

VariPhi® – The Patented Immersion Heater for Variation of the Φ -Factor in Thermal Runaway Tests

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Introduction

Accelerating Rate Calorimetry (ARC) is a method for studying worst-case scenarios and thermal runaway reactions. In contrast to other calorimetric techniques such as reaction calorimetry, combustion calorimetry or differential scanning calorimetry (DSC), ARC-type equipment allows for an adiabatic sample environment. Adiabaticity is essential in order to observe the most violent reaction progress possible. Decomposition reactions, which are of particular interest in this context, produce heat and pressure since the reactions are usually heavily exothermic and are forming decomposition gases. The adiabatic sample environment is realized inside the ARC-type calorimeter via a set of heaters surrounding the sample compartment and a clever temperature control regime. One aim is to detect the temperature at which the self-decomposition of a sample or a sample mixture starts. Another goal is to prevent any exchange of heat between the sample and its surrounding once the exothermic decomposition reaction has started. As soon as the self-heating rate exceeds a certain threshold (which is usually in the range of 0.02 K/min), all heaters surrounding the sample will track the sample temperature. Without heat exchange, there will be no heat loss to the surrounding, and if no heat dissipates, the entire heat of reaction remains inside the sample, thus increasing the sample temperature. The higher the sample temperature, the faster the rate of reaction will be. Such an experiment not only delivers the starting temperature of the decomposition reaction under quasi-isothermal conditions, it also allows for determination of the maximum temperature rise and the maximum pressure rise under adiabatic conditions.

The PHI-Factor (ϕ) or “Thermal Inertia”

From the two signals measured, temperature and pressure, the maximum rate can be calculated and predictions are usually made for the temperature at which the investigated reaction takes a minimum of twenty-four hours to reach its maximum temperature development rate, the time-to-maximum rate (TMR_{24h}).

$$\text{(equation 1)} \quad \phi = \frac{\Delta T_{\text{ad}}}{\Delta T_{\text{obs}}} = 1 + \frac{m_V \cdot c_{p,V}}{m_S \cdot c_{p,S}}$$

An essential parameter for the test scenario is what is known as the PHI-factor (ϕ). It gives the ratio of mass and specific heat of the sample to the sample vessel, where ΔT_{ad} is the temperature rise under adiabatic conditions, ΔT_{obs} is the observed temperature rise under given conditions, m is the mass, c_p is the specific heat capacity, s is the sample and v is the vessel [1].

The ϕ -factor, also known as thermal inertia, is better the closer it gets to 1, which means in the ideal case that the test results are defined through the sample and not through the influence of the vessel. On the other hand, the above-mentioned equation points out that the ratio of sample-to-vessel mass is somehow yielded by the reactivity of the sample itself, along with the maximum volume of the sample container and the materials available for the vessels. In order to show how these parameters will influence the ϕ -factor, table 1 summarizes ϕ -factors calculated for two samples (organic peroxides and hydrogen peroxide), two vessel materials (stainless steel and titanium) and for a realistic variety of sample masses.

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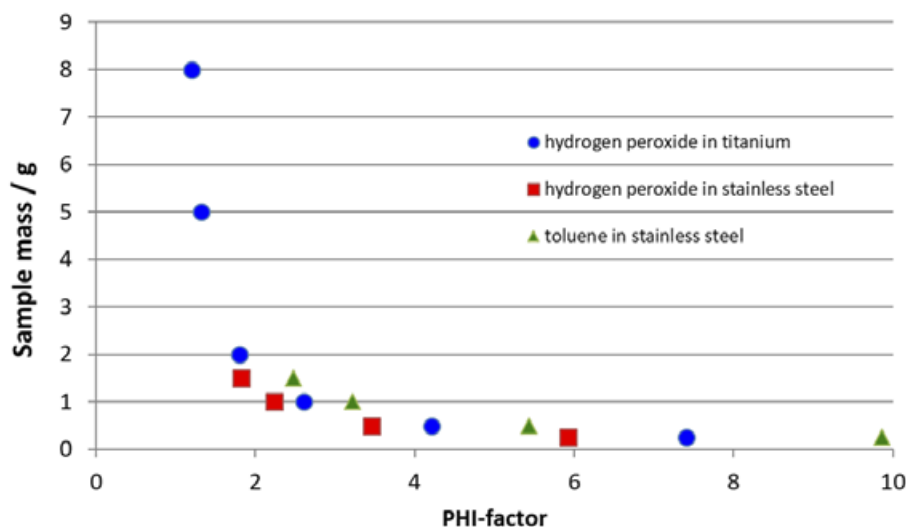
Tab 1. Calculated Φ -factors for various measurement conditions

