

Differential scanning calorimetry – methods, types of measuring instruments. A Review.

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Abstract: This article focuses on the essence of calorimetry, the calorimetric methods and the types of measuring instruments. Based on their specifics the calorimeters can be isothermal, isoperibol, adiabatic and scanning. Presented are the advantages and measuring techniques of calorimeters of leading manufactures like Setaram (France), Netzchs (Germany), Advance Riko, Inc.(Japan), etc. The article indicates the importance and the reliability of the differential scanning calorimetry (DSC) – one of the newest of the entrants in the high-temperature thermal analysis.

Key words: Calorimetry, Heat capacity, Differential scanning calorimetry, High-temperature DSC

Диференциална сканираща калориметрия – техники и видове апаратури. Обзор.

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Резюме

Тази статия се фокусира върху същността на калориметрията, калориметричните методи и видовете измервателни уреди. Въз основа на своите спецификации калориметрите могат да бъдат следните видове – изотермични, изопериболни, адиабатни и сканиращи. В настоящата разработка са представени предимствата и измервателните похвати на калориметри на водещи производители като Setaram (Франция), Netzchs (Германия), Advance Riko, Inc. (Япония) и др. Статията идентифицира значимостта и надеждността на диференциалната сканираща калориметрия – един от най-модерните подходи по отношение на високотемпературния термичен анализ.

Ключови думи: Калориметрия, топлинни ефекти, диференциалната сканираща калориметрия, високотемпературна диференциалната сканираща калориметрия.

Introduction

Thermal analysis include a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. [Brown, 1988, Wendlandt, 1985]

The basic units for Calorimetry are these three: Heat (J) – most experiments are carried out at constant pressure and Enthalpy (H) (used instead of total energy (U)). Heat capacity of constant (p, C_p) and Gibbs free energy (G).

The main principle: heat measurements involve determination of temperature changes, following of changes of state, or, comparison with chemical, electrical or mechanical energy.

There are three ways how the heat can be measured. In the first one, the change of the temperature in a known system can be observed and related to the flow of heat into that system. In the second one, one can follow the change of the state and can determine the accompanying flow of heat from the amount of material transformer in the known system. In the third one, the conversion to heat of know amount energy can be used to duplicate or compensate a flow of heat. [Wunderlich, 2005]

Once again has to be mentioned that the exchange of heat is measured by calorimetry. The atomic motion is the source of heat (Q) and its intensive parameter is temperature (T). The total heat content or internal energy of a substance is more difficult to assess. To find the heat content, one must remove all energy, i.e. cool the substance to the absolute zero of temperature, and the add heat successively under measuring conditions until one reaches the starting temperature again. The sum of the added Q is the internal energy or heat content. It is very much easier to measure the total mass (m). Perhaps the difference in ease of measurement of m relative to Q is one reason for a lag in learning about matter via energetics based on calorimetry relative to structural science. Another reason for a lag in learning about matter is the distance between macroscopic, human and the microscopic, atomic, scales in the two fields of knowledge. [Schlesinger, 1997]

Some application of calorimeters include purity determination, determination of thermochemical functions by measurement and computation, measurement of thermodynamic functions of carbon allotropes and paraffins. [Wunderlich, 2005]

Measurements of the enthalpy of a chemical reaction can be used to relate the thermodynamic properties of a given substance to obtain heats of formation, mixing and solid-state reactions. These calorimetric methods can be classified into two groups: direct in which the reaction studied is the one of interest and indirect in which the thermochemical cycle is used to obtain the enthalpy of interest. [Navrotsky, A., 1994]

1. Calorimeters

This is the combination of sample and measuring system, kept in well-defined surroundings, thermostat or furnace. Calorimetry uses the term environment and for precision, the environment should always be kept from fluctuating. The temperature should be controlled to ± 0.5 K and the room should be free of drafts and sources of radiating heat. [Wunderlich, 2005]

Calorimeters can be these types:

1. Isothermal - they have both calorimeter and surroundings at constant T_0 . [Wunderlich, 2005] These are calorimeters involving compensation of the thermal effect by phase transition or thermoelectric effects. [Sarge, 2014]

2. Isoperibol – the temperature changes with time, governed by the thermal resistance between the calorimeter and surroundings. [Wunderlich, 2005] These are calorimeters involving the measurement of a time-dependent temperature or temperature difference. [Sarge, 2014]

3. Adiabatic – the exchange of heat between a calorimeter and surroundings is kept close to zero by making the temperature difference small and the thermal resistance large. [Wunderlich, 2005] These calorimeters involve measurement of a time-dependent temperature or a compensation of the thermal effect by thermoelectric effects. [Sarge, 2014]

4. Scanning – the temperature of the surroundings or the measuring system is changed in a predetermined manner with respect to time. Calorimeters involve measurement of a temperature difference (heat flow) or with a compensation of the thermal effect by thermoelectric effects (power compensation). [Sarge, 2014]

To assess the heat losses have been developed twin calorimeters, which permit measurement in a different mode. In the scanning mode, called differential scanning calorimetry (DSC) is used a continuous, usually linear, temperature change of calorimeter or surroundings.

Perhaps the best-known isothermal phase-change calorimeter is the Bunsen ice-calorimeter, invented in 1870. This calorimeter is isothermal and practically has no heat-loss problem (the -loss or -gain of the calorimeter is eliminated by insulation with a jacket of crushed ice and water). Suited to measure very slow reactions because of its stability over long periods of time. A big disadvantage is that all measurements must be carried out at 273.15 K, the melting temperature of ice.

