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SAFETY SCREENING OF CHEMICALS

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ABSTRACT

Recent accidents in chemical plants involving compounds previously thought to have been harmless demonstrate the importance of complete safety screening.

Modern DSC instruments using rugged sensors and CRT graphics allow fast investigations of substances and mixtures in question.

Our paper copes with measurements of selected inorganic and organic samples that undergo decomposition in the applied temperature range of room temperature up to 600°C. The measurements are performed by the METTLER TA3000 System with the new computer graphics and evaluation software GraphWare TA72.

INTRODUCTION

Exothermic chemical reactions which get out of control constitute various hazards: formation of toxic or flammable gases or vapors, deflagration or even detonation as well as setting inflammable goods on fire. Thereby caused accidents in chemical plants and warehouses are a result of several unfortunate circumstances. But often there is still a lack of knowledge regarding potential exothermic reaction of chemical compounds. Chemical engineers of course know the hazard potential of the most popular substances such as peroxides, organic nitro and diazo compounds and certain mixtures e.g. gun powder and propellants but other compounds actually are in doubt.

Differential Scanning Calorimetry (DSC) allows the determination of any heat of reaction occurring in the covered temperature range of usually room temperature up to approximately 600°C. The small amount of sample required for such a screening test (approx. 1 mg) practically excludes any danger for the operating personnel. The use of air (oxygen) or nitrogen as a purge gas enables comparison of heat evolved by combustion/oxidation with the heat of decomposition in inert atmosphere. Volatile samples should be analyzed in pressure resistant sealed crucibles otherwise they can evaporate before the beginning of the reaction.

In addition DSC supplies information concerning drying, melting, purity, polymorphic transitions, sublimation and vaporization. The specific heat, cp, is also obtained and can be used to calculate the maximum possible temperature increase, ΔT, caused by the exothermicity. Here, it is assumed that the heat of reaction remains in the reaction material, namely that there is no heat exchange with the surroundings (adiabatic conditions):

$$\Delta T = \Delta H \,/\, Cp$$

The enthalpy change ,ΔH, can range from a few joules per gram up to several kJ/g.

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Usually an enthalpy change above 200 J/g (or an adiabatic temperature rise higher than 150°C) is thought to be of potential danger. Thus further investigations are required.

The shape of the reaction peak allows an insight into the reaction kinetics. Consecutive isothermal measurements, if possible at several isothermal temperatures, provide additional kinetic information, e.g. on autocatalytic behavior that signifies that the onset of the chemical reaction occurs only at the end of an induction period. Another approach is the use of several dynamic measurements with different heating rates [1]. Additional stages in the safety investigation concern non-thermoanalytical methods, e.g. the measurements of the deflagration behavior and the impact sensitivity of the reaction components and products. For scale up, that is the extrapolation to manufacturing conditions, fairly large batches (10...2000 g) are investigated in a reaction calorimeter under conditions reflecting actual practice [2, 3].

EXPERIMENTAL

In this work safety screening is performed at the examples of selected compounds that undergo decomposition in the applied temperature range of room temperature up to 600°C. The measurements are performed by the METTLER TA3000 System with its DSC20 cell with silver furnace and standard DSC sensor. The applied purge gas flow is 50 ml/min. Some studies include thermogravimetric measurements in the TG50 cell too.

Data storage, processing, on screen (CRT) curve comparison, numeric evaluation and recording the diagrams by a multi pen plotter is performed with METTLER GraphWare TA72 the new computer graphics and evaluation software. The computer hardware consists of an IBM PC/AT03 with 1.2 MB floppy disk drive, 30 MB fixed disk, coprocessor 80287, 1152 K RAM, EGA color display. An Epson HI80 with HP-GL ROM provides the diagrams.

RESULT AND DISCUSSION

A first measurement is performed at **constant pressure** using air as a purge gas (fig. 1 and 2). This treatment besides physical transitions indicates vaporizations and oxidative decompositions. An additional analysis under nitrogen often makes interpretation easier (fig. 3 and 4). Reweighing the sample after the san allows the determination of the total weight loss. A TGA curve provides more information (fig. 4).