Hydrogen peroxide mass / g	0.25	0.50	1.0	2.0	5.0	8.0
Φ for 10.0 g titanium vessel	7.41	4.20	2.60	1.80	1.32	1.20
Organic peroxide mass / g	0.25	0.50	1.0	1.5	5.0	8.0
Φ for 7.0 g stainless steel	9.86	5.43	3.21	2.5	-	-
Hydrogen peroxide mass / g	0.25	0.50	1.0	2.0	5.0	8.0
Φ for 7.0 g stainless steel	5.92	3.46	2.23	1.82	-	-

The correlation of sample mass and calculated ϕ -factor mentioned above is additionally shown in figure 1. Since the specific heat capacity of the sample to be investigated along with the specific heat capacity of the vessel material is usually given, the only parameter available for changing the ϕ -factor is the sample mass.

Increasing the sample mass can bring the ϕ -factor closer to 1, but there might be limitations to the volume of the vessel as well as limitations associated with the equipment itself. It is imperative to keep in mind the pressure range, temperature range and maximum tracking rate of the ARC-type calorimeter used in order to not exceed

one of them; otherwise, data might no longer be meaningful. It can be seen from figure 1 that, due to its total volume of 2.6 ml, the stainless steel vessel (figure 3) is limited to a sample mass of less than 2.0 g. Since vessels are usually not filled more than half, the expected ϕ -factor is between 2 and 4, depending on the specific heat capacity of the sample itself. Only with 1.5 mg hydrogen peroxide, which has a relatively high specific heat capacity, can a ϕ -factor of better than 2 be established. Even when using a titanium vessel offering 8.6 ml in volume, sample masses of more than 3.0 g and ϕ -factors in the range of 1.5 are somehow difficult to realize.



- 1** Correlation of the sample mass and Φ -factor for different samples and vessel materials according to equation 1. The associated titanium vessel is shown in figure 2; the associated stainless steel container in figure 3.



2 Spherical vessel, titanium, 8.6 ml, 10.0 g



3 Cylindrical vessels, stainless steel, 2.6 ml, 7.2 g

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4 NETZSCH MMC 274 *Nexus*[®] Multiple Module Calorimeter

All samples which exhibit thermal hazard potential are also characterized by increased risk with regard to handling in a laboratory environment. From a safety point of view, it is of course far better to handle risky samples in small amounts. In consideration of the above-discussed limitations, a dilemma ensues. The lower the ϕ -factor, the more meaningful the results should be. This, however, would require larger sample amounts. Yet decreasing the sample mass to address the safety issues will increase the ϕ -factor. In order to overcome this dilemma, the patented *VariPhi*[®] was used inside an ARC Module of the MMC 274 *Nexus*[®].

The Multiple Module Calorimeter (MMC 274 *Nexus*[®])

The MMC 274 *Nexus*[®] Multiple Module Calorimeter (figure 4) offers three different measurement modules [2]. The Coin-Cell Module is specialized for the investigation of batteries and the Scanning Module [3, 4] can be used to evaluate caloric data from a single heating run. The ARC Module (figure 5) can be used for thermal hazard studies and was employed for the results presented in this work.

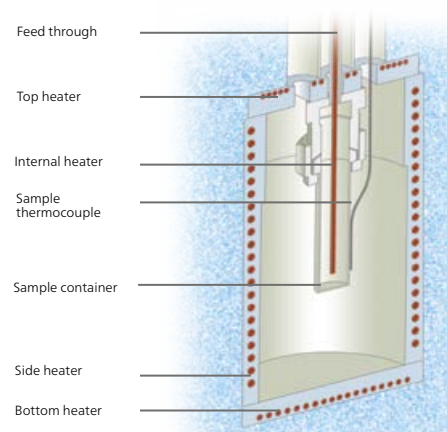
Test Substance: Hydrogen Peroxide Solution

Hydrogen peroxide (H_2O_2) thermally decomposes into water and oxygen. This decomposition reaction can be initiated thermally and is heavily exothermic. This is why hydrogen peroxide is usually handled as an aqueous solution of up to 35%. In terms of thermal safety studies, it is an ideal substance since it forms water and oxygen

during decomposition and this makes the cleaning and reuse of vessels quite convenient.

