APPLICATION **NOTE**

Hazard Potential of Decomposition Reactions Using the Example of Hydrogen Peroxide (H_2O_2)

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1 NETZSCH MMC 274 *Nexus*®

Hydrogen Peroxide

Pure hydrogen peroxide (H_2O_2) is a pale blue liquid, mixable in any ratio with water. Low-percentage aqueous solutions are widely used as bleaching agents due to their strong oxidizing properties. Besides for the bleaching of wood, paper or hair, hydrogen peroxide solutions are also used as oxidizing agents or in medical application as disinfectants. The tendency of hydrogen peroxide to decompose into water and oxygen (see equation 1 below) is the reason for its application as a liquid propellant in rocket engines.

(equation 1) $$2\,H_2O_2 \overset{\Delta T}{\rightarrow} 2\,H_2O + O_2$$

Multiple Module Calorimeter (MMC)

The NETZSCH Multiple Module Calorimeter MMC 274 *Nexus*® (figure 1) offers three different measurement modules [1]. The ARC Module can be used for thermal hazard studies; the Coin-Cell Module is specialized for the investigation of batteries; and the Scanning Module can be used to evaluate caloric data from a single heating run. In contrast to the widely used and well-known technique of differential scanning calorimetry (DSC), the Scanning Module of the MMC can handle samples up to a volume of 2 ml. For heating the samples, there are two options available: either a constant heating rate or a constant level of power. By using information about both the power supplied to the sample and the heating rate, a heat-flow signal can be calculated. Using metals such as indium, tin and bismuth, both the temperature and the sensitivity of the instrument can be determined. At 1000 to 9000 mg (sample volume about 1 ml), typical sample masses are considerably higher for the MMC than sample masses used for DSC, which are typically between 5 and 10 mg. Even so, the evaluated uncertainty for the Scanning Module of the MMC is about 1% for temperature determinations and less than 5% for enthalpy determinations.

This work studies the thermal decomposition behavior of hydrogen peroxide (35%) employing two MMC modules, the Scanning Module (see figure 2) and the ARC Module (see figure 3). Via an external heater which directly surrounds the sample vessel (figure 4), the Scanning Module can provide the sample with a constant level of power.

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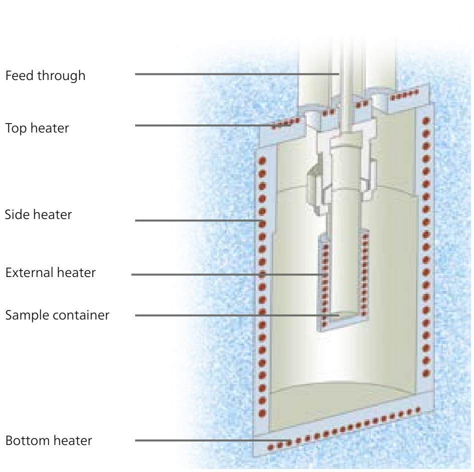
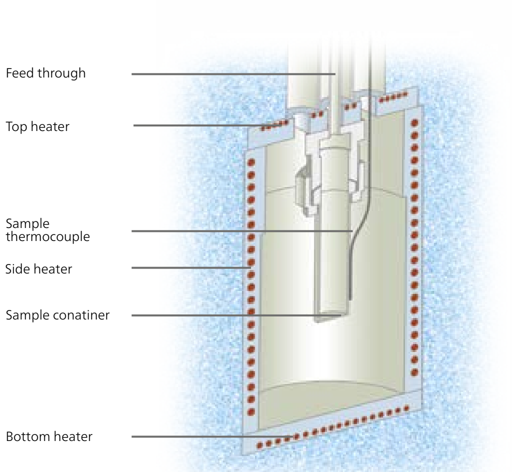


2 Schematic of the Scanning Module with external heater



3 Schematic of the ARC Module

4 Sample vessels for the NETZSCH MMC 274 *Nexus*®

Measurement Conditions

The measurement conditions are summarized in table 1. Hydrogen peroxide (Sigma Aldrich) was received as an aqueous solution (35%) and is stored at ambient temperature.

Results and Discussion

Depending on the change in the samples' heat capacity, the constant power input usually results in an almost constant heating rate at the sample. Figure 5 shows the outcome of heating hydrogen peroxide (35%) using a Scanning Module at a constant power input of 250 mW. The resulting heating rate is about 1 K/min for the first 60 minutes. After one hour, the decomposition reaction starts and produces additional heat. During the decomposition reaction, the heating rate rises to a maximum of 5.6 K/min and the detected pressure rises as well. According to equation 1, the decomposition reaction generates oxygen. Besides the evaporation of water, this gas formation is the major reason for the pressure increase during heating.