To make sure that the whole sample is exposed to the temperature program and no volatiles can escape a further measurement is performed in a high pressure crucible at **constant volume** (fig. 5). The METTLER high pressure crucible is made of Nimonic 80A with a volume of 270 µl. The burst disk withstands a maximum pressure of 10 MPa (~100 atm).The enclosed air (250 µl ~ 60 µg oxygen) is sufficient to oxidize approx. 30 µg organic matter. With a heat of combustion of 25000 J/g these 30 µg can cause an exotherm of 750 mJ! When using small amounts of sample (1...2 mg) this oxidation reaction can already contribute 500 J/g! To avoid the unwanted reaction which can hide decompositions it is necessary to flush the HP-crucible with nitrogen before closing them (glove box or laminar flow jet).

It is obvious that the non specific DSC method just measures the sum of all simultaneous thermal effects occuring at a time. In addition the respecitve chemical reactions are sometimes quite complex. A scientific investigation of thermally induced degradation reactions begins with DSC screening but other techniques, such as TGA and MS as well as chemical analysis of the obtained intermediate or end product, are required too.

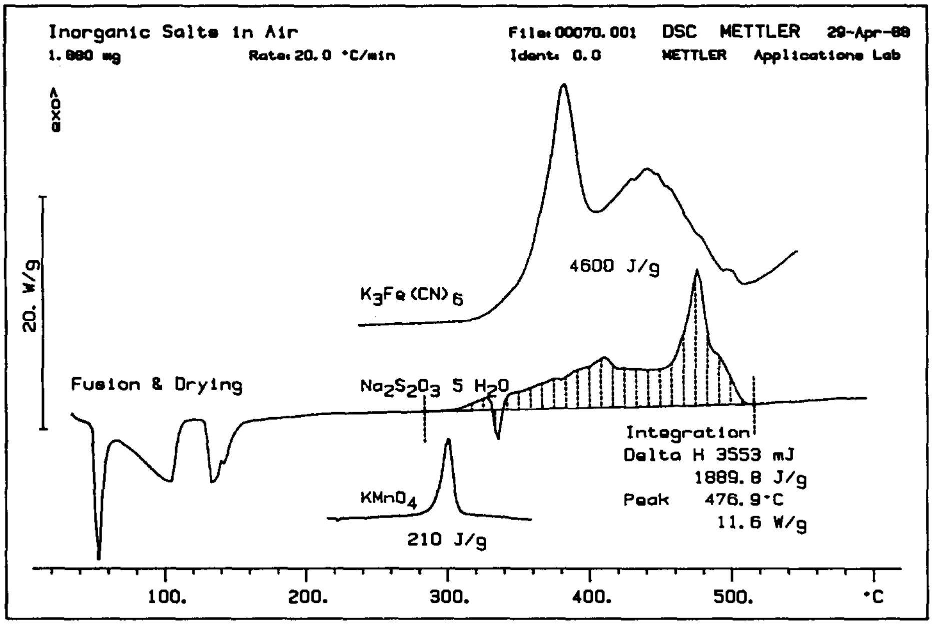

Figure 1: DSC curve of inorganic salts measured in pierced pans. Atmosphere: air, ordinate scale: normalized to the weight in watts per gram. Top: Oxidation of potassium ferricyanide with its high heat of reaction. Centre: Fusion, drying and oxidation of sodium thiosulphate with a transition endotherm at 330°C. Bottom: Decomposition of potassium permanganate.

