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A screening procedure for the thermal hazard assessment of biocidal products, wastes and chemical compounds by differential scanning calorimetry (DSC)
Procedura przesiewowa do oceny zagrożenia termicznego produktów biobójczych, odpadów i związków chemicznych metodą różnicowej kalorymetrii skaningowej (DSC)

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Abstract: *Thermal decomposition influences the safety of materials during use, storage, and their transport classification. The exothermal decomposition leads to the release of high energy and significant pressure growth and can lead to unexpected problems. Different reactions like polymerisation and oxidation or the catalytic effects of impurities may influence thermal reactions and safety and should be taken into consideration. Thermal stability can be initially estimated using differential scanning calorimetry (DSC). The standards for DSC measurements for safety purposes are described in ASTM E-537 standard as well as other documents like Manual of Tests and Criteria or Technical Agreements for Biocides. The standards in ASTM E-537 have been adapted for testing products like single compounds (hydrogen peroxide, ammonium nitrate), wastes (liquid sulphate waste following TNT synthesis) and commercial products (biocidal products based on permethrin), by specified measurement conditions, type of measuring cells, and heating rates. It allows primarily the classification of products such as explosives or self- reactive products, as well as registration processes for the approval of biocidal and pesticidal products for the market.*

Streszczenie: *Rozkład termiczny ma wpływ na bezpieczeństwo materiału podczas użytkowania, przechowywania i klasyfikacji transportowej. Rozkład egzotermiczny może doprowadzić do uwolnienia znacznej ilości ciepła i spowodować wzrost ciśnienia co może prowadzić do nieoczekiwanych problemów z bezpieczeństwem procesu. Różne zjawiska takie jak polimeryzacja i utlenianie oraz katalityczne działanie zanieczyszczeń mogą mieć wpływ na reakcje rozkładu i muszą być brane po uwagę. Stabilność termiczną można wstępnie określić za pomocą różnicowej kalorymetrii skaningowej (DSC) Założenia do zastosowania metody DSC zostały określone w normie ASTM E 537 jak również w innych dokumentach takich jak Manual of Tests and Criteria oraz Technical Agreements for Biocides. Zgodnie z normą ASTM E 537 przebadano produkty takie jak* *pojedyncze związki chemiczne (nadtlenek wodoru, saletra amonowa), ścieków (ługi posiarczanowe po syntezie TNT lub komercyjnych produktów chemicznych (produkt biobójczy na bazie permetryny) w określonych warunkach pomiarowych, typach naczynek i szybkości ogrzewania. To pozwala na klasyfikację produktów pod kątem transportu i bezpieczeństwa stosowania i określenie jako produkty wysokoenergetyczne jak również wypełnić wymagania rejestracyjne dla produktów biobójczych i pestycydów wprowadzanych na rynek.*

Keywords: *thermal analysis, differential scanning calorimetry, thermal hazard, sample pan, self-reactive substance*
Słowa kluczowe: *Analiza termiczna, różnicowa kalorymetria skanningowa, zagrożenie termiczne, naczynko pomiarowe, substancje samoreaktywne*

1. Introduction

Thermal hazards are defined as risks associated with the exothermic release of energy. These can occur during planned as well as unplanned chemical reactions, as well as during processing, storage and transport of the hazardous substance. The chemical reactions mentioned in such situations can lead to the release of volatile flammable products, and serious hazards if evolution of gases occurs in the closed space of a chemical reactor. This can in turn lead to the risk of excess pressure. Additionally, hazards can be a problem in the presence of other reactive and/or flammable chemicals, as this can cause fires and explosion. Thermal hazard assessment includes the identification of all potential exothermic reactions, establishing potentially dangerous scenarios, as well as assessing the probability and consequences of their occurrence.
Thermal safety studies have been necessary for the transport classification of bulk quantities as well as for those delivered in small quantities (for example, including research purposes). For small production volumes, it is, sometimes, not possible to adapt currently existing transport regulation test procedures to the classification of this group of products. Therefore, determining their safety based on DSC/TG measurements, has gained interest due to the small amounts of sample needed for testing and the speed of measurements. Differential scanning calorimetry (DSC) can be used to forego justification of the term's "explosives" and "self-reactive substances" in biocidal and pesticidal formulations.
Thermal hazard studies are based on laboratory test results. Such studies may include analysis of reaction mechanisms and the determination of its kinetics, as well as measurement of parameters such as heat of reaction and decomposition temperature. DSC can be treated as a screening tool in thermal stability studies. A small sample of product – a few milligrams, is enclosed in a sample pan and measurements are usually performed in an atmosphere of nitrogen/air and heated at a constant rate (usually between 2 to 10 °C/min). Temperature range measured was from ambient to 300-500 °C. The heat flow is measured as an endothermal or exothermal effect and registers as a peak on the thermoanalytical curve.
The absence of detected effects of decomposition is proof that a sample is stable. In a DSC experiment, the heating rate and the type of crucible used are two crucial factors. The observation of detectable exothermic activity allows decisions about the classification of the product as explosive or self-reactive to be made, thereby deciding on conditions of transport, storage and processing. In some cases, there is a necessity for further testing using other methods stipulated in the regulations. Thermal stability studies are often performed on organic molecules, which frequently have functional groups indicating explosive potential, to confirm that fact.
The first thermal stability tests using thermal techniques (TGA/DTA/DSC) were regulated in 1981 by the OECD guidelines [1]. The principle was to use thermal analysis techniques to determine if there are any changes (mass loss or exothermal /endothermal effects) during measurement at constant heating rates up to 150 °C. Sample mass change or the quantities of heat absorbed or given off, were measured and recorded. The substance was considered stable at room temperature if no decomposition or chemical transformation was found below 150 °C.

