

Screening of Hydrogen Peroxide Solutions by Means of Scanning Tests and ARC Tests

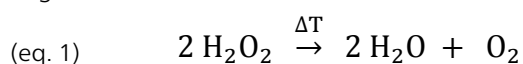
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1 NETZSCH MMC 274 Nexus®

Hydrogen Peroxide

Pure hydrogen peroxide (H₂O₂) 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 (equation 1 below) is the reason for its application as a liquid propellant in rocket engines.



The Multiple Module Calorimeter (MMC) Compared to Differential Scanning Calorimetry (DSC)

The NETZSCH Multiple Module Calorimeter MMC 274 Nexus® (figure 1) offers three different measurement modules [1]. The ARC Module can be used for thermal

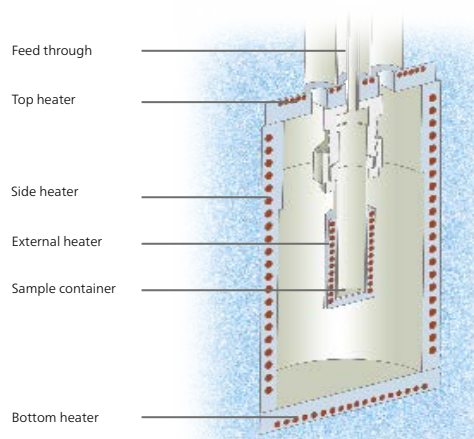
hazard studies; the Coin-Cell Module is specialized for the investigation of batteries; and the Scanning Module can be used to evaluate caloric data from a single heating run. In contrast to the widely used and well-known technique of differential scanning calorimetry (DSC), the Scanning Module of the 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.

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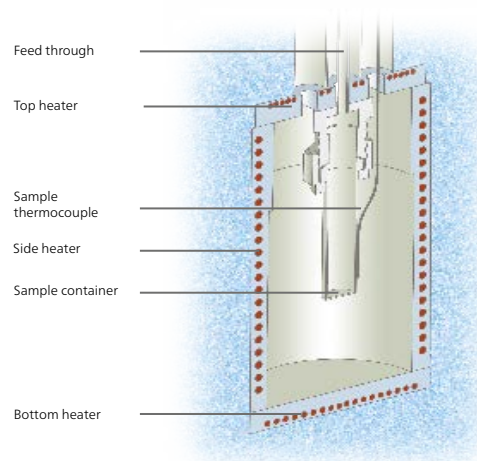
Scanning Module and ARC Module

This work studies the thermal decomposition behavior of aqueous hydrogen peroxide solutions of varying concentrations. Two MMC modules are employed for these studies: the Scanning Module (see figure 2) for screening

of the samples and the ARC Module (see figure 3) for heat-wait-search (HWS) studies. 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.



2 Schematic of the Scanning Module with external heater



3 Schematic of the ARC Module



4 Sample vessels for the NETZSCH MMC 274 Nexus®

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Measurement Conditions

Hydrogen peroxide (Sigma Aldrich) was received as an aqueous solution (35%) and stored at ambient temperature. The hydrogen peroxide solution was used as

received and was diluted with purified water in order to observe several lower concentrations. The composition of the diluted samples is summarized in table 1 and table 2. The measurement conditions for both the Scanning and ARC Modules are compared in table 3.

Tab 1. Sample compositions for screening (Scanning Module)

Sample Number	Sample Concentration/%	H ₂ O ₂ /mg	H ₂ O/mg	Total/mg
1	35	1.03106	0.0	1.03106
2	26	0.75757	0.25623	1.0138
3	17	0.5148	0.52494	1.03974
4	8.6	0.25169	0.7741	1.02579
5	4.3	0.12376	0.88605	1.00981
6	2.6	0.07316	0.92551	0.99867
7	1.1	0.03099	0.96707	0.99806
8	0.4	0.01215	1.00176	1.01391

Tab 2. Sample compositions for adiabatic testing (ARC Module)