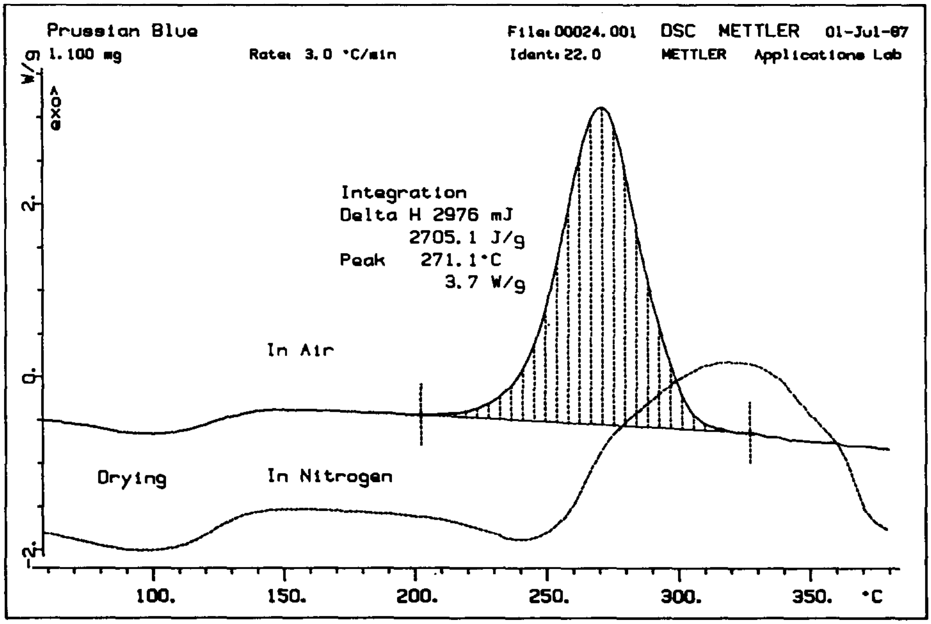

Figure 2: Glowing of prussian blue in air (top) and in nitrogen (bottom). The reaction in nitrogen is postponed to higher temperatures but it still occurs, probably due to the remaining 10ppm of oxygen.

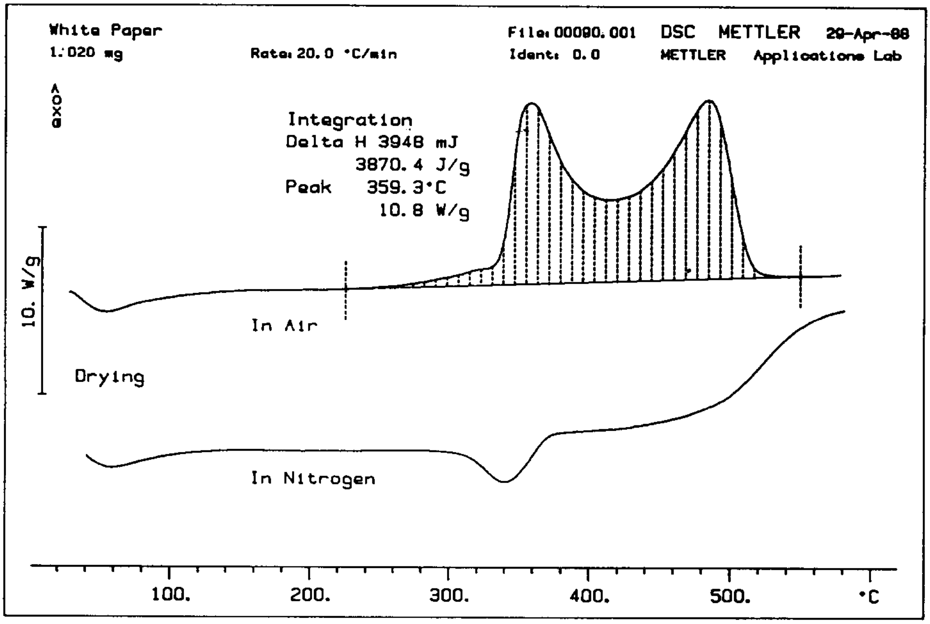

Figure 3: A familiar example of an exothermal oxidation reaction. Sample: recorder chart paper. The detected heat of reaction of 3900 J/g is not at all the total heat of combustion (some combustable volatiles escape for before self ignition).