For the assessment of thermal hazards and thermal stability testing, DSC tests are based on the established ASTM standard - ASTM E 537 [2]. This standard, developed by the ASTM E-27 committee, defines methods for determining the hazard potential of chemicals. According to this standard, safety tests using the DSC method are performed with use of sealed high-pressure vessels sealed hermetically. This test method uses DSC or pressure DSC, and is performed on solids, liquids, or slurries. It can be performed in an inert or a reactive atmosphere at an absolute pressure range from 100 Pa to 7 MPa and over a temperature range from 300 to 800 K (27 to 527 °C). This methodology is recognized as supporting the Manual of Tests and Criteria, version 8 [3] and the recommendations for testing contained in the Technical Agreements for Biocides [4]. As was emphasised, using DSC/TG, it is possible to initially determine whether the examined product has explosive or self-reactive properties.

The main group of substances subjected to attention are potential explosives. Explosives can be classified as Class 1, based on DSC measurements. It has been determined that organic substances containing chemical groups associated with explosive properties do not need to be classified as Class 1 explosives when: the determined exothermic decomposition energy is less than 500 J/g, or the onset temperature of exothermic decomposition is at or above 500 °C. Most known explosives have a decomposition energy of 2000 J/g or higher. Samples showing such energy usually require more thorough investigation and additional testing before transport.

The self-accelerating decomposition temperature (SADT) is defined in the United Nations recommendations as the lowest temperature at which self-accelerating decomposition occurs (e.g. in a transport package). The SADT value is a measure of the combined effect of ambient temperature, decomposition kinetics, package size and heat transfer properties of the substance and its packaging. SADT simulation requires a correct description of the process kinetics, i.e. the dependence of the reaction rate on temperature. The DSC test is a simple way of confirming or ruling out the nature of a substance as self-reactive.

Substances should be considered as self-reactive if the SADT value for a 50 kg package is 75 °C or less. These are thermally unstable substances which may undergo a strongly exothermic decomposition even without the participation of oxygen (air). Substances should be classified as self-reactive if they have a decomposition energy of 300 J/g or more and a SADT value of 75 °C or less. The classification of a substance as self-reactive does not apply if one of the two criteria is not met. Temperature control of a product is applied if the SADT is less than or equal to 55 °C.

The practical safety assessment of substances, based on DSC measurements, can be estimated by the "100 K" rule. This rule is used for a preliminary assessment of the SADT value and safe handling temperature. This temperature is described as the "distance" of 100 degrees from the beginning of decomposition expressed as T_{init} (the beginning of exothermal process, not T_{onset}). This temperature value defines the safe handling temperature, which should lead to the avoidance of uncontrolled thermal reactions. Thus, in the case of a decomposition starting at 180 °C, a handling temperature of 80 °C is considered safe. If the SADT is higher than 75 °C, it is possible to waive testing for self-reactivity.

To confirm the thermal stability of a material and the lack of need for temperature control, it is assumed that the material is thermally stable if SADT $\geq$ 60 °C. By applying the "100 K" rule, thermal stability is sufficient if decomposition starts at 160 °C or above. Small single exothermic peaks with an energy magnitude less than or equal to 20 J/g, need not be taken into consideration.

A more precise method of SADT determination than the "100 K" rule is based on the DSC thermal stress technique. This technique uses several isothermal measurements which followed non isothermal studies. The sample is subjected initially to a non-isothermal test to determine the beginning of the decomposition process. Another sample (taken from the same batch) is kept at a constant temperature in a closed system (isothermal test), for 24 h. The sample is then cooled to room temperature and is analysed again in a non-isothermal manner, like the first sample. If the decomposition curves of both samples do not change (shape and amount of decomposition energy) then the conditioning temperature in the isothermal stage is lowered by another 10 degrees and another sample is kept at a new temperature for 24 h. The process is repeated until the lowest temperature not showing changes in the DSC curve, is found. When it is found that the sample subjected to thermal stress at 60 °C has not changed, the material is considered stable.

There are several types of crucible used in DSC measurements mentioned in literature and practically applied. Details of application, advantages and disadvantages, are given in publication [5]. In a DSC experiment, evaporation or loss of gaseous decomposition products is common, which is registered as an endothermic event if an open or not hermetically crucible is used. Authors of this work propose that when analysing the thermal decomposition of potential energetic materials, only sealed high-pressure sample pans or alternatively, sealed glass ampoules, are the most suitable. Crimped aluminium sample pans are good for other DSC measurements (phase transitions) but inappropriate for hazard assessment because of rupturing, resulting in a sudden endotherm. The most popular aluminium pans, closed with a classic crimper, are cheap and easy to fill. The maximum pressure of aluminium vessels closed with a capper is relatively low. Only high-pressure DSC cells, available commercially for the purpose of assessing thermal stability, are suitable but are expensive for everyday use.

