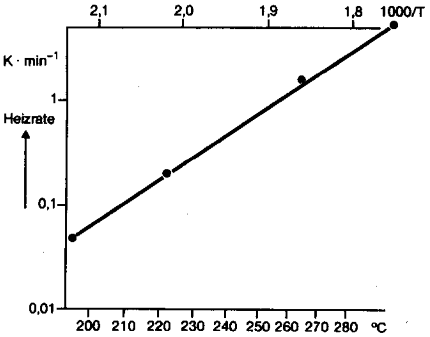
abgeschmolzene Glasampulle
HR : 5 K · min^{-1}
kritische Temperatur 374°C
kritischer Druck 225 bar
Wasser

3



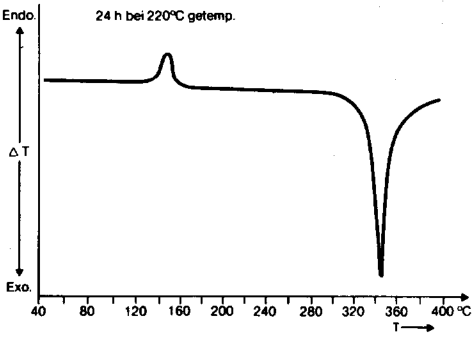
p-Nitranilin
HR 5K · min^{-1} abgeschm. Glasamp.

4



Heizratenabhängigkeit des Zersetzungsbeginns
p-Nitranilin

5



p-Nitranilin
HR 5K · min^{-1} abgesch. Glasamp. 20 mg

6

This test also revealed, by the way, that the glass ampoules can withstand pressures of more than 300 bar.

The next illustration (Fig. 4) shows the examination of p-nitroaniline in a sealed glass ampoule. Here, the endothermal melting heat and the exothermal decomposition heat can be clearly measured. Besides the melt temperature, it is also possible to measure a temperature, dependent on the heating rate, at the start of decomposition. This is the temperature at which the start of a change in the heat flow is recognized (300 °C). The decomposition temperature - as the temperature at the beginning of decomposition will subsequently be called - is in this case around 300 °C.

If we examine the beginning of decomposition for p-nitroaniline with different heating rates, we find that virtually any desired (high) decomposition temperature can be reached if the specimen can only be heated quickly enough, i.e. if the exposure time to the particular temperature is as short as possible.

In the following illustration (Fig. 5) the decomposition temperature is plotted in the familiar way for our standard substance o-nitroaniline as a function of the heating rate on the logarithmic scale.

The following decisive step prevents this disadvantage of a dynamic measuring method that has just been described. The specimen is exposed for the time necessary for the production stage (e.g. reaction, distillation, drying etc.) to the temperature required by the process.

We call this treatment "tempering". The tempering can be carried out at many temperatures and over many periods of time in suitable, comparatively cheap batteries of heaters. Our standard substance, p-nitroaniline, which has to be distilled during production, was tempered at several temperatures for a constant period of time (24 h). DTA is used for these measurements only as a very sensitive instrument for making comparisons between the specimen in its supply state and the tempered, i.e. thermally stressed, specimen (Fig. 6). The fact that the melting peak already seems to have changed and the area of the decomposition peak has decreased considerably shows that a decomposition has evidently taken place at 220 °C (tempering temperature), i.e. well below the decomposition temperature of 300 °C measured previously with a heating rate of 5 K min^{-1}.

From a quantitative evaluation of several temperings, we can determine by experiment a set of decomposition kinetics as a function of the exposure temperature at constant exposure time (Fig.7). Heat exposure at constant temperature and increasing time is frequently used to reduce the errors attributable to the apparatus.

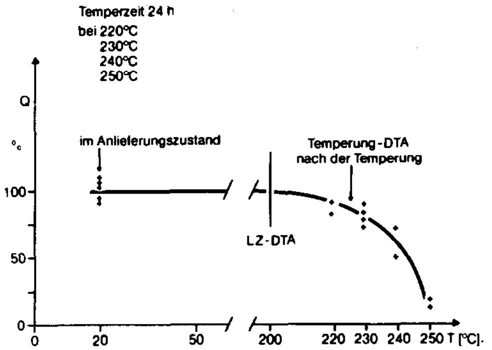
The sensitivity of this method can be illustrated with the aid of a further test. Let us assume that p-nitroaniline is to be stored for a continuous production process above the melt point (i.e. liquid) for a fairly long time. Somebody wants to know the decomposition heat to be cooled.