Tab 1. Measurement conditions

	MMC 274 *Nexus*®	
MMC Module	**Scanning**	**ARC**
Vessel material	Stainless steel	Stainless steel
Vessel type	Closed	Closed
Vessel mass	7176.38 mg	7233.59 mg
Heating	Constant power (250 mW)	HWS
Atmosphere	Air	Air
Purges gas rate	Static	Static
Temperature range	RT ... 250°C	RT .. 250°C
Sample mass	1031.1 mg	1008.1 mg

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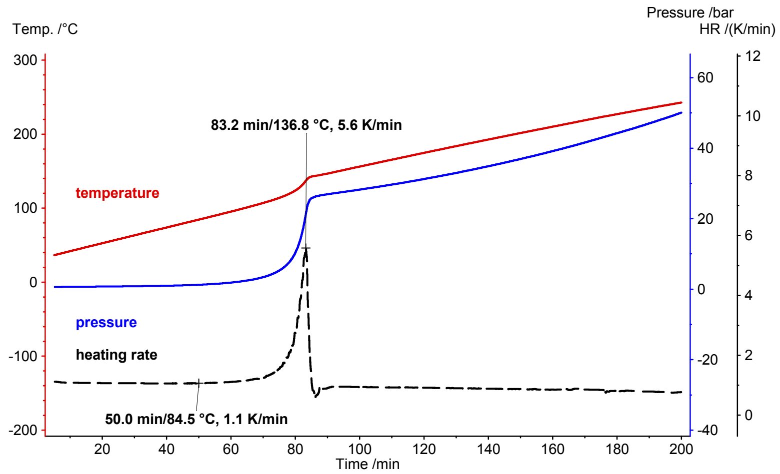
Comparison of the Behavior of H_2O_2, H_2O and Empty Vessel

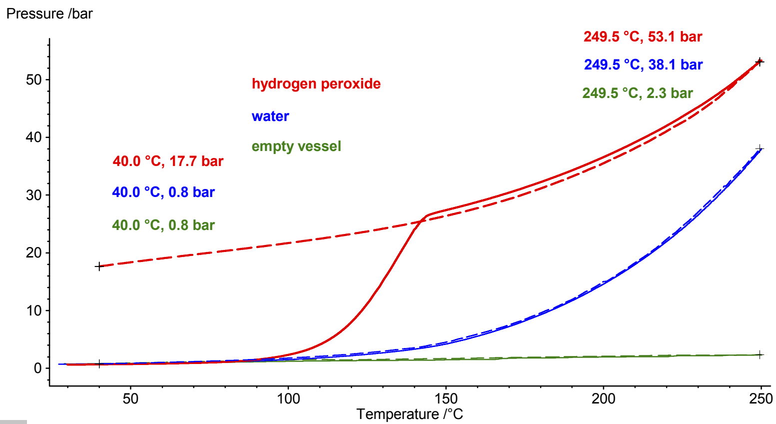
The results in figure 5 present exclusively the sample heating. Since the decomposition reaction of hydrogen peroxide is not reversible, the oxygen generated is not taken up again in order to form the initial hydrogen peroxide during cooling. Instead, the formed products of water and oxygen cool to ambient temperature as a liquid and a gas, respectively. The pressure signal indicates 17.7 bar at 40°C, which reflects the amount of oxygen being formed during decomposition (figure 6). Taking the same amount of water instead, the pressure also increases during heating, but since water remains chemically unchanged, all water vapor precipitates again during cooling. That's why the dashed blue line, indicating the pressure signal for water during cooling, shows values almost identical to the heating (solid lines). Just for comparison, the green lines show the course of the pressure signal during heating and cooling for an empty vessel.

Advantages of the Scanning Module

These results obtained by the MMC Scanning Module clearly demonstrate that the discontinuous course of the heating rate along with the pressure build-up are excellent indicators for hazard potential in terms of decomposition reactions or exothermic reactions. Even a small power level such as 250 mW, resulting in a comparably small heating rate of approximately 1 K/min, the heating for this exemplary measurement takes less than 4 hours. Therefore, the MMC Scanning Module is well suited to be used as a screening tool. In cases where pressure and/or temperature increase are detected, an adiabatic test should be the next step.



5 Results of thermal decomposition of hydrogen peroxide (35%); temperature (red), pressure (blue) and heating rate (black)



6 Results of heating and cooling of hydrogen peroxide (35%, red), water (blue) and empty vessel (green). Heating is shown with solid lines, cooling with dashed lines.