An alternative is the glass ampoule, developed over 30 years ago, which utilises a flame-sealed glass capillary as the container for DSC samples to assess their reactivity and thermal stability. It should be noted that aluminium can react with some materials such as oxidants, strong acids, strong bases and halogenated organics. Therefore, the steel and components can act as catalysts for decomposition reactions Thus, when planning DSC measurements, it is necessary to consider the proper choice of sample pans. The simultaneous use of TG measurement allows for additional observation of mass loss accompanying decomposition.

For measurements regarding decomposition kinetics, aluminium cells with a lid with a hole (pin hole) are also used, which to some extent allows for a controlled loss of mass during decomposition. DSC data generated using open cells are not suitable for assessing the extent of thermal stability. In the case of liquid samples or solid samples above their melting point, the endothermic effect of evaporation may occur, masking the signal from a possible exothermic decomposition, for example, the boiling point of the sample.

In practice, when conducting DSC measurements for safety tests in accordance with the ASTM standard, the following rules are followed:

– hermetic sample pans (HP) should be used,
– do not use of sample pans made of materials which may react with the test material,
– low heating rates should be used (2-10 degrees/min is recommended),
– the concept of the limiting temperature defining stability should be defined (extrapolated onset temperature T_{onset} or temperature related to the deviation from the baseline T_{init}),
– additional endothermic effects, related to the melting of the substance, should be considered,
– comparisons should be made for measurements performed under identical conditions.

There is currently no established convention for reporting safety data regarding thermal stability. It is generally accepted to define the onset temperature as the lowest temperature at which the exothermic heat flow is greater than the detection limit of the DSC instrument. This temperature is referred to as T_{init} or T_{onset}) and is suitable for determining the safety of the process. The T_{onset} is the extrapolated onset determined by the DSC software based on the steepest peak slope and is useful for comparisons between compounds. T_{init} temperature is the point of deviation from the baseline in the thermoanalytical curve.

The appearance of an exothermal peak during measurements determining thermal safety using the DSC is a point to confirm thermal decomposition considered in thermal hazard assessment. The absence of this peak may either exclude the recognition of the tested sample as having hazardous properties or other circumstances should be considered, for example the concentration of a potentially hazardous component is small, the composition of the mixture (water content, volatile solvents, the possibility of reactions with decomposition products, the effect of pressure). The heat of decomposition in the report is usually given as a negative value of J/g. and heats of exothermic decomposition peaks appearing at temperatures below 500 °C, are summed up.

2. Material and methods

Thermal decomposition studies were performed using the simultaneous thermal analyser Netzsch STA 449 F1 Jupiter, which enabled recording of the DSC and TG curves in parallel. The measurement method was based on a heating rate between 2-10 °C/min of the test sample. During the test, the thermobalance simultaneously recorded the change in sample mass. The preliminary tests were performed using aluminium concavus vessels with a capacity of 30 µl, closed using a crimper and steel, with the hermetic vessels, closed with a special dedicated sealer (Netzsch product: CrNi steel crucibles ø 6 mm, 27 µl, with hexagonal lids and golden sealing discs). The mass of the tested samples ranged from about 2 to 5 mg.

The final temperature depending on the type of sample, was 350-450 °C. The measurements were carried out in an inert gas atmosphere (nitrogen) at a flow rate of 70 ml/min. The apparatus was calibrated using metal standards such as In, Sn and Zn. Calibrations were performed for both types of crucibles in accordance with the manufacturer's instructions. The choice of examined products agreed with the requirements of the producers.

3. Results and discussion

3.1. Thermal decomposition of hydrogen peroxide (H_2O_2)

H_2O_2 is known for its oxidizing properties, and is a substance which easily decomposes at ambient. H_2O_2 solutions are used as the active ingredient in a biocide, often in the form of concentrate for further dilution. A 50% aqueous solution is defined as a strongly oxidizing hazardous material. Storage, transport and use must be carried out with caution. The biocidal product Belox with a concentration of 49.9% H_2O_2 is used as a disinfectant for type PT 2 and 4 products used against bacteria, fungi and bacterial spores in the food industry. There are also some products on the market with lower concentrations of H_2O_2. Hydrogen peroxide is also used as a bleaching agent in the fiber, food and cosmetic industries. It is an oxidizing agent in the production of polymers in the plastics industry. It is also used as a storable propellant. The determination of thermal safety is necessary in registration process.

DSC studies determining the energy activation of hydrogen peroxide were conducted by Anothairungrat [6] and by Scholl *et al.* [7]. Hermetic steel sample pans were used in both tests. DSC tests were performed in our laboratory on two biocides with concentrations of H_2O_2: 49.5% and 5% of H_2O_2 using aluminum and steel crucibles. Both results were presented in the form of superimposed thermoanalytical curves TG and DSC. Figure 1 shows two DSC curves for hydrogen peroxide at a concentration of 49.5%. First set of results - the solid line represents results obtained in an Al sample pan and second – the dashed line - results obtained in a steel hermetic sample pan.