In an isoperibol drop calorimeter the surroundings are at almost constant temperature and are linked to the sample via a heat leak. The recipient is a solid block of metal making it an aneroid calorimeter. The solid block eliminates losses due to evaporation and stirring that occur in a liquid calorimeter. But its drawbacks are less uniformity of temperature relative to the liquid calorimeter and the need of a longer time to reach steady state.

The liquid calorimeter also operates in an isoperibol manner. It is a simple bomb or reaction calorimeter, as is ordinarily used for the determination of heats of combustion. The reaction is started by electrically burning the calibrated ignition wire. The heat evolved during the ensuing combustion of the sample is then dissipated in the known amount of water that surrounds the bomb. From the rise in temperature and the known water value, the heat of reaction can be determined. The water value is equivalent to the heat capacity of a quantity of water, which equals that of the whole measuring system.

The accuracy in bomb calorimetry depends on the construction of the auxiliary equipment of the calorimeter. The heat flux into or out of the measuring water has to be at a minimum, and the remaining flux must be amenable to a calibration. It is possible to reach an accuracy of $\pm 0.01\%$. [Wunderlich, 2005]

1.1. Adiabatic Calorimeters

An attempt was made to follow the temperature increase of an internally heated calorimeter raising the temperature of the surroundings so that there is no net heat flux between the calorimeter and surroundings. The electrically measured heat input into the calorimeter, coupled

with the measurement of the sample temperature, gives the information needed to compute the heat capacity of calorimeter plus sample.

The first adiabatic calorimeter was described by Nernst in 1911. Modern calorimeters are more automated than the adiabatic calorimeter, but the principle has not changed from the original design by Nernst.

The main advantage of adiabatic calorimetry is the high precision. For the measurement of heat capacities of linear macromolecules, the sample has to be reproducible enough. Both chemical purity and the metastable initial state must be defined.

1.2. Compensating Calorimeters

Compensating calorimeters are constructed so that it is possible to compensate the heat effect with an external, calibrated heat source or sink. They often operate close to isothermal conditions between the calorimeter and surroundings. The simplest one is designed by Tian and Calvet, where the sample is contained in the central calorimeter tube across which the heat exchange occurs. The heat generated or absorbed by the sample is compensated by the Peltier effect of hundreds of thermocouples. If heat is generated the Peltier thermocouples are cooled. If heat is absorbed, the Peltier thermocouples are heated by reversing the current. This effect refers to a reversible heating or cooling which occurs at a contact point between two different conductors when current flows are in a given direction.

The main heat loss should be through heat conducted by the thermocouples. Another loss comes from the convection of air between calorimeter and surroundings. Finally, a fraction of the losses must go through the areas which are not covered by thermocouples.

These calorimeters can be used as heat-flux calorimeters for larger temperature differences. Because of the small losses, they have found application for the measurement of slow, biological reactions.

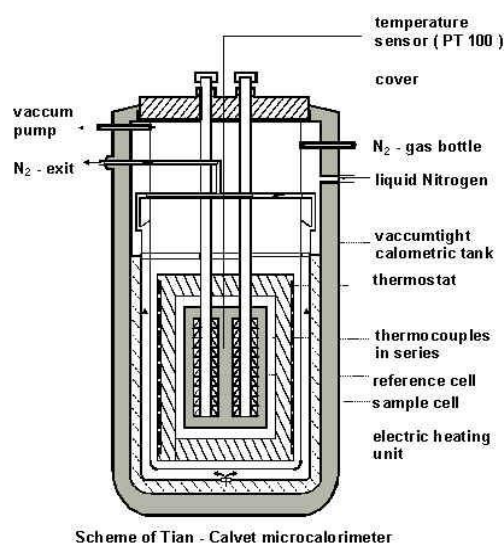


Fig.1.1. Scheme of Tian – Calvet microcalorimeter

1.3. Modern Calorimeters



Fig.1.2. Adiabatic Specific Heat Measurement System SH-3000 series, ADVANCE RIKO, Inc.
(http://advance-riko.com/en/products/sh-3000_en/)



Fig.1.3. C80 Calvet Calorimeter, SETARAM, France.
(<https://www.youtube.com/watch?v=nmjOKQyji9g>)

This is Sinku Riko ULVAC SH-3000 adiabatic (Fig.1.2. and 1.3.), scanning calorimeter - it provides a minicomputer control. Cooling water is provided to the surface of the calorimeter. The temperature range of the calorimeter is claimed to be 100K to 800K with two different calorimeter models. The sample mass can be several grams.

Another type is Setaram Calvet Calorimeter which can operate between 80 to 475 K. The key features are the heat flow detectors which carry practically all heat to and from the sample. It has extremely good insulation and has the ability to be cooled with liquid nitrogen. The temperature of the thermostat can be kept isothermal, or it can be programmed at rates from 0.1 to 1 K min. The cells may contain as much as 100 cm³ of sample. It is suitable for measurement of slow changes.

The stirred liquid bench-scale calorimeter duplicates laboratory reaction setups. The information about heat evolved or absorbed is extracted from the temperature difference between the liquid return and the reactor. This difference is calibrated with electric heat pulses to match the observed effect at the end of a chemical reaction. The sample sizes may vary from 0.3 to 2.5 liters. It can operate between 250K and 475 K.