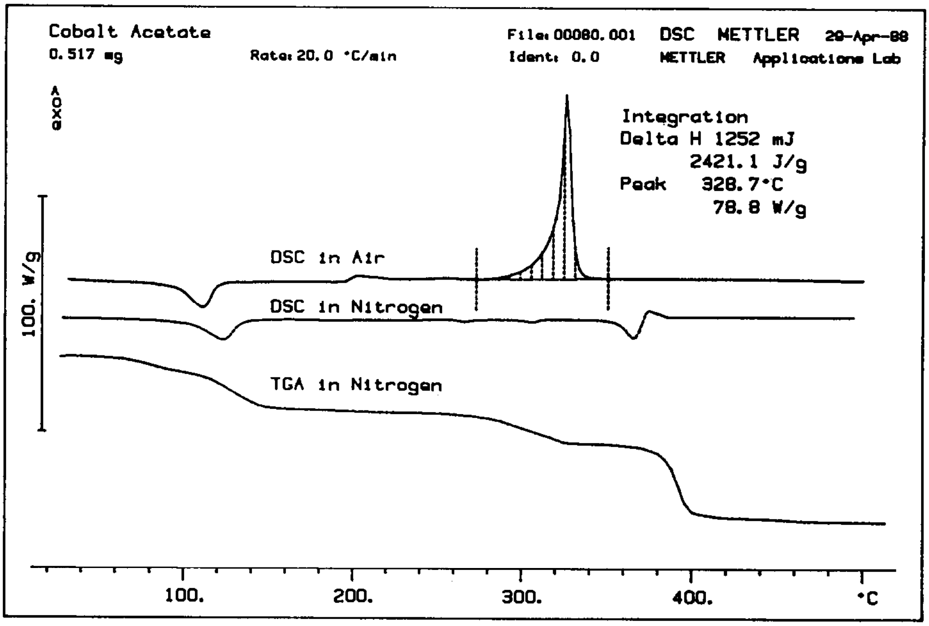

Figure 4: Cobalt acetate tetrahydrate splitts off water of crystallization at approx. 100°C. Around 300°C it begins to decompose. The formed combustable volatiles (carbon monoxide, acetone?) burn in air causing an exothermal reaction of 2400 J/g. Under nitrogen there is virtually no exotherm. The TGA curve shows two weight losses (60...150°C: 23% H_2O, 200...330°C: 13%, 330...500°C: 34%, residue 30% cobalt oxide).

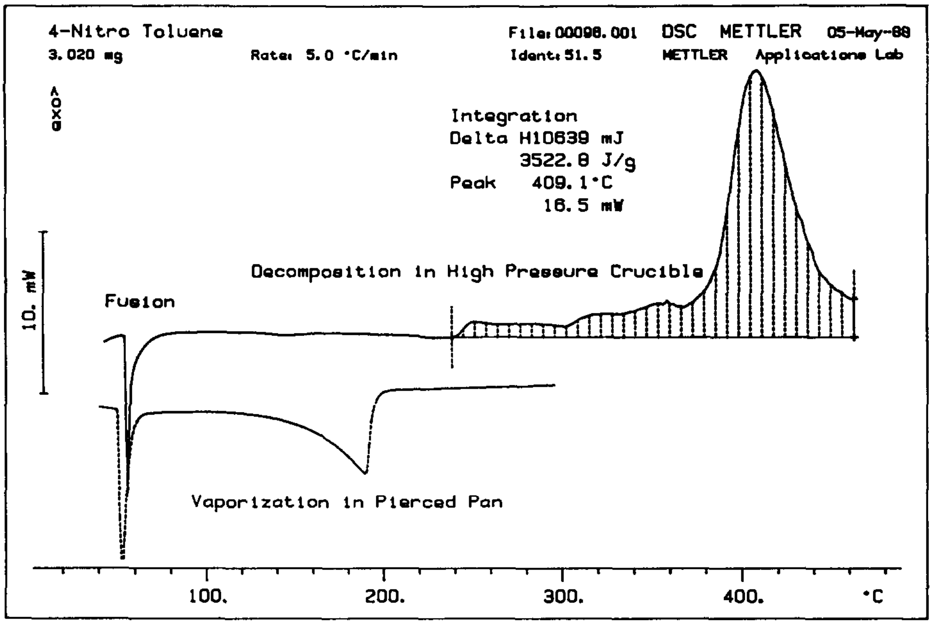

Figure 5: DSC curves of 4-nitro toluene. Bottom: measurement in pierced aluminum pan in nitrogen. Up to 200°C the sample is completely vaporized thus showing no decomposition. Top: the measurement at constant volume in a 270 µl high pressure crucible with burst disk up to 10 MPa (~100 atm) indicates the decomposition.

CONCLUSION

DSC-safety screening is a rapid means of testing the hazard potential of materials exposed to heat. Within a few hours a descision can be made whether the substance is harmless or may lead to exothermal reactions under certain conditions. A powerful graphics software package provides the necessary tool for efficient curve comparison and interpretation as well as quantitative curve evaluation.

REFERENCES

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