Sample Number	Sample Concentration/%	H ₂ O ₂ /mg	H ₂ O/mg	Total/mg
9	35	0	1.02157	1.02157
10	17	0.74935	0.52494	1.00359
11	8.6	0.51466	0.50962	1.02428
12	4.3	0.25036	0.77525	1.02561
13	2.6	0.14776	0.877248	1.02034

Tab 3. Measurement conditions

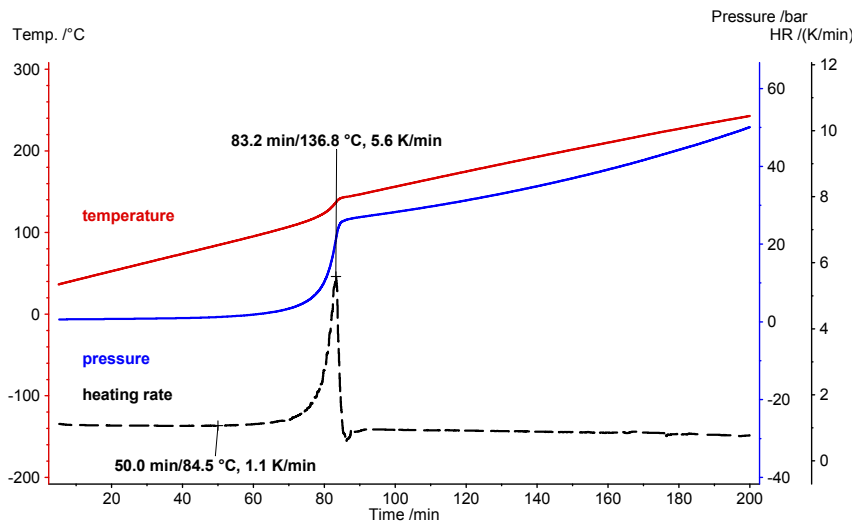
MMC 274 Nexus®		
MMC Module	Scanning	ARC
Vessel material	Stainless steel	Stainless steel
Vessel type	Closed	Closed
Vessel mass	7.0 to 7.25 mg	7.0 to 7.25 mg
Heating	Constant power (250 mW)	HWS
Atmosphere	Air	Air
Purges gas rate	Static	static
Temperature range	RT ... 250°C	RT ... 250°C
Sample mass	998.67 to 1039.74 mg	1003.6 to 1025.6 mg

Results and Discussion

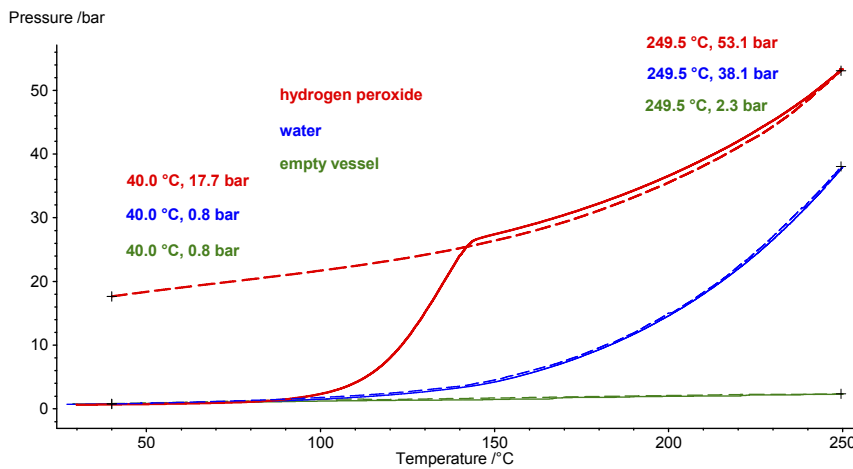
Depending on the change in the samples' heat capacity, the constant power input usually results in an almost constant heating rate at the sample. Figure 5 shows the outcome of heating hydrogen peroxide (35%) using the Scanning Module at a constant power input of 250 mW. The resulting heating rate is 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.