The C80 Calvet Calorimeter (Fig.1.4.) uses the latest evolution of the Calvet Design calorimetric detector in which a sample and reference cell are totally surrounded by an array of thermocouple detectors allowing for the measurement of all heat evolved (or adsorbed) including radiation, convection or conduction. Each measurement zone of C80 consists of nine concentric rings, each containing 38 thermocouples (324 in total) to form a cylinder that totally surrounds both sample and reference. Thus, the Calvet detector is up to 94% efficient whereas typical plate

DSC are between 20-40%, and as such the C80 provides a high precision of measurement independent of sample nature or matrix – solid, liquid, gas, powder etc.

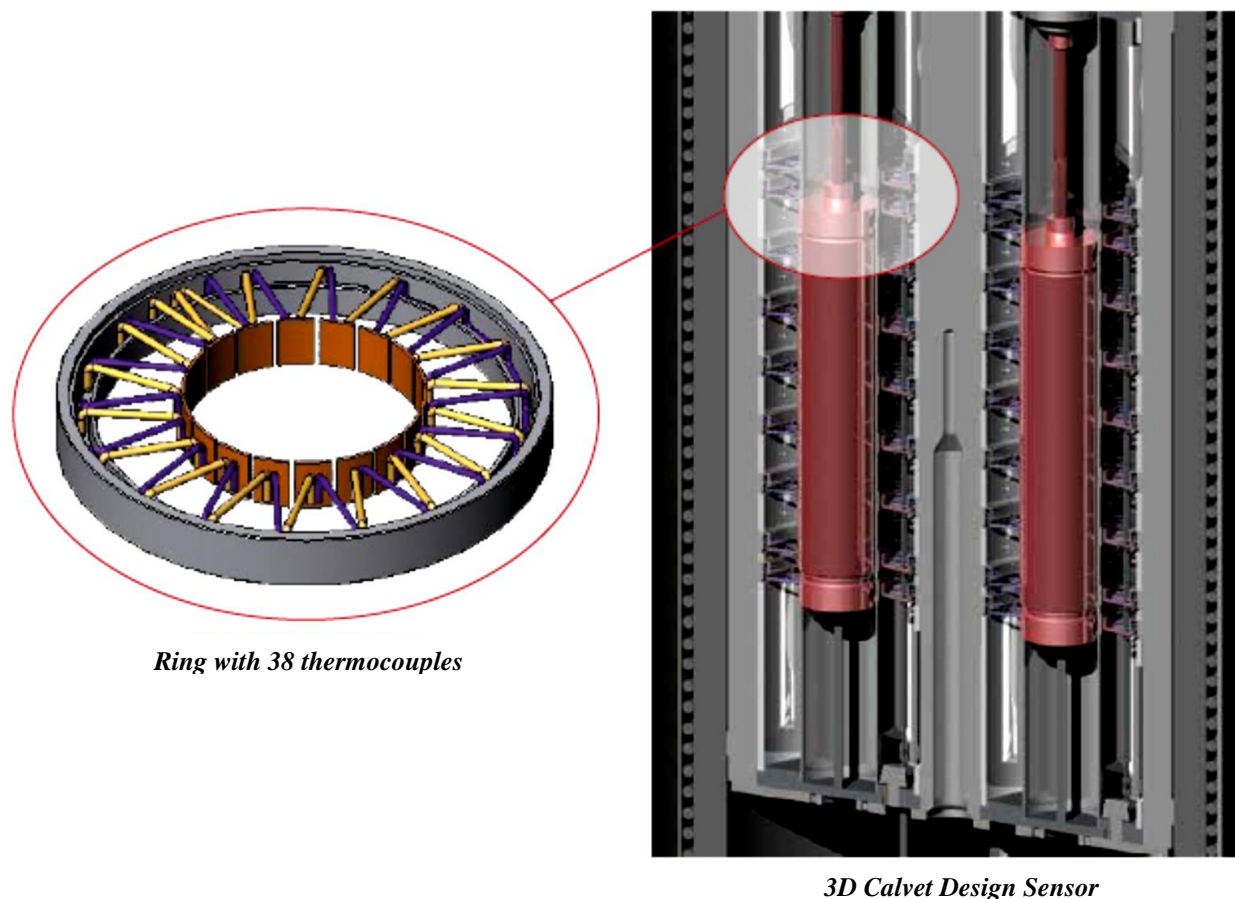


Fig.1.4. C80, Calvet Calorimeter, SETARAM, France

(<http://www.setaram.com/setaram-products/calorimetry/calorimetry-calorimetry/c80/>)

2. Drop calorimetry

Drop calorimeters are used for determination of enthalpy increments and specific heat capacities of solid or liquid materials in a temperature range between room temperature and more than 3000 K. The sample (rapidly dropped into the cavity of a well-insulated calorimeter block) should be nonreactive with the container and should have a low vapor pressure to avoid mass loss and significant contributions from heat of reaction or vaporization. The increase in temperature of the calorimeter block when it reaches equilibrium with the sample determines the sensible heat of the sample relative to the final temperature. [Schlesinger, 2004]

Their advantages include a constant heat capacity of the substance at a predetermined temperature, possibility of operating at high or low temperatures, elimination of any need for corrections for stirring or evaporation. The sample temperature may be above or below that of the calorimeter, but the initial and the final temperatures must be with a thermodynamically well-defined state.