For this purpose, the substance is tempered for about 90 days at various temperatures (Fig. 8). The sensitivity of the start of decomposition shown by this method is approx. 10 mW kg^{-1}. A comparison with other methods is shown in the next diagram (Fig. 9).

The method of adiabatic heat accumulation, which has the highest level of sensitivity shown in the illustration, with specimen quantities of approx. 1 l (liquids only) and up to a temperature of 100 °C is unsuitable for practical application, particularly as very complex apparatus is required (temperatures have to be measured with an accuracy of 10^{-3} °C over fairly long periods of time).

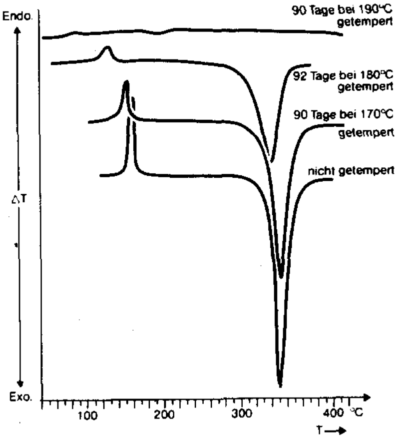
We have so far been examining the particular substance as regards its stability at the desired thermal exposure and could process it in a glass vessel or in an enamel-coated boiler. But not all containers for the further processing of a product can be made of glass or be enamel-coated. Besides this, the product to be processed may contain desirable or undesirable additions which, like the boiler materials, may enter into reactions with the product or exert a catalytic influence.

In the next illustration (Fig. 10), an examination was made of the reactive or catalytic influences on the product to be processed, azidophenyl acetic acid, through the addition of any boiler



p-Nitranilin

7 Restzersetzungswärme



p-Nitranilin

8 M 15 mg HR 4 K · min^{-1} abgeschmolzene Glasampulle

Methode	relative Empfindlichkeit mW/kg*	mW/kg**	DT$_{ad}$/dt (K/min)**	Tank kritische Wärmeentwicklung mW/kg	Volumen (m^3)
Exothermie im offenen Gefäß		75000	3,5		
DSC-1 B		30000	1,5		
DSC 2		20000	1		
TA 2000	5000	5000	0,2		
Sikarex 3	400–1000	500	0,02		
BAM-Wärmestau standard 0,5 L. 0,5 l. T$_{1/2}$ = 8 h	290	500	0,02	67,5	2
BAM-Wärmestau- 1 l, T½ = 50 h	50			29	30
Langzeit-DTA	< 25		< 0,003 ******		
Temperungs-DTA	10	Nach einer Temperung bei der Lagertemperatur für 30 bis 100 Tage****			
BAM-Adiabatische Lagerung	1		0,001 K/h		30000 kg****

* aus: Steidinger M., Wandrey P.A., Sicherheitstechnische Beurteilung von Verfahren. . .

** aus: Eigenmann K., Brogli F., Die Untersuchung thermischer Gefahren bei. . .

*** aus: Lemke D., Wärmestauverfahren und adiabatische Lagerung. . .

**** aus: BAM-Jahresbericht 1974 (anderer Zusammenhang als ***)

***** aus: Hentze Patent 2704871

****** aus: Hentze Patent 2704872

Anmerkung:
Die angeführten Werte aus der Literatur wurden nicht überprüft, es besteht aber kein Zweifel an ihrer Richtigkeit.

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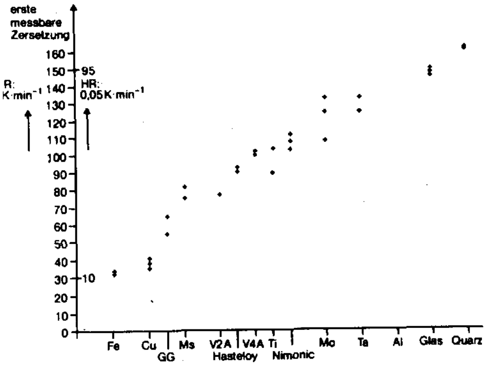
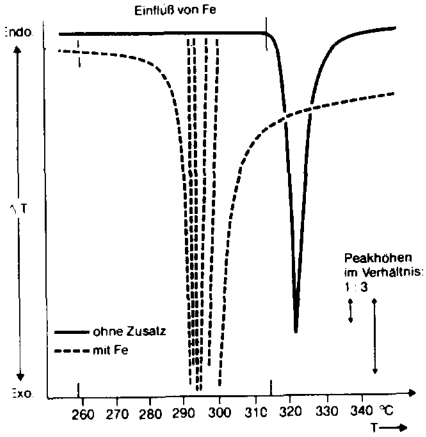


