DETERMINATION OF THE SHELF LIFE OF MATERIALS WHEN ONLY LIMITED AMOUNTS OF EXPERIMENTAL POINTS ARE AVAILABLE AND TIME IS OF THE ESSENCE

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One of the most important goals of the investigation of the kinetics of the thermal behavior of materials is the possibility of the application of the computed kinetic parameters for the prediction of materials' properties at temperatures higher or lower than those used during the data collection. The applications of the kinetic approaches for the extrapolation of materials' behaviors at lower or higher temperatures are well known, however, they are generally based on continuous data collection when plenty of experimental points are available for kinetic analysis. This study presents the possibility of a correct kinetic determination based on a limited amount of experimental points, which is a common situation for those working with e.g. stabilizers, ingredients, pharmaceuticals, vaccines, polymers, when very often only few experimental points can be collected in acceptable periods of time. In such situations, the kinetic analysis, based on scarce data, is impossible using the commonly applied isoconversional analysis [1] and requires another kinetic approach. In this study, we also propose the significant optimization of the experimental procedure required for the correct kinetic description of the investigated process. We illustrate how during the prediction of the shelf life of materials at ambient temperatures one can decrease the experimental temperature-time domains which, in turn, allows avoiding the necessity of the collection of the experimental points during few months or years. Proposed advanced methods [2] of the evaluation of the kinetic parameters from only a few points is based in this study on data collected by Heat Flow Calorimetry (HFC). The method was applied for the prediction of the thermal behavior of double base propellants used in defense applications. In the proposed kinetic analysis, the duration of the experimental domain was restricted to 21 days and 450 J/g whereas the arbitrarily chosen discontinuous data (Fig. 1, blue filled circles) were taken for the temperatures of 80 and 90°C only. Using a newly introduced kinetic approach [2], it was possible to simulate the reaction course in the range 50-90°C (solid lines) in Fig.1. For the verification of the method the experimental data collected at 50, 60 and 70°C were compared with the simulations based on the kinetic parameters derived from the data collected only at higher temperatures of 80 and 90°C. The results presented in Fig.1 clearly indicate that the data collected during 3 weeks can be used for the correct prediction of the reaction course even during 7 years (Fig. 1C) In addition, the proposed approach allows the determination of the prediction bands (e.g. 95%, dashed lines) for the calculated parameters and simulated dependences. As will be illustrated during the presentation, a proposed kinetics based method of the extrapolation of the thermal behavior to the required temperature zone can be applied with any few discontinuously collected data obtained by any experimental technique such as (i) High Performance Liquid Chromatography (HPLC) for stabilizer depletion, (ii) Vacuum Stability Test (VST) and (iii) ballistic firings (pressure peaks during the combustion process) for determining e.g. the chemical and ballistic stability of propellants. In the present study, it was possible to uncover the differences of the reaction course for the various propellant properties in different climates and storage conditions. The proposed method can be based on the data reporting the changes of many properties and for all sorts of materials.

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[2] B. Roduit, M. Hartmann, P. Folly, A. Sarbach, R. Baltensperger, Prediction of thermal stability of materials by modified kinetic and model selection approaches based on limited amount of experimental points, Thermochim. Acta, 579 (2014) 31-39.

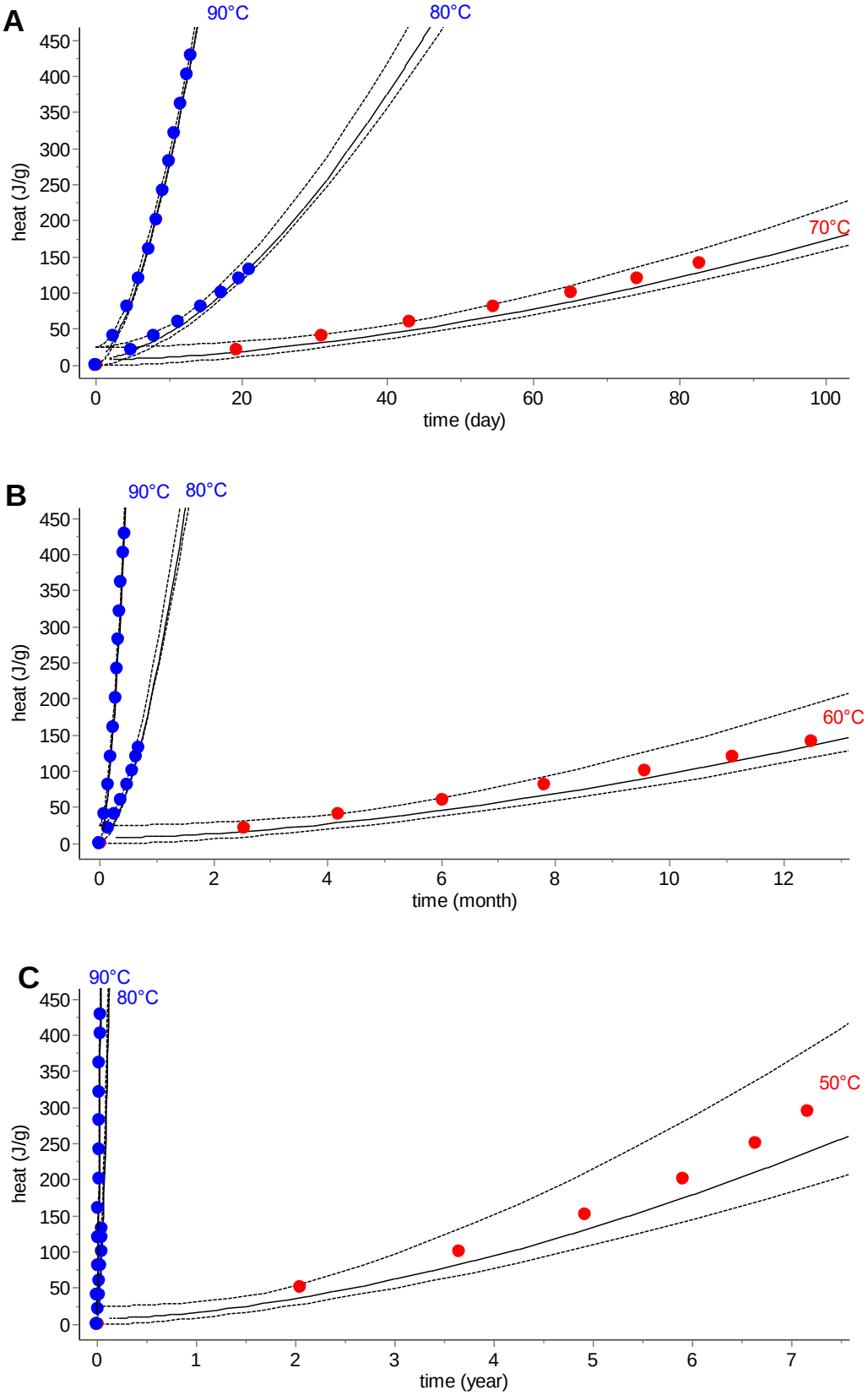

Fig.1 The arbitrarily chosen discontinuous data (blue solid circles) for temperatures of 80 and 90°C in the time zone of 21 days were used for the determination of the kinetic parameters allowing, in turn, the predictions of the amount of evolved heat (solid lines) at (A) 70°C, (B) 60°C and (C) 50°C during c.a. 85 days, 12 months and 7 years, respectively. Prediction curves were verified by the experimental results displayed as red solid circles. The prediction bands (95%), marked by the dashed lines were determined by the bootstrap method [2].