Blachnik et al. [Blachnik, 1996] described a calorimeter that involves the dropping of samples with temperature up to 1400 K into a copper block inside a brass vessel in a water thermostat at 298.15 K. A similar one was used by Yamaguchi and Itagaki [Yamaguchi, 2002] but with the temperature extended to 1850 K, to measure the enthalpy function of a silicon single crystal in the temperature region 700-1820 K. [Sarge, 2014]

Some of their disadvantages are that they are extremely slow, make only one measurement of sensible heat at a time, and do not have the best reproducibility. Also, the need to determine heat capacities as the derivative of a sensible-heat curve reduces accuracy.

They can be applied for determination of the specific heat of different materials, the heat of solution of metals in metal baths, oxides in oxide baths, calculation of thermal balances. [Sarge, 2014]

Navrotsky et al. [Linard, 2008] investigated the enthalpies of solution of La_2O_3 , TiO_2 , HfO_2 , NiO and CuO which were measured in sodium silicate melts at high temperature. They performed the study with high-temperature drop solution calorimetry method. The thermodynamic properties of these materials are interesting because of their application for optimizing composition and synthesis conditions for production of glasses and slags. They concluded that some determinations of the heat of solution of oxides in silicates melts provide constraints on the energetics of the melt speciation reactions.

Another study from Navrotsky et al. [Cowana, 2008] investigated the high temperature behaviour of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ by several techniques including drop solution calorimetry which was utilized to determine the enthalpies of formation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, RbHSO_4 and Rb_2SO_4 . Here the drop calorimetry revealed standard heats of formation. The heat of the decomposition reaction of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ indicated that the phase assemblages are similar in energy.

Also, Navrotsky [Navrotsky, 2005] (fig. 2.1.) used solution calorimetry and high temperature oxide melt solution calorimetry to study the templated materials which are inorganic or mixed organic-inorganic solids. Variety of approaches been applied to study the stability of their crystalline or amorphous frameworks, their interaction with organic templates and their evolution during synthesis and processing.

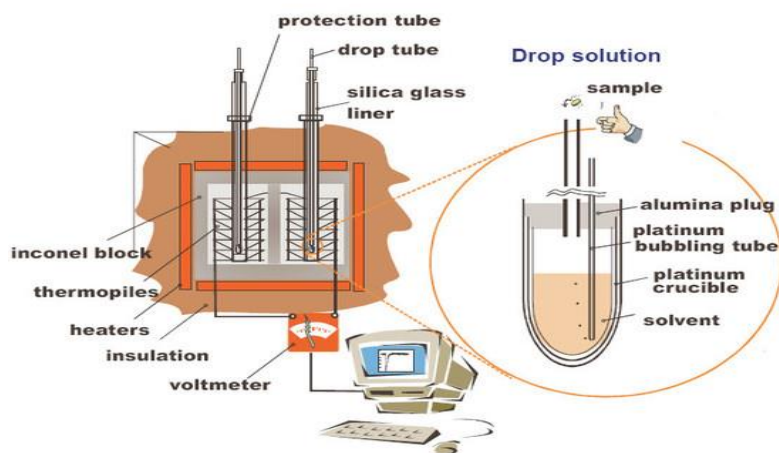


Fig.2.1. High temperature oxides melt solution calorimeter

(http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Thermodynamics/Calorimetry/Applications_of_calorimetry)

3. Adiabatic calorimetry

All heat produced by or in the sample stays there and changes its temperature. No heat leakage occurs. It is achieved in these three ways:

- The sample is isolated from the surroundings, so the thermal resistance between the sample and surroundings is infinitely large.
- The temperature of the surroundings is equal to the sample temperature by a proper control circuit.
- The heat production is so rapid and the measurement of the temperature so fast that there is no heat exchange.

The heat capacity determination is the main application field of adiabatic calorimetry.

Calorimeters with thermally isolated sample have such a structure that the sample have to be positioned inside a vacuum container and fixed there with as little thermal contact as possible. [Sarge, 2014]

Another method in the adiabatic calorimetry is the Pulse calorimetry which uses a pulse of electric current to heat the sample, using the sample's electric resistance. As the voltage drop across the sample, the temperature increase is measured. If the heat loss from the sample is known (or estimated through a calibration procedure), the sensible heat change can be determined; if this is done over short temperature intervals, the value approaches the true heat capacity.

Pulse calorimetry is fast, reproducible, and, with proper calibration, accurate. However, its use is limited to conductive materials and its usefulness for measuring thermodynamic properties other than heat capacity is less certain. [Schlesinger, 2004]

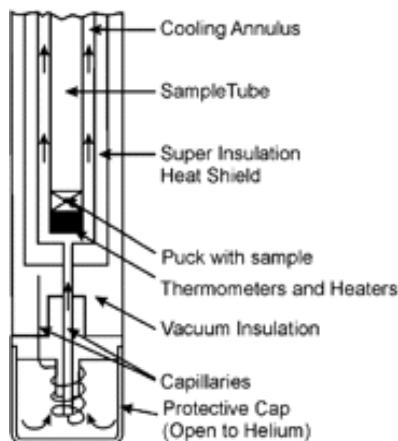


Fig.3.1. Calorimeter for measurement of specific heat capacities at low temperatures

Eucken [Eucken, 1909] developed a calorimeter for measurement of specific heat capacities at low temperatures. Nernst [Nernst, 1910, 1911] used a similar one for measurement of a large number of specific heat capacities to a temperature of 23 K (Fig. 3.1).