Azidophenylessigsäure

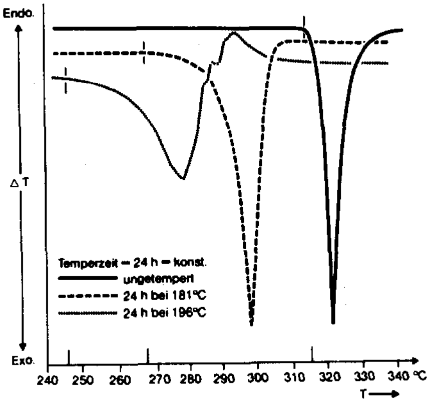
10



3,4-Dichloranilin

11 HR 5 K · min^{-1} abgeschm. Glasampulle 30 mg

Restzersetzungswärme und erste messbare Zersetzung als Funktion der Tempertemperatur



3,4 Dichloranilin

12 HR 5 K · min^{-1} abgeschm. Glasampulle 30 mg

materials or other impurities. It can be seen that even glass exerts a catalytic influence and lowers the decomposition temperature. Additional tests were therefore carried out in an ampoule made of quartz glass.

In the presence of iron, the decomposition temperature falls to 50 °C under the exposure times resulting from heating up at a rate of 5 K per min^{-1}. In order to obtain results that can be used in practical application, tempering should also be carried out here in accordance with the exposure time and processing temperature.

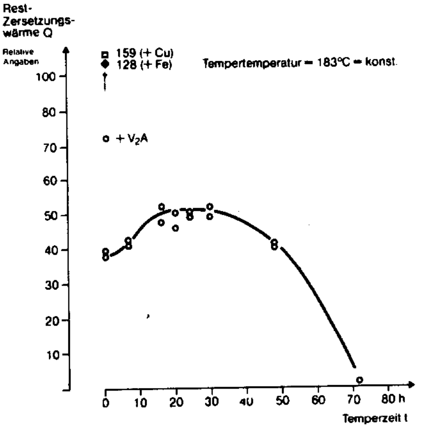
Many substances and substance mixtures have a tendency to autocatalytic reactions and decompositions. A few years ago, it was not yet possible to examine them accurately enough with differential thermal analysis. Back in 1976 our tempering method enabled us to find substances that have a tendency to autocatalysis under thermal load. This can be shown particularly clearly with 3.4-dichloroaniline.

Even in the presence of iron, the decomposition temperature falls considerably. The decomposition mechanism also changes, since the heat released on decomposition is much greater than that with straight dichloroaniline (Fig. 11). If the substance is tempered either at constant time and variable temperature or at constant temperature and variable time, we find an autocatalytic behaviour (Fig. 12).

Not only is the decomposition temperature shifted towards lower temperatures in the direction of the storage temperature (Fig. 13), the decomposition heat also becomes greater as long as the concentration conditions permit (Fig. 14).

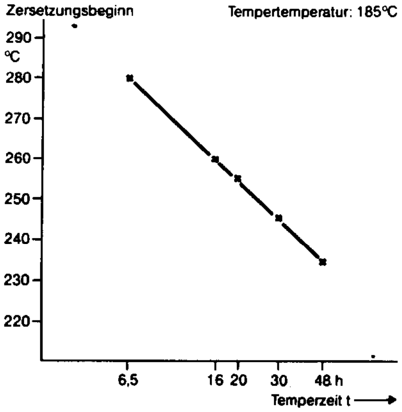
The autocatalytic behaviour of explosives can also be examined far more accurately using this method than with previous methods (Figs. 15, 16).

In order to be absolutely certain when assessing the stability of substances and mixtures and in order to obtain data as accurate as possible on the cooling of desirable and undesirable reactions, a further process was developed, namely long-term DTA.



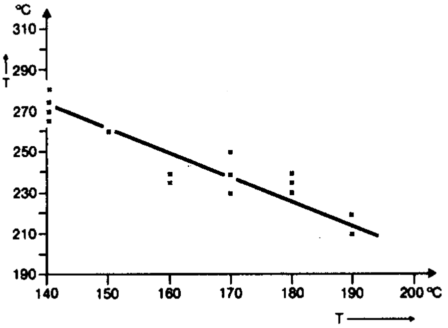
3,4-Dichloranilin

13 Restzersetzungswärme als Funktion der Temperzeit



Zersetzungsbeginn als Funktion der Temperzeit

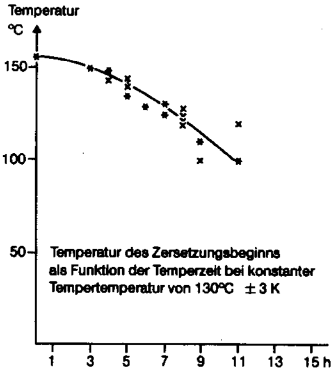
14 3,4-Dichloranilin



Trinitrotoluol:

Temperatur der ersten messbaren Zersetzung als
Funktion der Tempertemperatur bei konst. Temperzeit (48 h)
Meßbedingungen: HR 3 K · min^{-1} M = 2,5 mg

15

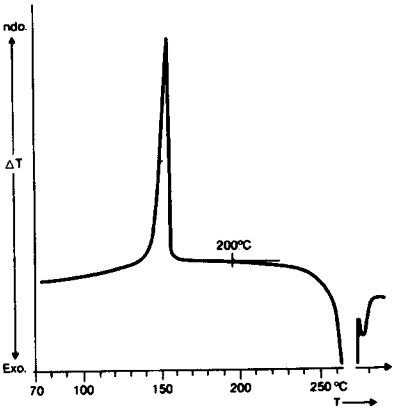


Temperatur des Zersetzungsbeginns
als Funktion der Temperzeit bei konstanter
Tempertemperatur von 130°C ± 3 K

abgeschmolzene Glasampulle
HR : 3 K · min^{-1}
m: 2,5 mg

Nitropenta

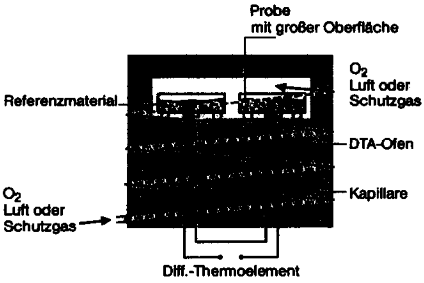
16



p-Nitranilin

HR 0058 K · min^{-1}
geschl. V_4A · Gefäß 8,8 g

17



DTA-Ofen für Trocknungsverfahren

18

For this, specimens weighing 3 g to 10 g are heated up at rates of between 0.01 K min^{-1} and 0.1 K min^{-1}. Through the integral thermal load (if necessary over several days) during the slow heating up, we get decomposition temperatures which approach those from the tempering method under similar thermal exposure.

The next illustration (Fig. 17) shows a long-term measurement performed on our standard substance p-nitroaniline. We find a decomposition temperature of approx. 200 ^{o}C. If we plot this in our kinetics diagram, we find good confirmation of our measurements.

Through the partial integration of the decomposition peak, it is possible to determine the heat production generated at the particular temperature. The maximum sensitivity with which we can recognize a start of decomposition at minimum heat production rate is, in this case, 25 mW kg^{-1}.

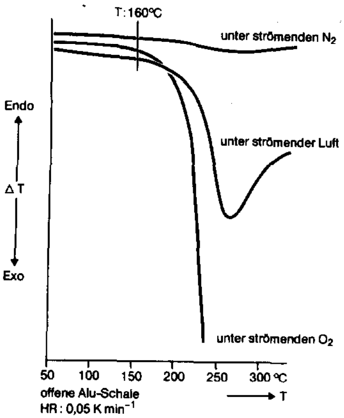
Since the drying of dusts may well incur a certain risk through decomposition or oxidation, we have developed DTA apparatus in which the specimen is accommodated in sample containers of large surface area, and which can be heated up at a very slow rate (Fig. 18).

Different gases can be passed over the specimen after they have been heated up to the particular heater temperature in a capillary wound around the DTA heater (Fig. 19).

Explosions occur through the build-up of pressure during decomposition. For this reason, it is important to recognize the increase in pressure as a function of temperature for a given period of exposure.

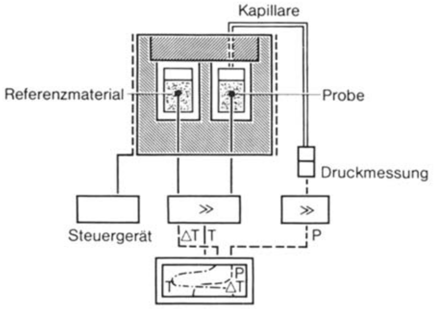
The apparatus developed for this purpose is shown in the following illustration (Fig. 20). A measurement performed on our standard substance p-nitroaniline shows the build-up of pressure during decomposition as well as a DTA measurement with melting heat and the decomposition range (Fig. 21).

