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Microcalorimetry in Historical Aspect, Status and Prospects. Part II

Part II of the article highlights the main applied areas of practical use of microcalorimeters of various types, including microcalorimeters with thermoelectric sensors. The role of microcalorimetric methods in materials science, pharmacy, biology and medicine, in the study of food products, for environmental monitoring, in astronomy and elementary particle physics is considered. The future of calorimetry is discussed, namely: areas of application and potential achievements that can be expected when integrating with artificial intelligence, in establishing a connection with other analytical methods that deepen the understanding of thermal phenomena, in the development and use of simulation models, and in improving miniaturization.

Keywords: microcalorimetry, areas of application of calorimetry, potential achievements of calorimetry.

Examples of applications of modern calorimetry

***1. Materials science*:** Calorimetry is essential for characterizing the behaviour of polymers, designing composite materials, and aiding the development of thermoelectric devices. Understanding heat spreaders is key to developing materials for electronics that can withstand extreme conditions and for other applications.

Since microcalorimetry is an important experimental method for quantifying reactions occurring between a solid material and reagents adsorbed on the surface, in the case of flotation used for the enrichment of mineral ores, surface reactions occurring between water and reagents are estimated as the enthalpy of immersion or adsorption. Their measurement by

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microcalorimetry has shown that these are very good methods for determining the adsorption of water or collector, respectively, on a mineral. The immersion enthalpy has been shown to be a good indicator of the hydrophobicity of a pure mineral or a mineral on which a collector is adsorbed, as indicated by its close correlation with the measured contact angle values [1].

As an effective analytical method for studying solid-liquid interfacial interactions, microcalorimetry can provide the simplest thermodynamic information (including changes in enthalpy, entropy, and Gibbs free energy during solid-liquid binding/dissociation processes), which is extremely important for understanding the directionality and limitations of the interaction [2].

Adiabatic calorimetry and thermodynamics are used to solve critical problems in materials science, namely: condensed gas calorimetry and the third law of entropy, phase transition and polymorphism in simple molecular crystals, incommensurate phase transitions, the effect of particle size on phase transitions in ferroelectric/ferroelastic crystals, relaxor ferroelectrics and multiferroics, and some other areas in materials science and technology [3].

The review [4] is devoted to highlighting the key role of common microcalorimetric methods, including differential scanning calorimetry, isothermal titration calorimetry, and immersion microcalorimetry, in the study of immersion and solid-liquid adsorption processes.

Obtaining information about crystallization kinetics is crucial for understanding the transformation rate of phase transition materials and selecting materials for phase transition memory. In [5], ultrafast differential scanning calorimetry was used to study the crystallization kinetics of In-doped Sb_4Te with different compositions and found that $In_{20}(Sb_4Te)_{80}$ has the fastest crystallization rate (~ 7.1 m/s at 726.2 K). The $In_{20}(Sb_4Te)_{80}$ film exhibited a high crystallization temperature (~ 503 K), superior data retention (~ 418.7 K for 10 years), and ultrafast crystallization with strong non-Arrhenius behaviour. These results indicated that $In_{20}(Sb_4Te)_{80}$ is a promising candidate for use in phase transition materials.

A new experimental calorimetric method based on oxidative solution calorimetry was developed to determine the enthalpies of formation/mixing of eutectics for binary Ga–In, ternary Ga–In–Sn, and quaternary Ga–In–Sn–Zn systems. Fusible alloys, in particular gallium-based alloys that are liquid below room temperature (Ga-LMA), find applications in soft robotics, microelectronics, self-healing battery components, and the synthesis of 2D materials, making the study of their thermodynamic properties critical for the improvement and development of hybrid materials. The experimental method presented can be extended to a wide range of liquid alloy systems at room temperature or below [6]. Global production of polymer products currently exceeds 400 megatons per year. To ensure efficient and environmentally responsible use of this vast resource, it is important to optimize product properties, which requires precise control of the internal structure of polymers. Depending on the materials used, polymers can exist in either an amorphous or semi-crystalline state. Processing is often done from the molten state, so the cooling rate plays a crucial role in determining whether the resulting products are amorphous or semi-crystalline, along with other process parameters such as pressure and shear rate. Since all these processes are associated with thermal effects, calorimetry is universally used here, namely fast scanning calorimetry or nanocalorimetry, which concern nanogram samples. Studies with controlled cooling rates up to 1×10^6 K/s have become possible using special chip sensors, which allows studying the properties of materials under extreme conditions [7].