Low-temperature calorimeters are used to measure the heat capacity at as low temperatures as possible to get the thermodynamic potential functions. At low temperatures, the accuracy of measurement must be very high. The specific heat capacity decreases and the effect of heat leakage increases. Almost all the calorimeters of this type work with pulse-like electrical heating of the sample and the proper energy of the pulse must be carefully selected so to avoid temperature steps that are too large. Wolf, Bohmhammel and Wolf [Wolf, 1998] described such kind of calorimeter for the temperature range of 15-300 K with helium refrigerator system. [Sarge, 2014]

Adiabatic calorimeters allow numerous measurements in a given experiment. They can also be used to measure enthalpies of reaction or mixing, if the enthalpy changes are small enough. They have good accuracy at high temperatures (up to 1,500°C). However, their construction is complicated and grows increasingly so at high temperatures. Because each energy input requires some time to equilibrate, radiation losses become an increasing concern as the temperature increases. One disadvantage is that they are still relatively slow for making exact measurements. [Schlesinger, 2004]

An interesting investigation is a study from Navrotsky [Snow, 2011] about iron oxides. These oxides exist into anhydrous and hydrous polymorphs. The heat capacity of the lepidocrocite and akaganéite (hydrous polymorphs) was measured within the temperature range 0.8 to 38 K using the semi-adiabatic calorimeter. There was lack of thermodynamic data and an interest to understand their relative stability and reactivity.

Also, some of the adiabatic calorimeters are applied into seeking stability of nanophase materials. Navrotsky et al. [Navrotsky, 2007] combined solution calorimetry and adiabatic calorimetry to learn about titania systems. They worked on the synthesis of samples of anatase and rutile and measured their heat capacities and enthalpies of adsorption of water.

Majzlan et al. [Majzlana, 2005] studied the thermodynamic properties of monoclinic $\text{Fe}_2(\text{SO}_4)_3$ by acid solution calorimetry, adiabatic calorimetry and semi-adiabatic calorimetry and this served as a basis for understanding the thermodynamic properties of a number of ferric iron sulfate. They determined the enthalpy of formation and the entropy as standard temperature and pressure of monoclinic $\text{Fe}_2(\text{SO}_4)_3$.

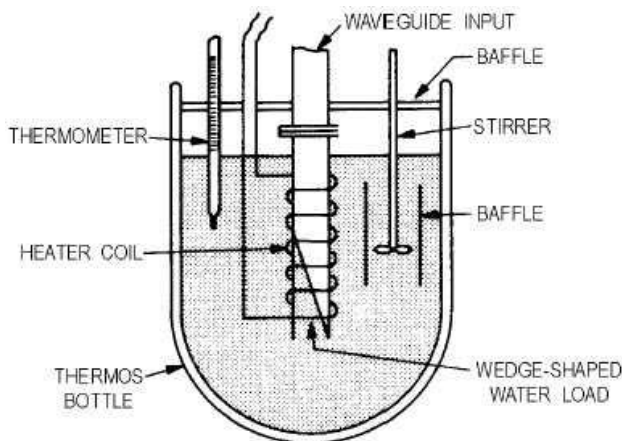


Fig.3.2. Adiabatic calorimeter

(http://electriciantraining.tpub.com/14193/css/14193_110.htm)

4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is the newest of the entrants in the high-temperature thermal analysis. A pan containing a sample and a second pan containing a reference material are heated by separate heating elements at the same rate. The difference in the electrical power required to keep the two pans at the same temperature is proportional to the difference in the heat capacities of the two samples.

The use of an internal reference standard improves the reliability of DSC measurements. DSC is capable of directly measuring the enthalpy changes associated with other thermal events: melting, solid-state phase transitions, even chemical reactions. [Schlesinger, 2004]

This technique measures the energy, which is necessary to establish a nearly zero temperature between a substance and an inert reference material, while the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

There are two types of DSC systems in common use: power-compensation DSC where the temperatures of the sample and reference are controlled independently and heat flow DSC where the sample and reference are connected by a low-resistance heat-flow path. [Bhadeshia]

1) Heat-flux DSC when used for quantitative measurements the thermal behaviour of the calorimeter and the heat path has to be independent of the possible non-steady-state conditions within the sample and of the heat capacities of the sample and reference. In the ideal steady state, the sample and the reference have the same temperature. The heat capacity and the thermal resistance of these calorimeters must be large compared to that of the sample and reference substance, because this affects the sensitivity of the calorimeter.

There are several types of heat flow DSC and two basic groups. The first one is based on the idea of Boersma [Boersma, 1955] to develop differential thermal analysis into quantitative calorimetric methods. The second is based on Calvet's idea to use the difference temperature sensor as the heat transfer medium between the furnace and sample or reference. One disadvantage of heat flow DSCs is the temperature difference between the sample and furnace and the reference and furnace.

The high-temperature DSC (HTDSC) has some similarities to power-compensated DSC: the heating of a reference material and the experimental sample at the same time. A single heater heats a block containing both sample pans. Thermocouples mounted under the pans measure the temperature of each as the block heats. The difference in temperature of the two pans is related to the difference in their heat capacities.

There are two types of HTDSC. The first is the plate type, the second is a cylindrical "Calvet" type. The "Calvet" type is more accurate for heat-capacity measurement than the plate type. It can be used for any type of material. It is fast, easily standardized, and operates at temperatures of 1,500°C or higher, depending on the model. It is theoretically capable of the same variety of measurements as power-compensated DSC.