Comparison of the Behavior of H₂O₂, H₂O 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



5 Results of the 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 portrayed with solid lines; cooling with dashed lines.

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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.

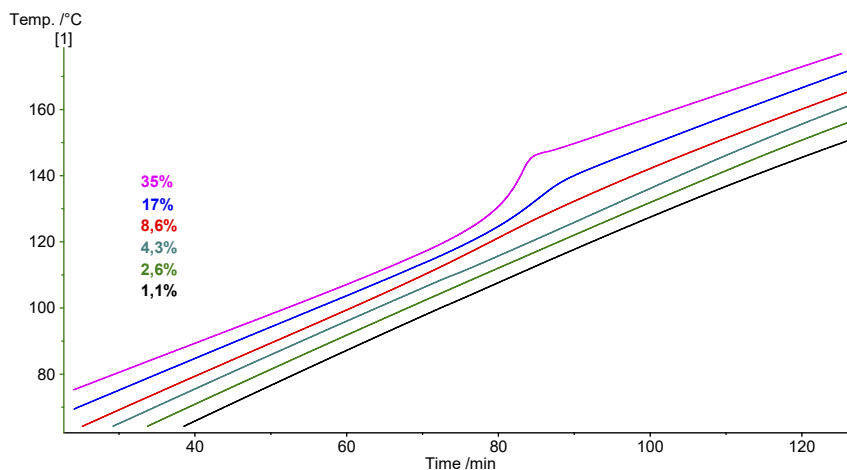
H₂O₂ with Various Concentrations

Especially when comparing with water, it can be seen that evaporation – which occurs to some extent even inside a closed vessel system – is always reversible. This is confirmed by the pressure signal at 40°C after the cool-down. On the other hand, the decomposition reaction of hydrogen peroxide produces a specific amount of gas. Therefore, the pressure signal is

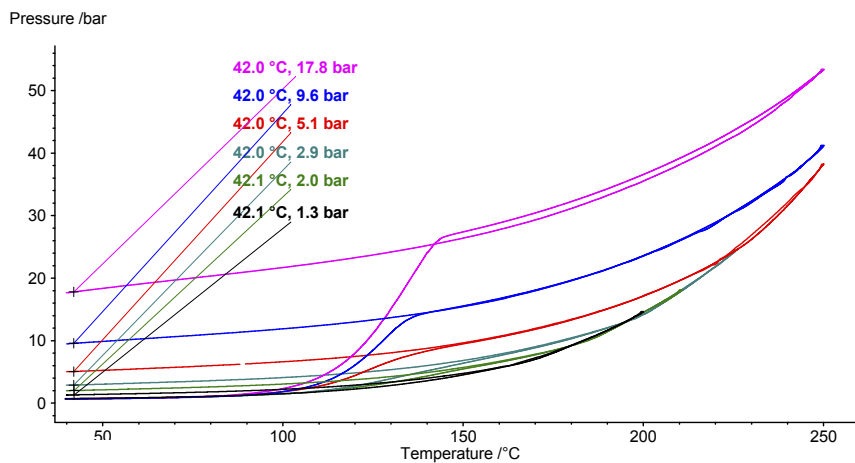
expected to be proportional to the absolute amount of hydrogen peroxide inside the solution. When repeating these tests with samples of various hydrogen peroxide concentrations, the pressure build-up during the test should be proportional to the hydrogen peroxide concentration. Figure 7 compares the heating results for samples 1 to 6. The associated hydrogen peroxide concentrations are summarized in table 1.