2. Pharmacy, biology and medicine: In drug formulation, calorimetry helps to understand stability and efficacy by analyzing the effects of temperature on the physical state of drugs, thus managing storage conditions.

The study of metabolism at the level of individual cells is related to all intracellular biochemical reactions, which is the basis of fundamental research in biology. Heat production or heat consumption characterizes all biological processes. Microcalorimetry is a very sensitive method of measuring heat transfer for various applications, so the development of ultrasensitive microcalorimeters provides tools for bioanalysis at the level of individual cells or even subcells, as well as for precise calorimetric detection [8].

Microcalorimetry is an effective and powerful tool for measuring heat changes during biological reactions and heat production at the level of individual cells, reflecting cell activity. The heterogeneity of cellular metabolism characterized by different species demonstrates the advantage of biodiversity [9].

Real-time monitoring of energy balance is essential for studying and characterizing the thermodynamics of physical, chemical, and biological processes, especially in active matter such as mammalian cells and unicellular organisms. Understanding metabolic mechanisms in these organisms offers the potential to reveal information about life. Given that energy monitoring at such a scale (micro/nano) is technically challenging, microcalorimetry is essential for the label-free characterization of molecular interactions to estimate enthalpy, entropy, Gibbs free energy, specific heat capacity, and many other parameters. It is widely used to assess and analyze resolution, mixing, and chemical/biochemical reactions, as well as to assess protein binding and cellular processes such as cellular metabolism and apoptosis [10].

The droplet-based differential microcalorimetric platform described in [11] is characterized by a small thermal time constant of ≈ 1.5 s, therefore it allows for dynamic monitoring of bioprocesses in real time without limitations. It is important to note that energy balance for biologists refers to the difference between energy input, such as chemical energy from nutrients, and energy output, such as heat, motor activity, chemical energy of biomass, hydrolysis of ATP to ADP, etc. The energy balance of the system is considered from a physics perspective, as the total energy difference within an isolated calorimetric system is monitored. A single protist was placed in a ≈ 1 μL drop of culture medium that mimicked an unconstrained microenvironment. The temperature change of the drop was measured and the corresponding dissipated power and energy consumed were calculated, demonstrating the potential of this approach to study chemically induced bioprocesses in P. caudatum. The study could be used to analyze other bioprocesses such as cell division, differentiation, and apoptosis.

In [12], the design, fabrication, characterization, and measurement configuration of a microcalorimeter for microfluidic applications are described. The authors report that this calorimeter is capable of detecting temperature fluctuations of the order of $70 \cdot 10^{-3}$ °C, and when used with the proposed circuit configuration, it is expected to be able to monitor even smaller temperature fluctuations. In current studies, this microfluidic device has been used to detect and study biomolecular interactions, such as DNA-DNA hybridization kinetics and DNA-inaccessible RNA.

The importance of microcalorimetric measurement of heat production in human erythrocytes is shown in section 5.2 of the book [13].

Microcalorimetric studies of human blood cells in relation to various diseases and assessment of the effects of certain hormones and pharmacological agents are shown in [14, 15].

The study of human blood cells is relevant at this stage, in particular, the study of erythrocytes in patients with peripheral arterial disease who received cilostazol highlights the potential of differential scanning calorimetry as an auxiliary method for assessing the effectiveness of treatment of peripheral arterial disease at the cellular level [16].

The importance of microcalorimetric studies in pharmacy and medicine is also reflected in [17].

