

APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO CORE ANALYSIS

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ABSTRACT

The differential scanning calorimetry (DSC) technique allows one to measure transient differential heat flow between the two cells of a differential scanning calorimeter. The measurements can be done either at constant temperature (isothermal mode) or during the controlled change of temperature (scanning mode) of the calorimeter furnace. High accuracy and versatility of the DSC devices lead to a broad use of this technique in many modern industries.

The application of the high-pressure high-temperature (HPHT) DSC technique to laboratory core analysis can provide a lot of valuable information with unprecedented accuracy; some common applications are outlined in this manuscript.

One of the common applications for a DSC technique is the determination of the specific heat capacity (SHC) of a sample – cleaned or saturated core samples can be studied at different pressure and temperature conditions. The existence of relatively large surface areas in reservoir core samples allows one to study these samples with the DSC methods that are commonly used to study media with high surface area to volume ratio such as catalysts and catalyst supports, colloids or thin films for example. In particular: pore size distribution (PSD); wettability and surface area of the core samples can be studied.

DIFFERENTIAL SCANNING CALORIMETRY SETUP

Differential scanning calorimetry means the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program. The characteristic feature of all DSC measuring systems is the twin-type design and the direct in-difference connection of the two measuring cells of the calorimeter (sample cell and reference cell) which are matching pairs [1] (Figure 1). Both of the cells are situated in the furnace at the same temperature controlled with high accuracy. Difference configuration allows one to substantially decrease the influence of the base line signals and thus to increase the accuracy of the DSCs.

There are several types of differential scanning calorimeters commercially available now; this manuscript concerns only one of them: heat flow Calvet-type DSC. Calvet-type sensor consists of a great number of thermopiles that are connected in series between the cell and the furnace. The cells are thermally decoupled from each other. The thermocouples are dominating the heat conduction path from the sample to the furnace

thus ensuring high accuracy of this device and its capability to capture more than 95% of the heat produced in the cells. By the known thermocouple response the measured electrical signal ΔU is converted to a temperature difference between the cells which in turn can be converted to the difference in differential heat flow if proper calibration is done. A Setaram BT2.15 calorimeter was utilized in this work for the measurements.

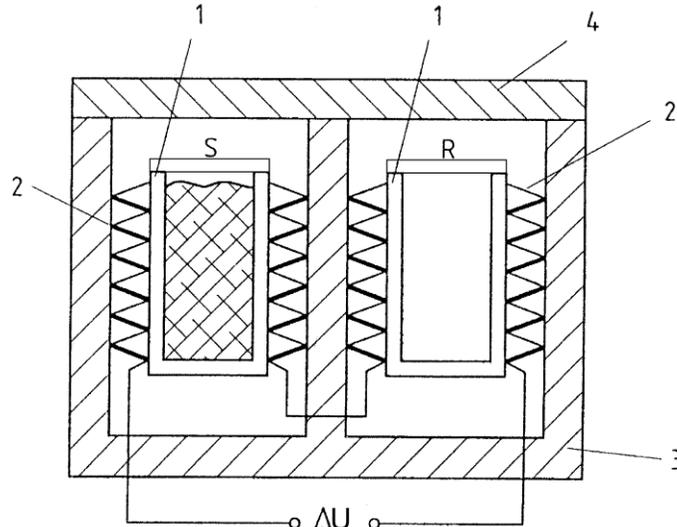


Figure 1. Heat flux DSC with Calvet cylinder-type measuring system. 1 – Sample and reference cells, 2 – thermopiles, 3 – furnace, 4 – lid

PROCEDURES

Specific Heat Capacity Measurements

The thermal properties of core samples are of high value in the oilfield industry [2]. DSCs are particularly useful for SHC measurements. With the DSC, SHC measurements can be done either in a continuous mode (continuous furnace temperature variation) or in a step mode (step temperature change). Step mode allows the sample to reach thermal equilibrium after a temperature step, giving the method greater precision compared to continuous temperature variation method, at the same time step mode is much more time consuming if SHC at different temperatures is required.

Both of the methods preferentially use reference sample SHC measurements in order to increase the accuracy of the method. In the preferred embodiment of the method reference sample heat capacity should be close to the investigated sample heat capacity. Al_2O_3 material which is very stable and well characterized is often used as a standard reference sample for such experiments. Three identical experiments are required for the accurate determination of the SHC: experiment with empty cells (blank experiment - B), experiment with a reference sample (R) and experiment with the sample (S). The resulting SHC is calculated by the following formula:

$$c_p(T) = \frac{c_{pR}(T) \left(\frac{m_R}{m_S} \right) (HF_S - HF_B)}{(HF_R - HF_B)} \quad (1)$$

where HF_S , HF_B , HF_R – are the heat flows in the corresponding experiments, m_R , m_S – are the masses of the reference and the investigated sample; $c_{p,R}(T)$ – is the reference sample specific heat capacity. The examples of SHC measurements in the step mode and at the scanning mode are shown in Figure 2.