Several factors affect accuracy and reproducibility, including:

- * Heating rate - the lower the heating rate, the greater the precision;
- * Sample mass - higher sample mass is a potential concern over a thermal lag between the instrument and sample temperatures;
- * Sample form - measurements should not be overly dependent on material form;
- * Cover gas (argon) flow rate;

- * Measurement technique - can be operated using a scanning technique or an enthalpic technique;

Some of the main applications of heat flow DSCs are: polymer and material science; quality control; investigation of thermally activated reactions and transitions. [Sarge, 2014]

The DSC 404 F1/F3 Pegasus® instruments stand out as first-rate vacuum tight high-temperature DSCs. Practically every component is constructed to fulfill the requirements of high vacuum and high-purity gas applications. Various pump systems are available to evacuate the system down to 10^{-4} mbar. Automatic evacuation is of course possible, as is backfilling with various kinds of purge gases.

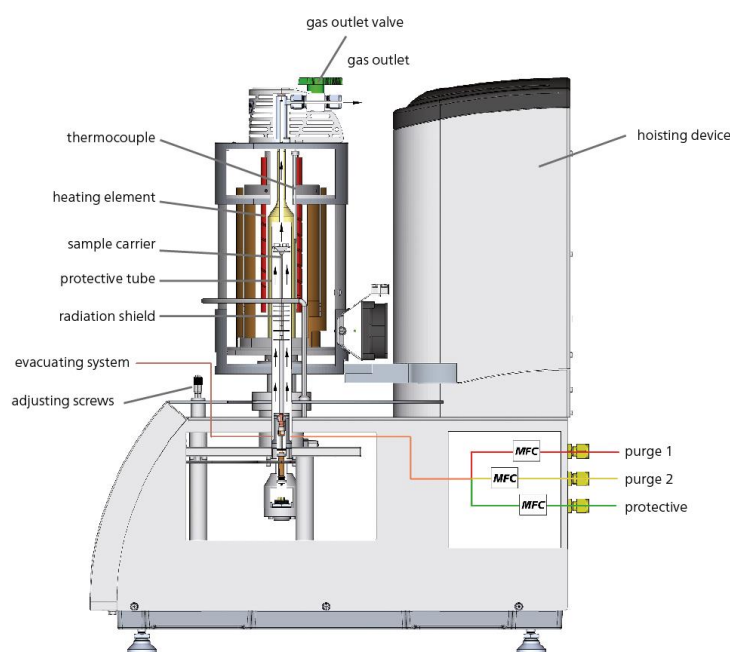


Fig.4.1. DSC 404 F1/F3 Pegasus®, NETZCHS, Germany

(<https://www.netzsch-thermal-analysis.com/en/products-solutions/differential-scanning-calorimetry/>)

In the DSC 404 F3 Pegasus®, the purge or reactive gas flow is generally controlled via frits, manual control systems or tailor-made mass flow control systems (MFCs). The DSC 404 F1 Pegasus® comes standard-equipped with integrated metal-housed mass flow control systems for three different gases. Both MFC systems allow software controlled gas switching and purge gas rates as well as recording of the flow rates in the software.

2) Power-compensated DSC has become a highly popular thermal analysis tool in a variety of fields. However, radiation heat losses at temperatures above 650°C make the stability and repeatability of the baseline signals increasingly unreliable. Power-compensated DSC is not recommended above this temperature. [Schlesinger, 2004] It is developed by Watson et al [Watson, 1964]. The sample and reference are placed in two furnaces in a massive aluminum

block whose temperature is kept constant. They are heated so that their temperature average corresponds to the present temperature according to the heating or cooling program. Additional heating power is added to both furnaces. An internal gas flow serves for a heat exchange between the furnaces and the thermostatized block by convection. The large heating and cooling rates are advantages. Another advantage is the rapid heat exchange between the sample and furnace. One disadvantage is the fact that the differential heating power and the output signal should be zero in empty device, but it never occurs because of huge heat exchange between the furnaces and the cold surrounding block.

This calorimeters are used for precise and fast determination of specific heat capacities in dependence in temperature from which the thermodynamic potential functions of the respective substances can be calculated and for the applications which heat-flux DSC has. [Sarge, 2014]

Some interesting investigations of DSC include these:

- applied in pharmacy characterization and engineering of manufacturable drug products; it analyses proteins in dilute solutions and in solid states [Demarest, 2015]
- used to measure the denaturalization heat of some proteins [Romanini, 2013]
- can measure changes in the thermodynamic properties of phospholipid membranes and into hydrocarbon chains and polar head group [Smith, 2013]
- can be used to evaluate the differences in water and organic matter contents and composition between soil types and thus estimate organic matter loss after fires [Ushakov, 2011]

Navrotsky et al [Costa, 2014] studied onion-like carbons (OLC). These carbons are interesting in material science because of their storage applications due to structural and electronic properties. They made investigation of the enthalpies of formation of OLC at 25°C measured by high-temperature oxidation calorimetry. The results confirm more stable state in enthalpy and that organic functional groups on the OLC which are synthesized at 1300°C add energetic stability.

Another investigation made by Navrotsky [Perrya, 2012] includes cobalt-based spinels. They are intriguing because of their electrical, optical and magnetic properties, and their application in catalysts, batteries and sensors, pigments. They confirmed by DSC that a solid-solution exists in the spinel phase at 800°C. The AlexSys is a high-sensitivity Calvet calorimeter optimized for high temperature solution calorimetry in molten solvents at temperatures to 1000°C. Its most important element is a differential 3D Calvet sensor made of an array of thermocouples (thermopile) which completely surrounds the measuring zone and is connected to a constant temperature block. This design captures over 90% of the heat flow in or out of the sample.