Correlation Between H₂O₂ Concentration and Pressure

The decomposition reaction of hydrogen peroxide is indicated by the increase in heating rate measured at the sample as well as by the build-up of pressure. In figure 8, the signal of the remaining pressure after the reaction



7 Comparison of scanning tests with hydrogen peroxide samples of various concentrations



8 Comparison of the pressure signal for various hydrogen peroxide concentrations during heating and cooling

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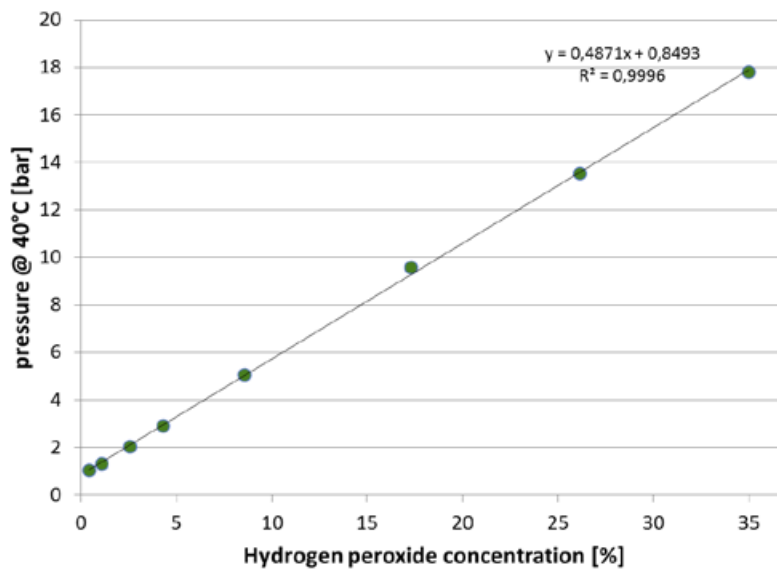
and after the cool-down to 42°C is evaluated. There is an almost perfectly linear correlation of the pressure with the hydrogen peroxide concentration of the sample. This correlation is depicted in figure 9.

Various concentrations of H₂O₂ investigated with the ARC Module

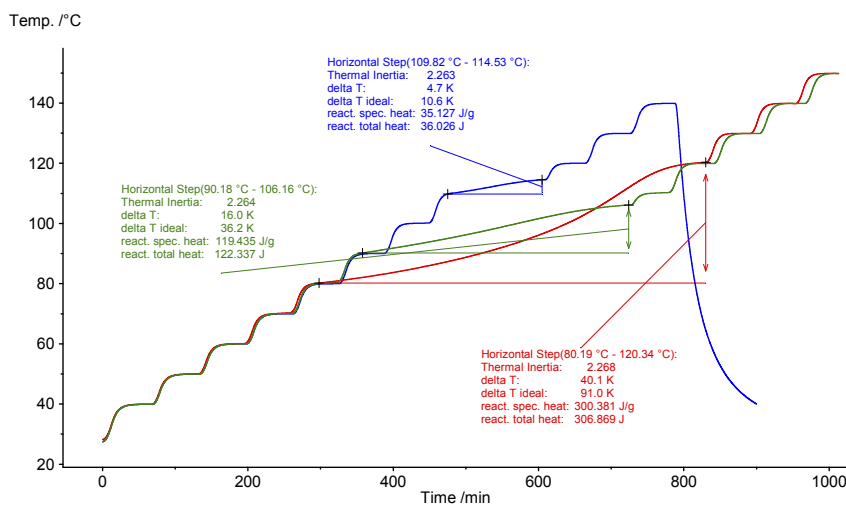
A similar series of aqueous hydrogen peroxide concentrations was also investigated using the MMC's ARC Module (figure 3). The associated hydrogen peroxide concentrations are summarized in table 2. The ARC Module can

be employed to specifically determine the temperature of the beginning of decomposition by means of a so-called heat-wait-search (HWS) program. With the help of the sequence of heating, equilibration and detection, the self-heating rate of the sample is determined under quasi-isothermal conditions and then, the sample is investigated in adiabatic mode [1, 2].