The ARC Module with *VariPhi*[®]

Figure 5 shows the setup of the MMC's ARC Module. The sample container is placed inside the calorimeter compartment and the sample temperature is detected via a thermocouple clamped directly to the outer wall of the sample container. The vessel itself is connected via a feed-through to a pressure gauge. Right in the center of this setup, the internal heater, called *VariPhi*[®], is placed inside the sample.



5 Schematic of the ARC Module with internal heater (*VariPhi*[®])

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This patented *VariPhi*[®] heater is the solution to the above-described dilemma. On the one hand, it can be used for a screening run in order to quickly detect whether or not an unknown sample exhibits hazardous potential. In this case, constant power would be supplied to the *VariPhi*[®] heater. Along with the resulting heating rate, a heat-flow signal can be calculated in order to distinguish between endothermic and exothermic sample effects. On the other hand, the *VariPhi*[®] heater can also be used to partially or fully compensate for the influence of the sample vessel (ϕ -factor; eq. 1). In this case, the *VariPhi*[®] heater applies the amount of heat to the sample which would usually be lost by warming up the sample container. Since the sample is the warmest part during a self-heating decomposition reaction, heat would be lost to warm up the vessel prior to being detected via the thermocouple which is clamped outside the vessel (figure 5). According to equation 1, the ϕ -factor can be either partially or completely compensated to achieve the ideal conditions with respect to the ϕ -factor. This way, it is possible to adjust the ϕ -factor to a value which reflects the real conditions of a reactor or it can be adjusted to $\phi = 1$ in order to study worst-case scenarios. The required power input for compensation is given by the mass and specific heat capacity of the vessel.

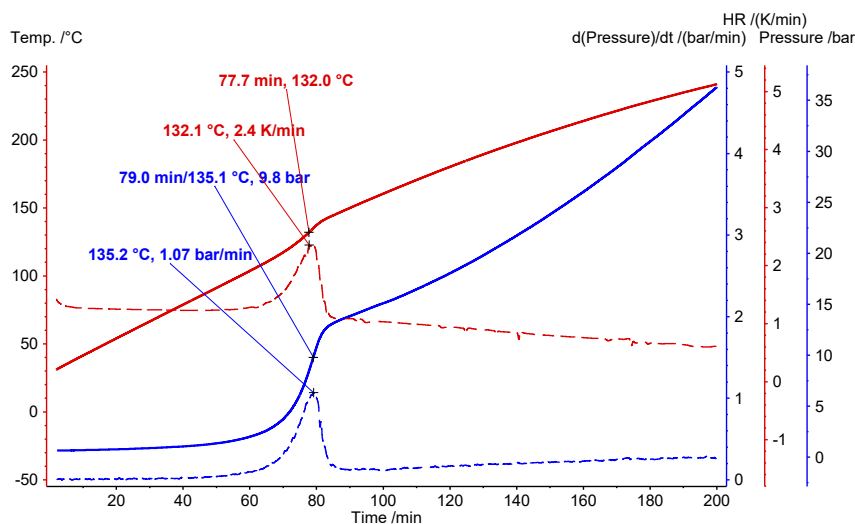
If a thermal hazard screening test has detected self-heating and pressure build-up (figure 6), it is imperative to carry out an additional thermal-runaway test. The results for such a heat-wait-search (HWS) test are depicted in figure 7. It compares the differences between the

compensated measurement results (red curve) and non-compensated ones (black curve). The measurement conditions are summarized in table 2.