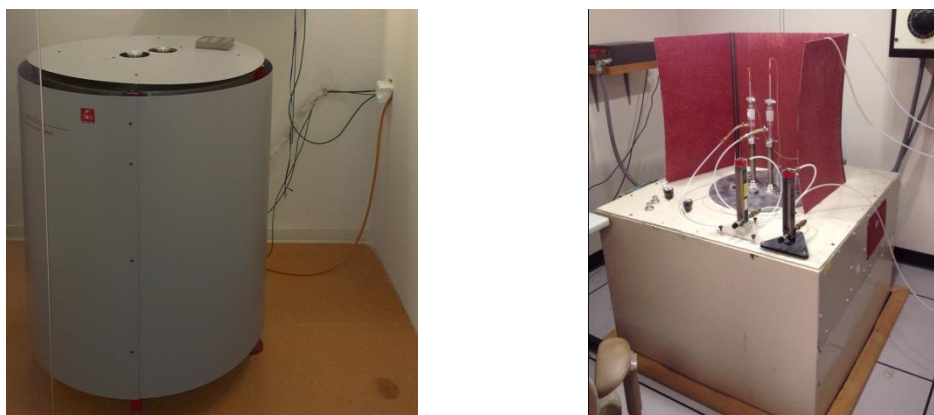


Fig.4.2. AlexSys – High Temperature 3D Calvet Calorimeter, SETARAM, France
(<http://tu-freiberg.de/fakult5/iww/forschung/analysemethoden>)e

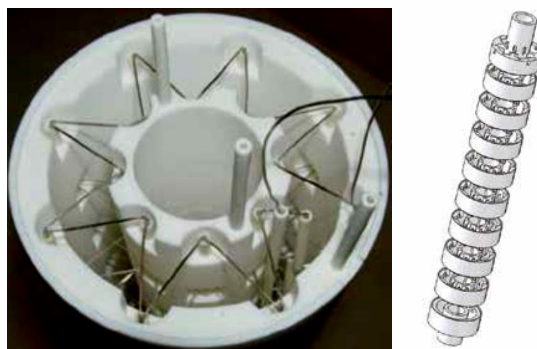


Fig.4.3. 3D Calvet sensor

(<http://www.setaram.com/setaram-products/calorimetry/calorimetry-calorimetry/alexsys/>)

The 3D Calvet sensor provides high sensitivity and exceptional precision. The system is twinned – it has two thermopiles per calorimeter for additional signal stability and greater experimental throughput. The calorimeter is calibrated using a drop method in which a sapphire pellet (or other calibrant) is dropped into an assembly similar to that used for the experiment. Such calibration can be done periodically rather than after each experiment because the calibration factor is accurate and stable over time.

CONCLUSION

This article represents various types of calorimetric methods and measuring instruments. This article represents various types of calorimetric methods and measuring instruments. Firstly, the article illustrated the adiabatic calorimetry, described by Nernst in 1911 in connection of the first adiabatic calorimeter. The main advantage of these calorimeters is the high precision.

Modern calorimeters are more automated than the adiabatic calorimeter, but the principle has not changed from the original design by Nernst. Compensating calorimeters are constructed so that it is possible to compensate the heat effect with an external, calibrated heat source or sink. They often operate close to isothermal conditions between the calorimeter and surroundings. For instance, the C80 Calvet Calorimeter provides a high precision of measurement independent of sample nature or matrix – solid, liquid, gas, powder etc.

Drop calorimeters are used for determination of enthalpy increments and specific heat capacities of solid or liquid materials in a temperature range between room temperature and more than 3000 K. Their advantages include a constant heat capacity of the substance at a predetermined temperature, possibility of operating at high or low temperatures, elimination of any need for corrections for stirring or evaporation.

Differential scanning calorimetry (DSC) is the newest of the entrants in the high-temperature thermal analysis. This technique measures the energy, which is necessary to establish a nearly zero temperature between a substance and an inert reference material, while the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The DSC 404 F1/F3 Pegasus® instruments stand out as first-rate vacuum tight high-temperature DSCs and are used for precise and fast determination of specific heat capacities in dependence in temperature from which the thermodynamic potential functions of the respective substances can be calculated.

REFERENCES

- Blachnik, R., Besser, J., Wallbrecht, P., Dreyer, K., An isoperibol drop calorimeter. *Thermochim. Acta*, 271, 1996, 85-92.
- Boersma, S. L., A theory of differential thermal analysis and new methods of measurement and interpretation. *J. Am. Ceram. Soc.*, 38, 1955, 281-284.
- Brown, M. E., *Introduction to Thermal Analysis. Techniques and Applications*. Chapman and Hall Ltd., New York, 1988.
- Brown, M. E., *Introduction to Thermal Analysis. Techniques and Applications*. Second Edition. Kluwer Academic Publishers, 2001.
- Costa, G. C. C., McDonough, J. K., Gogotsib, Y., Navrotsky, A., Thermochemistry of onion-like carbons. *Carbon*, 69, 2014, 490-494.
- Cowana, L. A., Morcos, R. M., Hatadac, N., Navrotsky, A., Hailea, S. M., High temperature properties of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ at ambient pressure: Absence of a polymorphic, superprotonic transition. *Solid State Ionics*, 179(9-10), 2008, 305-313.
- Demarest, S. J., Frasca, V., *Differential Scanning Calorimetry in the Biopharmaceutical Sciences. Biophysical Characterization of Proteins in Developing Biopharmaceuticals*, 2015, 287-306.
- Eucken, A., Über die Bestimmung spezifischer Wärmen bei tiefen Temperaturen. *Phys. Z.*, 10, 1909, 586-589.
- Hatakeyama, T., Quinn, F.X., *Thermal Analysis. Fundamentals and Applications to Polymer Science*. Second Edition. John Wiley & Sons Ltd. 1999.
- Linard, Y., Wilding, M. C., Navrotsky, A., High temperature calorimetric studies of heat of solution of NiO, CuO, La_2O_3 , TiO_2 , HfO_2 in sodium silicate liquids. *Geochimica et Cosmochimica Acta*, 72(2), 2008, 590-601.
- Majzlana, J., Navrotsky, A., Stevens, R., Donaldson, M., Woodfield, B. F., Boerio-Goates, J., Thermodynamics of monoclinic $\text{Fe}_2(\text{SO}_4)_3$, *The Journal of Chemical Thermodynamics*, 37(8), 2005, 802-809.