If, for reasons of safety, decomposition tests are carried out on organic products, it is often desirable to identify the decomposition products using mass spectroscopy. For this reason,



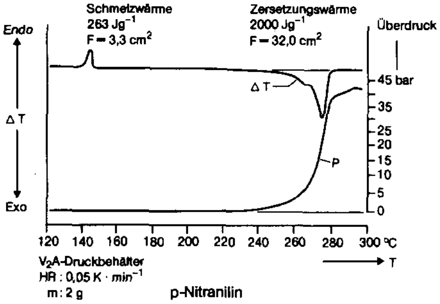
Scharlach Rot

19



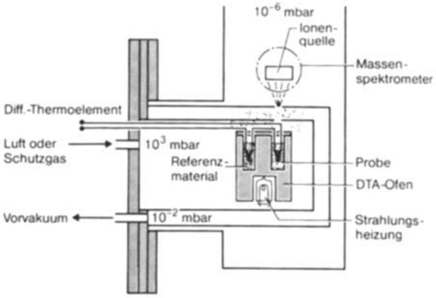
DTA-und Druckanstiegsmessung

20



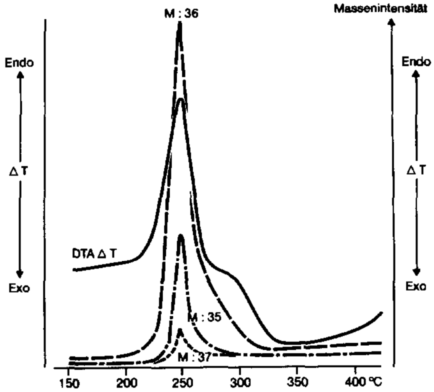
DTA-und Druckanstiegsmessung

21



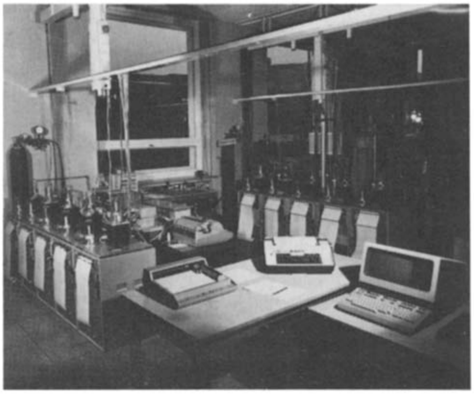
DTA-MS-Kopplung

22



Polyvinylchlorid DTA-MS

23



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several DTA-MS couplings were developed. Particular importance was attached to a high intensity. One of these DTA-MS couplings is shown in the next illustration (Fig. 22).

Here, a radiation-heated DTA heater having a very low heat capacity is installed inside a leakage system. This set-up makes it possible to limit the distance between the sample container - in which the decomposition products are formed - and the ion source of the mass spectrometer to approx. 2 cm. The fact that they are only 2 cm apart produces a high intensity of the masses to be identified.

The leakage system with the radiant DTA heater can be operated in any desired gas atmosphere or also in a vacuum. A study of the decomposition of PVC is particularly easy to follow and is shown in the next illustration (Fig. 23). Besides the DTA curve, we see the mass intensity plotted as a function of temperature.

Using the control device of the mass spectrometer, the maxima of mass numbers that had been programmed in were continuously scanned and plotted out over the particular DTA temperature. In this case, it was the masses Cl_{35}, Cl_{37}, (chlorine), HCl_{36} (hydrochloric acid). The isotopes Cl_{35} and Cl_{37} are shown very well in the curve in the same ratio as they occur in nature, i.e. approx. 1 : 3.

In this report I have endeavoured to introduce you to some of the instruments and processes that we have developed. The step-DTA developed by Dörr should also be included in the list of measuring methods. The shortage of time prevents me from dealing with it in detail, and this is also true of the isothermal DTA methods used by Eigemann and Broglie. For the methods I have described for carrying out safety tests, we have around 25 commercial DTA instruments and apparatus in use, which are based on our own development work (Fig. 24).

The wealth of data gathered from the tests and the calculations that have to be performed with them, e.g. reaction and decomposition heat, kinetic calculations etc., necessitate a data processing system of the HP 1000 type with an external storage of 20 mbytes.

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p 2704870	5.2.1980	DTA-Ampullenhalterung
p 2318340	6.5.1976	Vorrichtung zur Durchführung von DTA-Untersuchungen
	8.3.1982	DTA/Δp-Messungen
	16.7.1982	DTA/MS-Kopplung
	16.7.1982	DTA/MS Kopplung Vorrichtung zur Emissionsgasanalyse