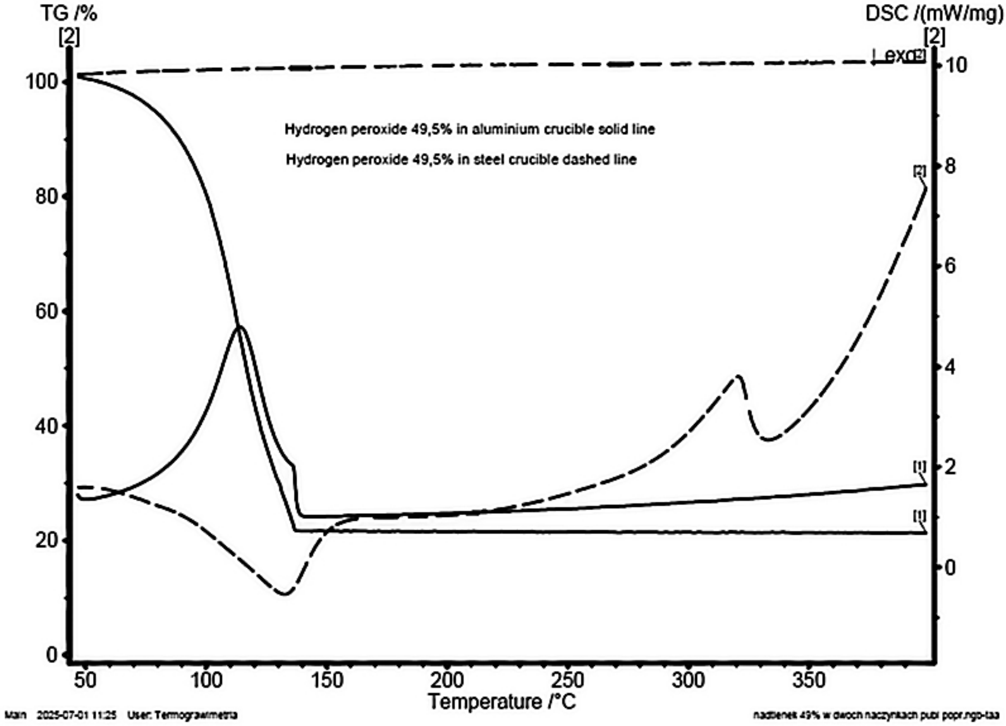

Figure 1. Pair of thermoanalytical curves (TG and DSC) for H_2O_2 at a concentration of 49.5% obtained in aluminium (solid line) and steel sample pans (dashed line)

The DSC curve obtained from the aluminum sample pan shows a large endothermal peak and immediate mass loss due to release of gaseous decomposition products, to 150 °C (calculated 85% of mass loss). The curve obtained from measurement in the hermetic sample pan has a flat TG curve and shows a great exothermic peak with an onset temperature of about 94 °C together with a decomposition heat of 759.6 J/g. Both measurements were carried out at a heating rate of 5 °C/min. The sample mass measured in the hermetic sample pan was 3.9 mg and in the Al sample pan was 4.7 mg. For the 5% H_2O_2 solution the same test was performed under the same conditions. The results are presented as Figure 2.