- Materials and Their Characteristics: Overview. Dipartimento di Fisica. Università degli Studi di Genova.
<http://www.fisica.unige.it/~rocca/Didattica/Material%20Science/I%20-%20Materials%20Overview.pdf>
- Missen, R. W., Mims, C. A., Bradley, A. S., Introduction to Chemical Reaction Engineering and Kinetics, Department of Chemical Engineering and Applied Chemistry, University of Toronto. 1999.
- Navrotsky, A., Calorimetric insights into the synthesis of templated materials. *Current Opinion in Colloid & Interface Science*, 10(5-6), 2005, 195-202.
- Navrotsky, A., Calorimetry of nanoparticles, surfaces, interfaces, thin films, and multilayers. *The Journal of Chemical Thermodynamics*, 39(1), 2007, 1-9.
- Navrotsky, A., *Physics and chemistry of Earth materials*. Cambridge University Press, 1994.
- Nernst, W., Der Energiegehalt fester Stoffe. *Ann. Phys.* 4. Folge, 36, 1911, 395-439.
- Nernst, W., Untersuchungen über die spezifische Wärme bei tiefen Temperaturen II. *Sitzungsber. K. Preuss. Akad. Wiss.*, 1910, 262-282.
- Perrya, N. H., Masona, O. T., Mab, C., Navrotsky, A., Shic, Y., Bettingerc, J. S., Toneyc, M. F., Paudeld, T. R., Lanyd, S., Zungere, A., $\text{Co}_3\text{O}_4\text{-Co}_2\text{ZnO}_4$ spinels: The case for a solid solution. *Journal of Solid State Chemistry*, 190, 2012, 143-149, doi:10.1016/j.jssc.2012.02.022.
- Ramachandran, V.S., Paroli, R. M., Beaudoin, J. J., Delgado, A. H., *Handbook of Thermal Analysis of Construction Materials*, Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario, Canada.
- Romanini, D., Braia, M. J., Porfiri, M. C., Applications of Calorimetric Techniques in the Formation of Protein-Polyelectrolytes Complexes in: "Applications of Calorimetry in a Wide Context - Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry", 2013, doi: 10.5772/54260.
- Sarge, S. M., Hohne, G. W. H., Hemminger, W., *Calorimetry: Fundamentals, Instrumentation and Applications*. Wiley-VCH, 2014.
- Schlesinger, M. E., Jacob, S., *Advances in High-Temperature Calorimetry: A comparison*. JOM, 2004.
- Smith, E. A., Dea, P. K., Differential Scanning Calorimetry Studies of Phospholipid Membranes: The Interdigitated Gel Phase in: "Applications of Calorimetry in a Wide Context - Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry", 2013, doi: 10.5772/51882.
- Snow, C. L., Smith, S. J., Lang, B. E., Shia, Q., Boerio-Goatesa, J., Woodfield, B. F., Navrotsky, A., Heat capacity studies of the iron oxyhydroxides akaganéite ($\beta\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$). *The Journal of Chemical Thermodynamics*, 43(2), 2011, 190-199.
- Speyer, R. F., *Thermal Analysis of Materials*. School of Materials Science and Engineering. Georgia Institute of Technology, Atlanta, Georgia. Marcel Dekker, Inc., 1993.



- Ushakov, S. V., Nag, D., Navrotsky, A., Application of scanning calorimetry to estimate soil organic matter loss after fires. *Journal of Thermal Analysis and Calorimetry*, 104(1), 2011, 351-356.
- Watson, E. S., O'Neill, M. J., Justin, J., Brenner, N., A differential scanning calorimeter for quantitative differential thermal analysis. *Anal. Chem.*, 36, 1964, 1233-1238.
- Wendlandt, W., *Thermal Analysis, Third Edition*, A Wiley-Interscience Publication. 1985.
- Wolf, U., Bohmhammel, K., Wolf, G., A simple low-temperature calorimeter based on a helium refrigerator system. *Thermochim. Acta*, 310, 1998, 37-42.
- Wunderlich, B., Learning about calorimetry. *J Therm Anal* 49, 1997, 7-16.
- Wunderlich, B., *Thermal Analysis of Polymeric Materials*. Springer, 2005.
- Yamaguchi, K., Itagaki, K., Measurement of high temperature heat content of silicon by drop calorimetry. *J. Therm. Anal. Calorim.*, 69, 2002, 1059-1066.