3. Food science**:** Calorimetric methods are used to assess the caloric content and nutritional quality of foods, thereby influencing food processing and preservation technologies.

The book [18] introduces the basic principles of food calorimetry and highlights various applications for characterizing temperature changes, including starch gelatinization and crystallization, lipid transitions, protein denaturation, and microbial inactivation in various food and biological materials. These changes are known to affect the storage stability and shelf life of foods. The book addresses important issues in the use of calorimetry in food systems, focusing on data collection, data interpretation, and the use of this data for process optimization and product development. Emphasis is placed on the use of calorimetry as a tool for assessing processing requirements to assess food industry performance and to characterize the impact of changes in formulation and processing conditions.

Microcalorimetry is a useful tool for measuring the degree of product aging and also for elucidating the aging mechanism. In a complex matrix such as a food product, this can be a challenging task. It can be used to monitor microbial activity, assess food stability, and study various reactions affecting food products. How isothermal microcalorimetry can be used for microbiological applications is discussed in [19].

Fermentation is important for the production of various food products such as bread, yogurt, beer, wine, etc. Isothermal microcalorimetry is a tool for monitoring various industrial fermentations and evaluating changes in the formulation and process [20].

Vitamin A was synthesized in 1948 and is very sensitive to chemical degradation caused by oxygen, light, heat and other stress factors. An important task is to determine the shelf life stability of vitamin A in feed, food and pharmaceutical products. This stability can be predicted quite easily from the initial heat flow in a simple microcalorimetric experiment. Compared to conventional stability tests, this provides savings in cost and time [21, 22].

Phase transition problems in the food and pharmaceutical industries have significantly affected these industries and, as a result, have attracted the attention of scientists and engineers. The study of thermodynamic parameters such as glass transition temperature, melting temperature, crystallization temperature, enthalpy and heat capacity can provide important information for the development of new products and the improvement of existing ones. Differential scanning calorimetry (DSC) is the preferred method for characterizing phase transitions because it allows the detection of transitions over a wide temperature range (from -90 to 550 °C) and facilitates quantitative and qualitative analysis of transitions. However, standard DSC still has some limitations that can reduce the accuracy of measurements. Modulated differential scanning calorimetry (MSC) has overcome some of these problems by using sinusoidally modulated heating rates, which are used to determine the heat capacity. Another variant of MDSC is supercooling, which allows the detection of more complex thermal events, such as solid-solid transitions, liquid-liquid transitions, and glass transition and de-glass transition temperatures, which are usually observed at supercooling temperatures. The main advantage of MDSC is the accurate detection of complex transitions and the ability to distinguish reversible events (dependent on heat capacity) from irreversible events (dependent on kinetics) [23].

The use of differential scanning calorimetry (DSC) for food authentication and traceability has led to significant improvements in the structure and stability of some structured food products. DSC remains a powerful thermal analytical tool used to study the mechanism of crystallization, polymorphism, and structural reconformation of biological substances. DSC is able to determine the state of food materials - stable or unstable, texture - soft, granular or rough, as well as polymorphic crystal forms and emulsion stability. Thus, the collection of information on thermal analysis using DSC has helped in establishing some model correlation between energy and structure in connection with changes in the chemical composition of some model oils and fats [24].

The study of the fat content and type of fat in foods is becoming increasingly important for health reasons, especially regarding the content of solid fats, saturated fats and trans fats in foods. Differential scanning calorimetry of fats in biscuits includes the study of the gelatinization and staling (retrogradation) behaviour of starches; the polymorphism of fats such as cocoa butter and chocolate. DSC provides information on the effects of moisture content or absorbed moisture, the effects of aging, protein denaturation, determination of fat content or solid fat index. It has been found that the behaviour of food fats during processing depends on the ratio of solid to liquid fat in the food sample. Power-compensated DSC or double oven gives exceptional results for food products, including the determination of the nature and content of fat. The fast response of power-compensated DSC provides the highest possible resolution, and this is vital for the classification of the different polymorphic melting forms associated with fats in food products [25].