In contrast to the scanning test, the corresponding heat-wait-search test of hydrogen peroxide detects the beginning of the self-heating already at 90°C (figure 7, black curve). The maximum self-heating rate was detected to be 0.08 K/min together with an temperature increase of 26.8 K (ΔT_{obs}). The observed temperature increase is evaluated by subtracting the onset temperature (T_{start} , beginning of the exothermal event) from the final temperature of the exothermal event (T_{final}) [1].

$$\text{(equation 2)} \quad \Delta T_{\text{obs}} = (T_{\text{final}}) - (T_{\text{start}})$$

The above-discussed measurement results, depicted by the black curve in figure 7, are carried out without making use of the internal heater, called *VariPhi*[®]; the associated ϕ -factor is 3.14. When employing the *VariPhi*[®] for the same sample setup and using its power to compensate for the mass and specific heat capacity of the vessel ($\phi = 1$), the measured temperature increase was determined to be 64.8 K (red curve, figure 7). This nicely confirms the expectation of a significant increase in both ΔT_{obs} and the speed of reaction. The lower the ϕ -factor, the less heat is lost in warming up the sample vessel; furthermore, all the heat of reaction can remain inside the sample vessel to speed up the self-heating reactions. The dashed



6 Measurement results for screening of hydrogen peroxide with pressure (blue), pressure rate (dashed blue), temperature (red) and temperature rate (dashed red)

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line in figure 7 confirms a self-heating rate almost ten times higher for the measurement using *VariPhi*[®] (red curve, figure 7) than for the non-compensated measurement. These results demonstrate the enormous impact of the ϕ -factor with respect to the expected hazard potential of chemical reactions.

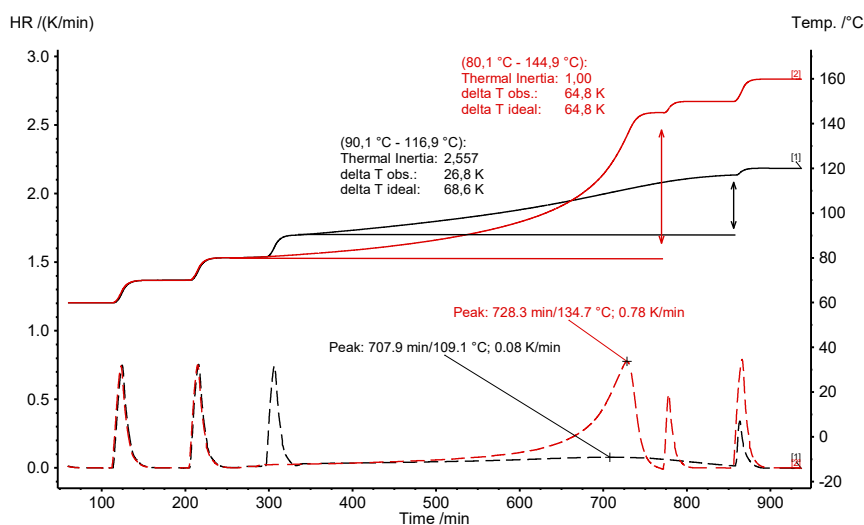
If *VariPhi*[®] is not available, measurements can usually not be carried out with low- ϕ conditions due to limitations caused by material properties of the sample container, maximum sample amount, expected pressure, etc. In this case, ASTM E1981 – 81(2012) suggests the following approximation for ideal measurement conditions.

$$\text{(equation 3)} \quad \Delta T_{\text{ad}} = (\Delta T_{\text{obs}}) (\phi)$$

The “delta T ideal” value is calculated as per equation 3 during data evaluation in NETZSCH *Proteus*[®] software. The non-compensated result (black curve in figure 7) indicates a “ ΔT_{obs} ” of 26.8 K and a ϕ -factor of 2.56. The assumption for a measurement result under ideal conditions ($\phi = 1$) expects “ ΔT_{ideal} ” to be 68.6 K. This assumption made via equation 3 is close to the measurement result of 64.8 K yielded by using the *VariPhi*[®] heater (red curve in figure 7).