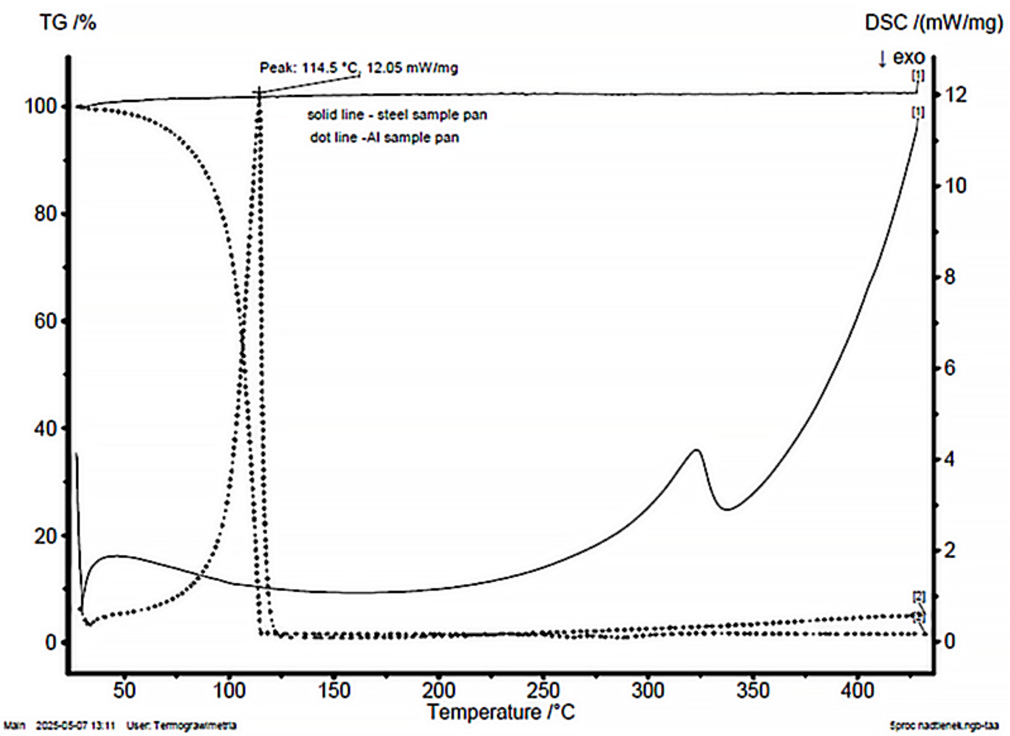

Figure 2. Thermoanalytical curves (TG and DSC) for decomposition of 5% solution of H_2O_2 in water – (dot line aluminum sample pan, solid line steel sample pan)

The mass of the sample in the steel vessel was 5.5 mg, while in the aluminum vessel it was 3.5 mg. The heating rate was also 5 °C/min, and the final temperature was 450 °C. Because of the low concentration of hydrogen peroxide, no exothermal peak was observed in the curve from the hermetic steel pan. There is also no evaporation visible in the TG curve for the steel vessel. The mass loss due to evaporation in the aluminum sample pan was 97.4% in the temperature range 100-120 ^{o}C of which can be attributed to water evaporation. The main component of this mixture is water. In this situation, where there is a low concentration of examined compound, the DSC results are not reliable. For the purpose of safety measurements, there is no need for DSC experiments with steel hermetic sample pans as well as aluminum ones.

3.2. Thermal decomposition of ammonium nitrate(V) (AN)

AN (NH_4NO_3) is of interest as a potential replacement for ammonium perchlorate as a solid propellant oxidizer. A review of the thermal degradation of AN is published by Chaturvedi and Dave [8]. It is known that AN can react violently with the addition of various substances or impurities. Pure AN is defined as safe due to its considerable stability at lower temperatures, but during production, storage or transportation it can be contaminated with products such as acids, oils, organic substances which can act catalytically, causing explosive reactions. The thermal degradation depends on pressure and temperature and experimental conditions such as sample size, rate of heating, and purity of compound monitoring techniques.

A measurement was made for AN using a steel hermetic sample pan and an aluminium sample pan. Pure, crystalline AN, measured by DSC, shows the presence of 5 transition endothermic peaks (designated as phases I, II, III, IV and V). All the peaks are below the melting point of AN, which is approximately 170 °C. Onset temperatures of these transitions obtained in the DSC curve were: 51-53, 85, 125.8-126 and 168.7-

168.8 °C, the endothermic transformation with a T_{onset} 167.8 °C is associated with the decomposition of AN and the release of gaseous decomposition products. The peak maximum of the decomposition peak is 260 °C. It decomposes around 230 °C at 760 mmHg. All these peaks (TG and DSC) are visible in Figure 3 which presents DSC measurements for pure AN made in aluminum sample pans (solid line) and steel hermetic crucibles (solid and dot line).

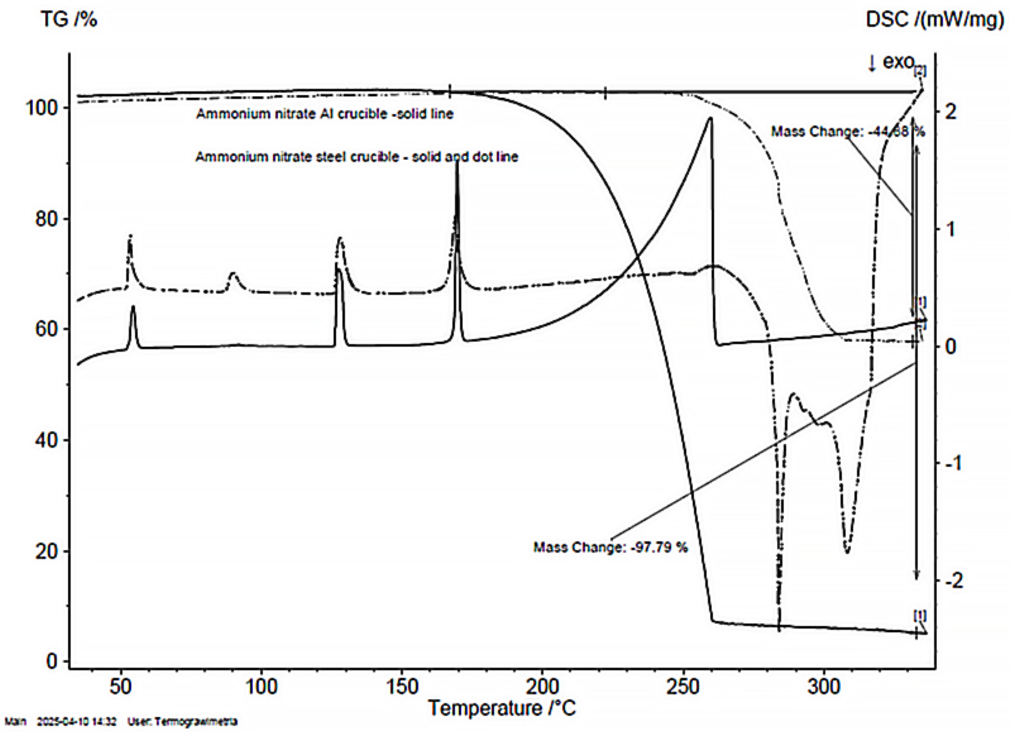

Figure 3. Superimposed DSC curves (TG and DSC) for AN obtained using two types of sample pans: aluminum sample pan (solid line) and steel hermetic pan (solid and dot line**)**