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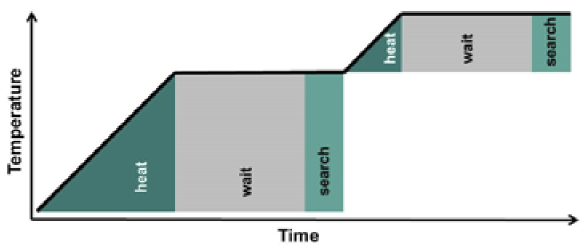
Accelerating Rate Calorimetry

Specialized calorimeters allow for sample investigation in accordance with the method of accelerated rate calorimetry (ARC). An ARC-type equipment offers an adiabatic sample environment in order to not allow any heat exchange and to detect even the smallest of self-heating reactions. The typical measurement mode is called heat-wait-search (HWS). The sequence of heating, equilibration and detection of even the smallest of self-induced temperature changes is a quasi-isothermal approach used in order to determine the temperature at which the decomposition reaction starts. A diagram depicting heat-wait-search is shown in figure 7.

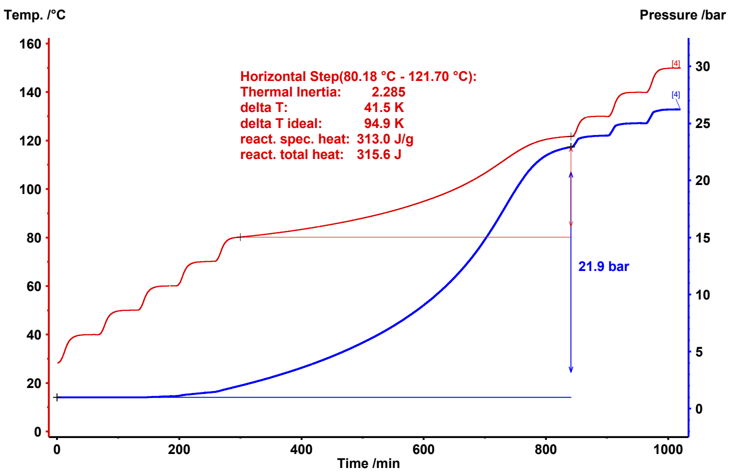
A cross-section of the MMC's ARC Module set-up is depicted in figure 3. If the self-heating rate of 0.02 K/min is exceeded during the detection period (search), the measurement changes from heat-wait-search to adiabatic mode. This means the surrounding heaters (top, side and bottom) no longer follow the above-mentioned sequence, but rather track the sample temperature. During this "adiabatic" mode, there is no temperature difference and thus no heat exchange between the sample and the calorimeter environment.

H_2O_2 in the ARC Mocule

Figure 8 depicts the results of the decomposition of hydrogen peroxide (35%) investigated with the MMC's ARC Module employing the heat-wait-search mode. The temperature increment in the stepwise heating was 10 K and the system was allowed to stabilize for 30 minutes during the wait segment. The answer to the question of whether or not an exothermic event is detected during the 10-minute search period depends on the exothermic threshold. Between 40°C and 70°C, self-heating during the search period was less than 0.02 K/min and the heat-wait-search sequence continued. At 80°C, the detected self-heating had exceeded that threshold and the calorimeter thus changed over to the adiabatic mode. The temperature increase (ΔT_{obs}) was detected to be 41.5 K. Taking thermal inertia [1] into account, the adiabatic temperature increase is calculated to be 94.9 K (ΔT_{ad}). The difference is based on the so-called PHI-factor which is mainly given by the ratio of mass times specific heat capacity of the container versus mass times specific heat capacity of the sample. In addition to the increase in temperature caused by self-heating of the sample during decomposition, the pressure increase can also be quantified. At the end of the adiabatic segment, the increase in pressure was more than 20 bar.



7 Sequence of the heat-wait-search (HWS) measurement mode



8 Results for the decomposition behavior of hydrogen peroxide investigated with the MMC's ARC Module and heat-wait-search (HWS) mode

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Conclusion

The decomposition behavior of a 35% aqueous hydrogen peroxide solution was investigated with the MMC's Scanning Module as well as with its ARC Module. Since the Scanning Module is operated using either a constant level of power (as was the case here) or a constant heating rate, these experiments are far less time-consuming than with the heat-wait-search method. Therefore, the Scanning Module is an excellent screening tool for investigating unknown samples with respect to self-decomposition or hazardous potential. In cases where an investigated sample exhibits unsteady temperature behavior during the scanning run, or in cases where a decomposition reaction is indicated by pressure build-up, any further investigation on the samples should be carried out using ARC-type equipment. Values such as pressure build-up as well as observed and adiabatic temperature rise are extremely important in assessing the hazardous potential of chemicals and can easily be obtained using the NETZSCH Multiple Module Calorimeter MMC 274 *Nexus*®.

References

[1] E. Füglein, S. Schmölzer, "Epoxy Curing Investigated by Means of the DSC 214 *Polyma* and MMC 274 *Nexus*®", NETZSCH Application Note 130, 2019
[2] E. Füglein, "Screening of Hydrogen Peroxide Solutions by Means of Scanning and ARC Tests®", NETZSCH Application Note 132, 2019

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