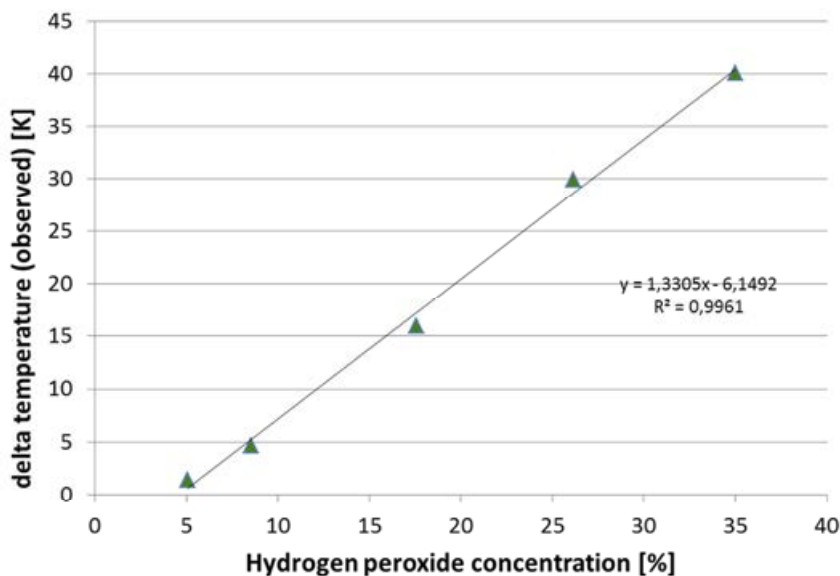
The results for hydrogen peroxide concentrations of 35%, 17% and 8.6% are presented in figure 10. As expected, the results confirm a smaller temperature increase (ΔT_{obs}) under adiabatic conditions for lower



9 Correlation of remaining pressure at 42°C with the hydrogen peroxide concentration of the samples



10 HWS test results for aqueous hydrogen peroxide solutions of 35% (red), 17% (green) and 8.6% (blue)



11 Detected temperature increase during adiabatic mode of HWS tests

hydrogen peroxide concentrations. The temperature at which the decomposition reaction is detected (onset) increases for lower concentrations due to the lower release of energy (90°C and 110°C). The maximum self-heating rate for hydrogen peroxide concentrations lower than 5% is less than 0.02 K/min. That’s why no exothermic events are detected in such a case. The temperature increase steps (ΔT_{obs}) detected during the adiabatic segments of several HWS tests are shown in figure 11.

Conclusion

These results nicely demonstrate the screening capability of the MMC Scanning Module. In the case of strongly exothermic reactions, the self-heating rate will increase significantly – to above the level of roughly 1 K/min – as a result of the constant power input. Thus, when an unknown sample exhibits an exothermic decomposition reaction, this can be recognized within several hours. As soon as hazardous potential is recognized, an adiabatic test is recommended using an MMC ARC Module [1].

Such an HWS test can easily take a full day but on the other hand, is much more pertinent to thermal equilibrium than a scanning test [2].

Additionally, the results presented above nicely demonstrate the usefulness of the pressure signal. The constant power input of 250 mW enables a heating rate of approximately 1 K/min for an aqueous sample of 1 g. Samples having a concentration of hydrogen peroxide lower than 5% do not exceed this heating rate via the energy released during the decomposition reaction. This means that, through the self-heating rate of the sample, the decomposition reaction for low concentrations is masked by the power input. The pressure signal, in contrast, is unaffected by the power input. Therefore, it can be taken as a significant indicator as to whether or not a decomposition reaction has occurred, especially in the case of lower concentrations.

References

- [1] E. Füglein, S. Schmölzer, “Epoxy Curing Investigated by Means of DSC 214 *Polyma* and MMC 274 *Nexus*®”, NETZSCH Application Note 130, 2019
- [2] E. Füglein, “Hazard Potential of Decomposition Reactions using the Example of Hydrogen Peroxide (H_2O_2)”, NETZSCH Application Note 131, 2019