Calorimetric methods have been used to rapidly detect and identify hardening reactions in protein bars. Hardening and texture changes in protein bars are among the most common causes of shelf life violations in this product category [26].

Safety and quality testing is an integral part of any industrial fermentation process. Isothermal microcalorimetry is a rapid, reliable and easy-to-perform method that can handle samples containing very high initial bacterial loads and can be easily incorporated into an in-house testing routine. Samples taken directly from the real fermentation process were tested using isothermal microcalorimetry, which resulted in much faster test execution, higher experimental reproducibility, and better sensitivity when observing different samples [27].

***4. Environmental monitoring*:** Calorimetry helps to study heat flows in ecological systems, contributing to our knowledge of climate change and energy use in natural processes. Microcalorimetry plays a significant role due to its thermodynamic capabilities in a wide range of fields of environmental research. The developed instrumental methods are easily applicable to various fields of research using microcalorimeters and are commercially available. Effective areas of application include the study of trace elements, living organisms, the interaction of solutes with solvents, sorption processes, and the determination of the stability of technical products. The combination of microcalorimetry with various specific analytical methods plays an effective role in solving complex problems in environmental sciences. Microcalorimetric analysis can also be applied in ecotoxicological branches of environmental sciences, such as wastewater treatment [28].

Better catalysts and electrocatalysts are essential for the production and use of cleaner fuels with less pollution and increased energy efficiency, for the creation of chemicals with less energy and environmental impact, for pollution control, and for many other future technologies needed to achieve a cleaner energy supply and develop the chemical industry. Measurements of surface reaction energies involving many of the most common adsorbates formed as intermediates on late transition metal surfaces in catalytic and electrocatalytic reactions are of interest for energy and environmental technologies. Calorimetric measurements of the heats of molecular and dissociative adsorption of gases on single crystals allow direct determination of the heats of formation of adsorbed intermediates in well-defined structures [29].

The presence of pharmaceuticals in the environment can lead to potentially hazardous situations. In soils and sediments, pharmaceuticals can be partially immobilized due to interactions with humic substances. These interactions can strongly influence their mobility and bioavailability. Thermodynamic parameters are usually calculated based on sorption experiments. In the study [30], the thermal effect of interactions between fulvic acids and ibuprofen, diclofenac and sulfapyridine was directly measured. Isothermal titration calorimetry provided a complete set of thermodynamic characteristics of the main processes - interaction enthalpy, entropy and Gibbs energy. All studied interactions were found to be exothermic with heat release from -496 to -9938 J/mol. The lowest enthalpies were obtained for sulfapyridine and the highest for ibuprofen (on average). The Gibbs energy changes were very similar for all studied interactions (20–28 kJ/mol). The largest entropy change was determined for ibuprofen (73 J/mol·K); the values obtained for diclofenac and sulfapyridine were comparable (57 and 56 J/mol·K, respectively).

To assess the impact of catalytic activity of microbial communities on soil functions, microbial turnover processes were analyzed in a model soil modified with an easily metabolizable substrate (glucose) and three commercial isothermal microcalorimeters. It was found that a small variation in the elemental composition of biomass can cause changes in the microbial community, which can affect not only the kinetics of matter and energy flows, as expected, but also the stoichiometry of the process [31].

The study [32] reviews the formulae for both melting and freezing calorimeters for estimating the volumetric liquid water content of snow. These results highlight the accuracy and practical advantages of melting calorimetry as a reliable field tool for quantifying the liquid water content of snowpack.