For the AN sample tested in the hermetic steel sample pan, the beginning of very strong exothermic decomposition can be observed at 270 °C, with a heat of decomposition of 2754 J/g. It should be noted that the mass loss in these conditions is around 44%, up to a temperature of 300 °C. When using aluminum pans, the mass loss is over 95%, which indicates the complete release of the gas phase through the openings in the sample pan closure.

The rapid decomposition of AN was caused by the catalytic action of Cr, present as a component of steel. Chromium compounds in particular show greater catalytic action than other cations for AN. Arthur *et al.* [9] suggest that the catalytic effect of some metals being the material of the sample pan (in this case CrNi steel) can act as a catalyst and cause changes in the mechanism of decomposition. Both stainless steel and gold can catalyze certain decomposition reactions. It is anticipated that reactions between steel and several of the materials tested may occur. Gold, from which the gaskets are made, is chemically inert in these measurements.

In an aluminum sample pan, decomposition has an endothermal character with the release of volatile products up to 250 °C. The boiling point of AN according to literature, is approximately 210 °C, undergoing decomposition, releasing nitrous oxide and other gases.

3.3. Thermal decomposition of liquid sulphate waste after 2,4,6-trinitrotoluene (TNT) synthesis

DSC was carried out in measuring the thermal safety of the liquid by-products of TNT production. This product is the concentrated sulphite lye, a waste product generated in the purification (sulphiting) of TNT and is intended for disposal (so-called red waters). The chemical composition of this mixture is 4-6% sodium nitrate(III), a mixture of sodium dinitritoluene sulphonate isomers (20-22%) and trinitrotoluene (0.4-0.6%), the remainder being water.

A measurement of thermal decomposition was performed to compare the results obtained in an aluminium pan and a hermetic steel sample pan. The heating rate of the samples was 5 °C/min, the temperature range was from 30 to 400 °C and the sample mass was from 2.5 to 4.9 mg. Figure 4 shows the results as DSC and TG curves from both types of sample pans (solid line – steel, dotted line aluminum sample pans).

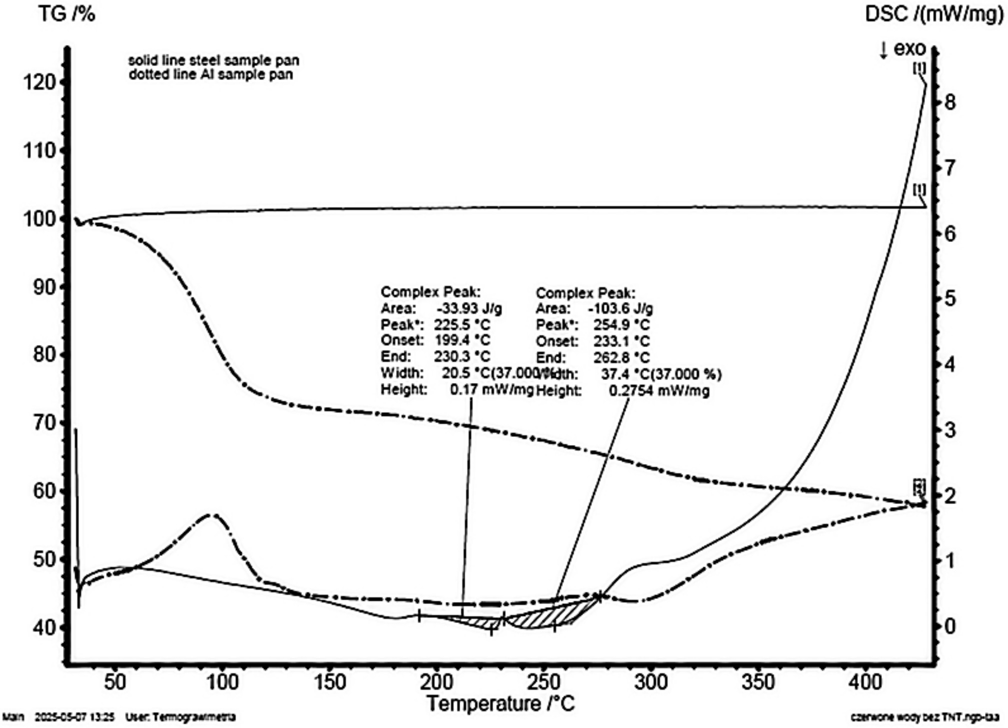

Figure 4. DSC thermoanalytical curves (TG and DSC) of sulphate wastes analyzed by DSC with steel and Al sample pans

Because of the presence of significant amounts of water, the evaporation endothermal peak in the DSC curve obtained from the aluminum sample pan is visible. The calculated heat was about 1550 J/g and the mass loss on the TG curve was about 75%. As thermal decomposition of pure TNT occurs in the temperature range of 200 to 340 °C, no exothermal peak was observed under these measurement conditions. In the steel sample pans two small exotherms (between 220-250 °C) were detected with the total heat of reaction being about 140 J/g. No evaporation was observed. It is rather difficult to attribute thermal properties to a product taking into account these results because the high content of water.