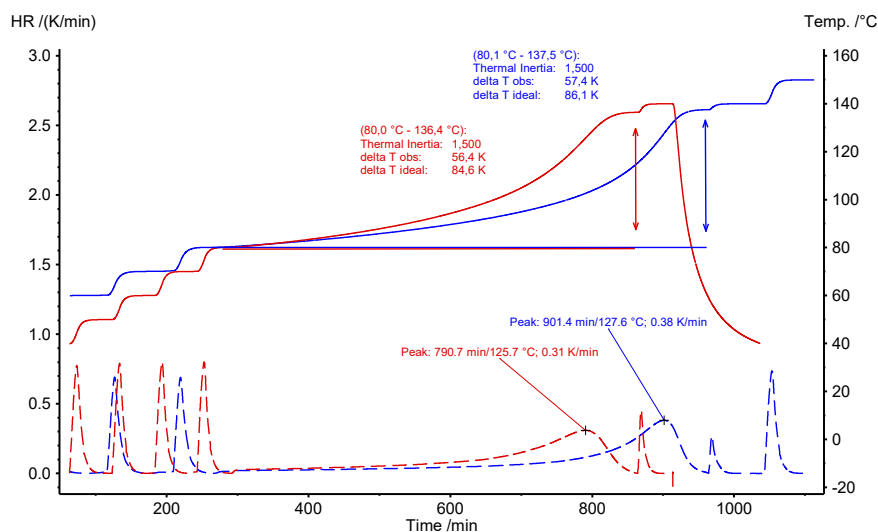
Tab 2. Measurement conditions for scanning (figure 6) and the heat-wait-search tests (figure 7)

MMC 274 Nexus [®]			
MMC Module	Scanning	ARC	
		ARC without compensation	ARC with compensation
Vessel material	Stainless steel	Stainless steel	Stainless steel
Vessel type	Closed	Closed	Closed
Vessel mass	7176.00 mg	7119.74 mg	7119.66 mg
Heating	Constant power (250 mW)	HWS	HWS
Atmosphere	Air	Air	Air
Purge gas rate	Static	Static	Static
Temperature range	RT ... 250°C	RT ... 250°C	RT ... 250°C
Sample mass	512.35 mg	749.79 mg	749.46 mg
Φ -factor	4.15	3.14	3.14
Φ -factor (comp.)		3.14	1.00



7 Measurement results for a heat-wait-search (HWS) test on hydrogen peroxide with compensation of the ϕ -factor (red) and without (black)

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8 Comparison of two heat-wait-search (HWS) tests with different measurement conditions, both compensated to $\phi = 1.5$

A further advantage of the *VariPhi*[®] heater is to compensate for the ϕ -factor to improve the comparability of different measurement conditions. Figure 8 compares two measurements on different amounts of hydrogen peroxide. The red curve represents a measurement on 0.500 g of H_2O_2 ($\phi = 4.21$) and the blue measurement was carried out using 1.00 g ($\phi = 2.60$). Due to the different sample masses, the ϕ -factors are significantly different: 4.21 and 2.60, respectively. The *VariPhi*[®] heater was employed to compensate both measurements to $\phi = 1.5$. The evaluated results are very similar for the two measurements, including the onset temperature (T_{start}), the self-heating rate (HR) and the observed temperature increase (ΔT_{obs}).

Conclusion

The decomposition reaction of hydrogen peroxide (H_2O_2) was investigated as a test scenario to demonstrate the use of an additional heater inside ARC-type equipment. The patented *VariPhi*[®] heater can be employed to compensate the test setup to either a real world ϕ -factor or to the ideal value of $\phi = 1$. This setup of compensation for heat loss allows low- ϕ measurements on even small sample amounts. From a safety point of view, the ability to vary the ϕ -factor turns out to be a great advantage for laboratories testing the hazardous potential of chemicals and reaction mixtures.

References

- [1] ASTM E1981 – 98(2012), “Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry”, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959.
- [2] E. Füglein, S. Schmolzer, “Epoxy Curing Investigated by Means of DSC 214 *Polyma* and MMC 274 *Nexus*”, NETZSCH Application Note 130, 2019
- [3] E. Füglein, “Hazard Potential of Decomposition Reactions Using the Example of Hydrogen Peroxide (H_2O_2)”, NETZSCH Application Note 131, 2019
- [4] E. Füglein, “Screening of Hydrogen Peroxide Solutions by Means of Scanning Tests and ARC Tests”, NETZSCH Application Note 132, 2019