5. Astronomy, particle physics: To provide unprecedented understanding of the physics of galaxy formation, to study galaxy clusters and supernova remnants with high spectral resolution, including feedback between stars and black holes, and to study the fluxes of baryonic matter into and out of galaxies, a linear emission mapper (LEM) is being developed, which includes lightweight X-ray optics with a large-format microcalorimeter array, i.e., an X-ray microcalorimeter. The LEM detector uses a 14-thousand-pixel Transition Sensor Array (TES) capable of providing a spectral resolution of <2.5 eV in the energy range of 0.2 to 2 keV, and a field of view of 30 arcminutes. The TES-based anti-coincidence detector will flag and reject cosmic ray-induced events that could be confused with photons in the LEM science range. Operation at cryogenic temperatures (<100 mK) provides extremely high spectral resolution over a wide bandwidth, with a resolution of ~3000 at 6 keV routinely demonstrated. Transition-edge sensors (TES) are a type of microcalorimeter based on superconducting thin films [33].

Mergers between galaxy clusters can produce high velocities of turbulent and bulk flows in the intracluster medium and thus provide useful diagnostic information in the X-ray spectral lines of heavy ion emission regarding the possibility of a large head-on cluster merger. Hitomi, during observations of the constellation Perseus, suggested that measurements of gas velocities in clusters from high-resolution X-ray spectra would be achievable with future X-ray calorimeters [34].

As a result of observations using a working X-ray microcalorimeter, the possibility of limiting the velocity field of an interzone moisture storage array in a large merger of star shadow clusters was investigated [35].

To study the effective mass of the electron neutrino at the subelectronvolt level by analyzing the finite region of the electron capture spectrum, a new generation of high-resolution magnetic microcalorimeters with built-in 163Ho was developed and characterized. During electron capture, an electron from the inner shell of the 163Ho atom is captured by the nucleus and an electron neutrino is emitted. As a result, the excited daughter atom relaxes to the ground state, emitting cascades of electrons and, in a small number of cases, also X-rays. The minimum energy required to create a neutrino corresponds to its mass, and therefore the maximum energy in the measured energy spectrum after de-excitation is reduced by this amount. Therefore, the shape of the spectrum at the final point depends on the finite mass of the neutrino [36].

Another experiment that uses cryogenic microcalorimeters to measure the spectrum of EC 163Ho in order to study the mass of electron neutrinos is HOLMES [37].

An international conference on calorimetry in particle physics was held in Japan in 2024. This was a continuation of a series of conferences that have brought together experts in calorimetry and its applications for almost 30 years, which indicates a high interest in calorimetry in the scientific community [38].

It should be noted that advances in computational methods in the late 20th and early 21st centuries have effectively complemented calorimetric studies. In particular, molecular dynamics simulations allow researchers to study thermal behaviour at the molecular level, reinforcing data obtained from experimental calorimetry. For example, in [39], the modeling and simulation of an isothermal heat flux microcalorimeter capable of measuring heat fluxes of a few μW in microliter test samples is considered. The microcalorimeter model is obtained and analyzed using computational fluid dynamics methods. The only unknown parameter of the model is a thin layer of thermal paste between the microcalorimeter rim and the aluminium block, which is used to stabilize the reference temperature. The thickness of the thermal paste layer cannot be measured physically, but it has a significant impact on the sensitivity of the microcalorimeter. To determine the thickness of the thermal paste layer, a calibration procedure is proposed, which includes two numerical environments (ANSYS Fluent and Simplorer). The calibrated model is used to study the effect of the thickness of the thermal paste layer or the air gap on the sensitivity of the microcalorimeter and its dynamic behavior. The results clearly show that even a small change in the thickness of the thermal paste layer can significantly affect the sensitivity of the microcalorimeter and its response speed.

Thus, previous advances in calorimetry have enriched our understanding of thermal phenomena in many fields. Calorimetry continues to be a cornerstone technique that improves our understanding of energy transformations and material behavior, leading to innovations that profoundly impact society, validating the need for calorimetric research in scientific experiments.

Advances in micro- and nanocalorimetry allow the investigation of thermal properties of materials at the microscopic level. These techniques allow researchers to study heat flow in small quantities of materials, which is especially relevant in fields such as nanotechnology and drug delivery systems.