3.4. Thermal decomposition of permethrin-based biocidal/pesticide products

Permethrin (CAS number 52645-53-1) is a widely applied insecticide from the group of synthetic pyrethroids, commonly used as a plant protection product and a component of biocidal products. Its melting point is 34-39 °C, the boiling point being above 290 °C (at 1013 hPa). It is not known as an explosive, but there is a requirement to test thermal safety for registration purposes due to pesticide and biocide regulations.
Results of investigations into thermal decomposition of pyrethroids in oxidizing atmosphere were published and presented at Conference CORESTA in Paris in 2006 [10]. The results of experiments indicate that pyrethroids such as permethrin undergo evaporation and oxidative pyrolysis, Evaporation occurs at a temperature of about 250-300 °C, sometimes in parallel with oxidative pyrolysis. When the temperature rises above 350-400 °C, a more extensive process occurs, degradation to low molecular weight compounds. Oxidation and the associated production of CO, CO_2 and H_2O dominate when the temperature rises above 400-500 °C. Permethrin is not classified as an explosive or a self-reactive substance. DSC measurements were performed on permethrin in an aluminum vessel and in a steel, hermetic vessel and the graphs were superimposed. These are shown in Figure 5.

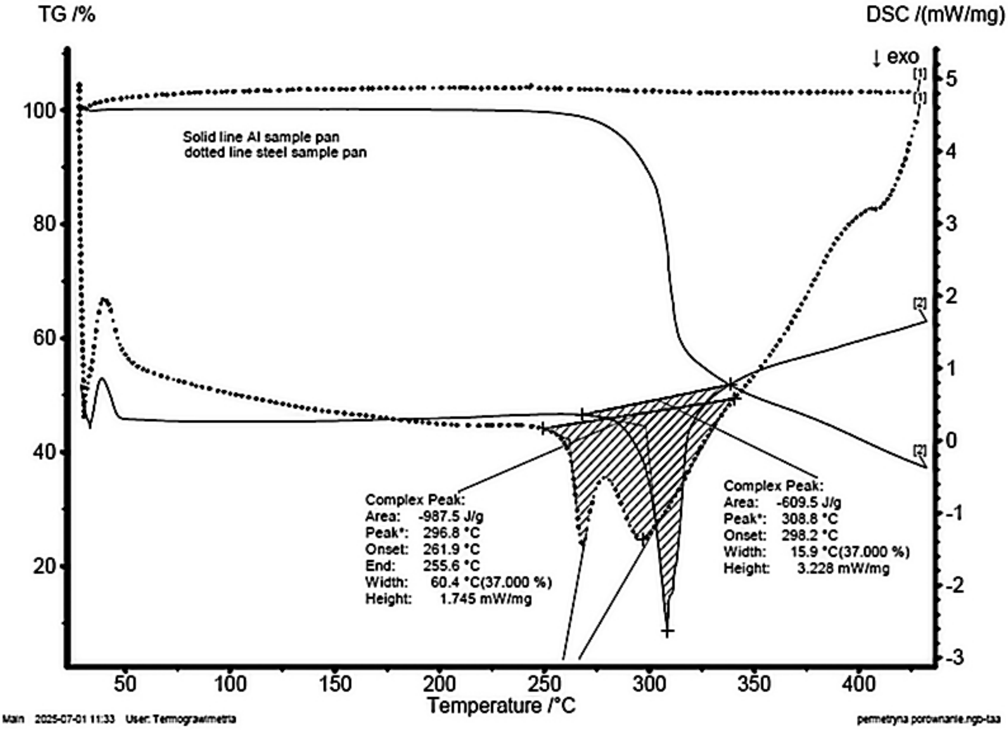

Figure 5. DSC curves (TG and DSC) of permethrin in two types of crucibles – steel and Al (sample masses are 3.4 mg – in steel and 5.5 mg in an aluminum crucibles, respectively)

As can be seen in the figure, the result for sample analyzed in an aluminum crucible in the area of boiling temperature for permethrin shows the exothermic decomposition and certain mass loss. The exothermic peak visible on the DSC curve obtained in a hermetic sample pan also shows the decomposition. The thermal effect for exothermal decomposition for sample in the Al crucible was 609.5 J/g and onset temperature was 298.2 °C, for the hermetic steel sample pan the heat of reaction was 987.5 J/g and onset temperature was 261.9 °C. For solid product containing Permethrin in lower concentrations (about 20% in product which is used after dilution in water for application), only a small exothermal peak is observed with the heat of reaction being about 33.4 J/g as can be observed in Figure 6.