Calorimetry, combined with various spectroscopic techniques such as Fourier transform infrared spectroscopy and nuclear magnetic resonance, provides a complete understanding of thermal spreaders along with molecular interactions. This connection helps to elucidate the complex behaviour during phase transitions, thereby providing the opportunity to improve material performance.

Adapting calorimetric methods to high-throughput formats allows for rapid analysis of large sample sets, which is important in pharmaceutical research as it allows for rapid evaluation of compound libraries in drug development.

The versatility of calorimetry is also reflected in its application in various industries.

As we move into the 21st century, the future of calorimetry looks promising, where ongoing innovations will undoubtedly contribute to a deeper understanding of energy transfer and thermal interactions in various scientific fields [40].

The future of calorimetry: potential advances and applications

As we look to the future of calorimetry, it is increasingly clear that the field is on the verge of significant advances and innovative applications that could transform our understanding of thermal processes. The convergence of advanced technologies, interdisciplinary approaches, and new scientific challenges will drive calorimetry forward in the coming years. There remains a vast amount of thermodynamic information, such as that on solid-liquid interactions, that awaits exploration using calorimetry.

The global microcalorimeter market is projected to reach approximately US$ 1.2 billion by 2035, growing at a compound annual growth rate of 7.5% from 2025 to 2035. The growth of this market can be attributed to the increased demand for accurate and reliable thermal analysis in various industries such as pharmaceuticals and biotechnology. In addition, advances in microcalorimetry technology, which allow researchers to perform highly sensitive and accurate measurements, are also driving the market expansion. Increased focus on research and development in materials science and a significant need for energy-efficient processes are further fueling this market. As more industries recognize the importance of thermal analysis, the microcalorimeter market is expected to witness significant growth in the coming years [41]

Potential advances in calorimetry can be expected in several key areas:

1. Integration with artificial intelligence. Applying machine learning algorithms to analyze complex calorimetric data opens up the prospect of uncovering hidden patterns and insights. As datasets become larger and more complex, artificial intelligence can accelerate the interpretation of thermal behavior, allowing researchers to make predictions based on historical findings.
2. Miniaturization improvements: With the continued push for smaller, more efficient devices, future calorimeters could evolve into compact, portable devices capable of performing a variety of thermal analyses. These innovations will increase accessibility, allowing for real-time data collection in a variety of environments, from laboratories to the field.
3. Improved connectivity with other analytical techniques. The synergy of calorimetry with techniques such as mass spectrometry, chromatography, and NMR will deepen our understanding of thermal phenomena. This integrated approach will facilitate the multifaceted analysis of chemical reactions, allowing scientists to comprehensively investigate both thermal and kinetic parameters.
4. Sustainable practices in calorimetry: As environmental concerns grow, future calorimetric research will increasingly focus on sustainability. Methods that involve energy efficiency, minimal waste, and environmentally friendly materials will be crucial in the development of new calorimetric devices.
5. Advanced simulation models: Integrating calorimetric data with computational models will allow for more accurate predictions of the thermal behaviour of complex systems. Using computational chemistry to model heat flows could improve experimental designs, ultimately increasing the reproducibility and reliability of calorimetric results.

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Мікрокалориметрія в історичному аспекті, стан та перспективи. Ч.II

У ч. II статті висвітлені основні прикладні напрямки практичного використання мікрокалориметрії різного типу, в тому числі мікрокалориметрів з термоелектричними датчиками. Розглянуто роль мікрокалориметричних методів у матеріалознавстві, фармації, біології і медицині, у дослідженні харчових продуктів, для проведення екологічного моніторингу, в астрономії та фізиці елементарних часток. Обговорюється майбутнє калориметрії, а саме: області застосування та потенційні досягнення, яких можна очікувати при інтеграції зі штучним інтелектом, у встановленні зв'язку з іншими аналітичними методами, що поглиблюють розуміння теплових явищ, розробці та використанні імітаційних моделей, удосконаленні мініатюризації.

Ключові слова: мікрокалориметрія, області застосування калориметрії, потенційні досягнення калориметрії.

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