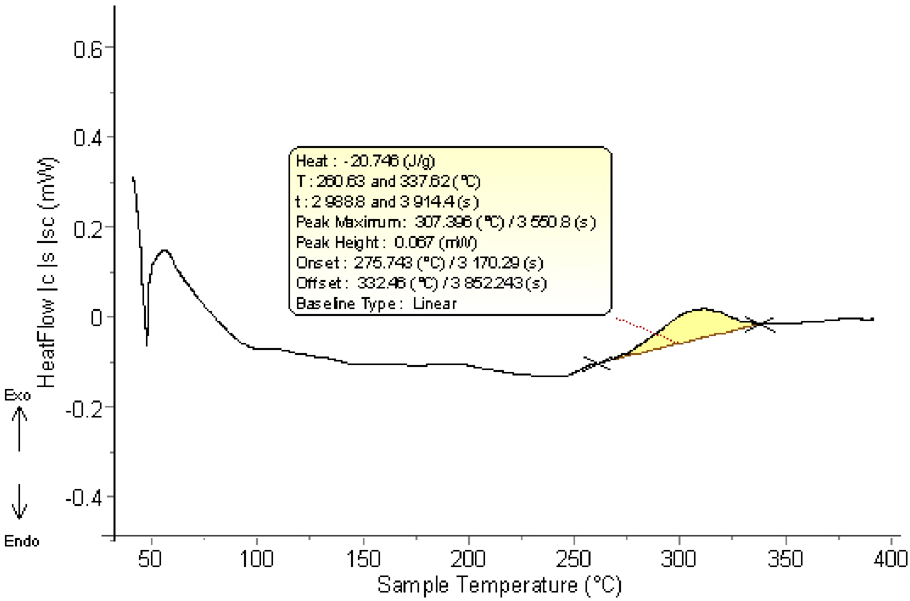

Figure 6. DSC curve for commercial solid product with 20**%** of permethrin content

It can be concluded that the presence of permethrin in commercial products has a rather negligible impact on the thermal safety of these products. Some commercial permethrin formulations are used as biocidal products against mosquitos, and contain different amount of active ingredient. As can be observed, the decomposition of permethrin appears in the range of boiling temperatures of about 290 °C. The decomposition can give a strong exothermic effect in the pure compound, but will not be visible in formulations, because of the much lower concentration of active ingredients.

4. Conclusion

- The DSC method is approved as a method of determination of thermal safety for numerous group of compounds, products of reactions or, mixtures. DSC enables a preliminary assessment of the thermal hazards of potentially energetic materials. Using unsuitable sample pans can lead to incorrect. conclusions about the presence of exothermal decomposition. For example, in the case of hydrogen peroxide measurements. In a typical aluminum sample pan an endothermic peak with a simultaneously great mass loss of volatile decomposition gaseous products is observed. In hermetic steel sample pan, an exothermic peak is observed accompanied by a high enthalpy of decomposition. In the case of hydrogen peroxide products at high concentrations, these should be tested in a steel high pressure sample pan since exothermal decomposition includes the area of water evaporation.
- Biocidal and pesticidal products should be subjected to thermal stability tests because of legal reasons, to assess whether they are explosives or self-reactive substances. The DSC technique seems to be relatively simple and quick and there is great interest in using DSC as a universal tool for thermal safety measurements.

- In some cases, there are certain factors which need to be considered before designing an experiment. It is also a fact that the use of hermetic sample pans protects from the release of solvents and gaseous decomposition products. If there are no signs of exothermal decomposition appearing as visible peaks, there is no reason to use this method.
- Most explosives show exothermal peaks of decomposition in commonly used sample pans made from aluminum. There is another situation in the case of liquid products. The use of aluminum pans with limited pressure resistance allows for the release of solvent with the endothermic peak overlapping the exothermic decomposition peak. There is also the problem of concentration of active ingredient in the tested product. For diluted solutions of hydrogen peroxide-based products, the exothermic decomposition peak is small and not visible even using a high-pressure pan.
- Sometimes there are visible examples of a reaction between the tested substance and sample pan material. In the case of ammonium nitrate(V) there is strong decomposition with an exothermal peak which can be attributed to the reaction being catalyzed by the steel sample pan material (Cr). Total decomposition has an endothermal character with the release of gaseous products.
- In pesticide formulations and biocides, whether mixed with water or inert components, the effect of thermal degradation will be not observed in either aluminum or steel sample pans. Testing biocidal products or pesticide formulations containing significant amounts of neutral substances like water, sugar, solid inorganic substances and small concentrations of the active substance, use of the DSC technique sometimes will not lead to reasonable results being obtained. The obligatory using of steel hermetic sample pan given by guidance [4] is unjustified. When using hermetic pans, the cost of such a method grows significantly. For the DSC analysis of biocidal/pesticide or industrial products, it is advisable to know earlier the thermal behavior and concentration of active substances and other components like water or solvents. Although aluminum sample pans are not suitable for thermal hazard studies, in some cases they can be used as a first step prior to detailed investigations. However in some cases, they are irreplaceable.

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