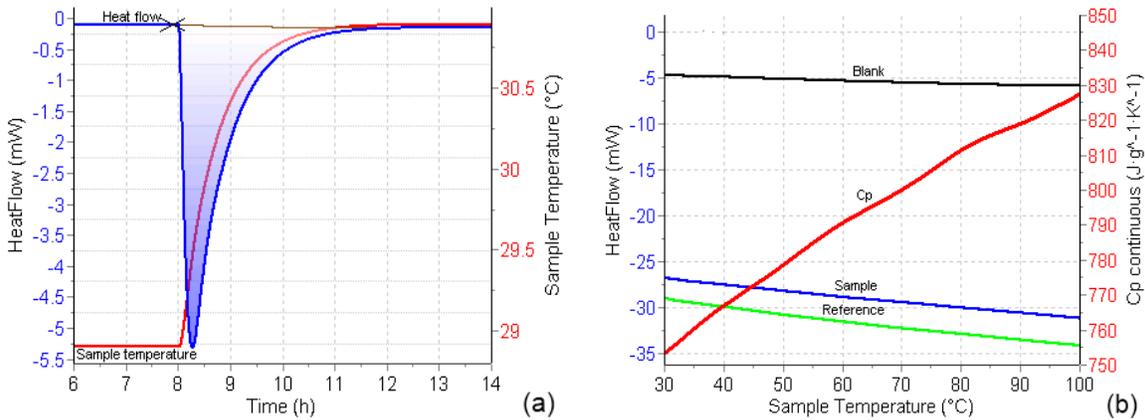


Figure 2. (a) Heat flow (heating scan) versus time and sample temperature versus time profiles obtained during step change (29 – 31 °C) SHC measurements experiment; (b) Heat flow profiles for sample, reference and blank experiments and resulting SHC versus sample temperature profiles obtained during continuous temperature variation SHC measurement experiments on a core sample

Depending on the calorimeter parameters, sample size and availability of the proper reference sample, the precision of the experiments may vary in these experiments. With the calorimeter that is utilized in these experiments we were able to reach ~ 1 % precision for the step mode of operation and ~ 1.7 % precision for the continuous mode of operation wherein the precision dominates over the accuracy in the experiments. It is possible to work with cleaned or saturated cores as well as saturated cores at high-pressure conditions if high-pressure cells are utilized for the experiments. Temperature range is determined by the calorimeter parameters (-196 to 200 °C for BT2.15 DSC).

Pore Size Distribution Measurements

A standard method for PSD measurements in core analysis is mercury injection capillary pressure method. Although superior to many other methods by its range of applicability (~ 4 nm to 400 μm) and accuracy, this method has serious limitations due to first of all health and environmental issues (another concern is that high mercury pressure may crush or deform the pores when small pores are studied), which drives continuous research on this theme. DSC thermoporometry [2] is one of the alternative methods for PSD measurements. This method covers much narrower range of pores in the mesopore and macropore range of pores with characteristic sizes up to 1 μm [3].

Thermoporometry are methods for assessing porosity and PSD in systems with a high surface area to volume ratio (SV ratio). In these systems additional contribution of the surface energy to the total Gibbs energy leads to a shift of temperature of phase transition in the media with a high SV ratio. Simply speaking, a drop of liquid bounded by a pore

wall would exhibit phase change temperature depression as compared to a bulk liquid phase transition temperature. DSC scanning over phase transition temperature of the confined liquid allows the measurement of the quantity of liquid exhibiting given temperature depression in a liquid-saturated porous material thus allowing one to estimate SV ratio of this part of liquid.

PSD by its definition is a derivative $\frac{\partial V}{\partial r}$ as a function of r , where V – is the pore volume and r – is the pore radius (or characteristic width if the pore is not cylindrical). In order to obtain PSD from the DSC heat flow profile versus sample temperature one has to convert the temperature record into an equivalent length scale (pore radius for example) while the heat flow should be converted into a differential pore volume. The theoretical basis for relating temperature depression ΔT to pore radius is through the Gibbs equation:

$$\Delta T = T_m^0 - T_m = SV_{CL} T_m^0 (\gamma_{SC} - \gamma_{SL}) / \rho_C \Delta H, \quad (2)$$

where T_m – is the bounded phase transition temperature, T_m^0 – is the unbounded (bulk) phase transition temperature; SV_{CL} – is the surface to volume ratio of the condensed phase (ice); γ_{SC} – is the solid (rock surface)-condensed phase surface tension; γ_{SL} – is the solid-liquid surface tension; ρ_C – is the condensed phase mass density and ΔH – is the enthalpy of the phase transition. The geometrical considerations are very important for correct interpretation of DSC thermoporometry results, e.g. for a long cylinder of radius r : $SV_{CL} = 2\pi r l / \pi r^2 l = 2/r$.

Controlled pore glasses (CPGs) are glass materials that as a rule have uniform narrow distribution of pores ($\sim 80\%$ of pores within $\pm 10\%$ of the mean pore diameter) and are ideal model media for reference experiments on PSD measurements with the DSC thermoporometry.

In Figure 3 one can see the results of one of the experiments that were conducted with a mixture of a CPG powder of 3 different sizes of pores. Four endothermic peaks are distinguished in the figure – three of which correspond to liquid inside the pores of different CPGs while the biggest one is attributed to bulk water phase transition.

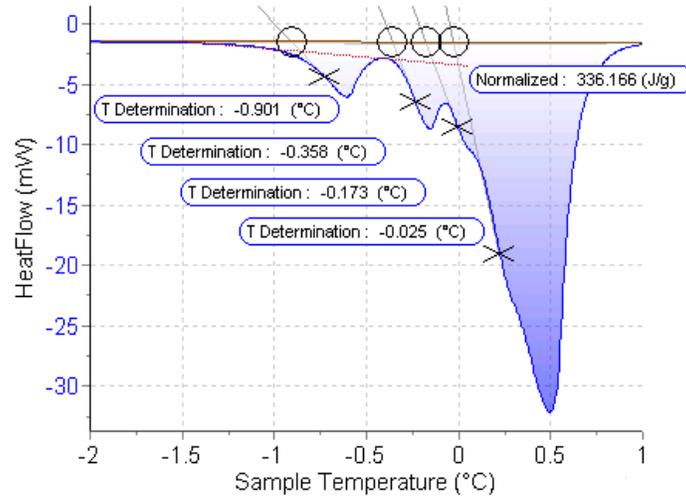


Figure 3. (a) Heat flow (heating scan) versus sample temperature for a mixture of CPG samples (50 nm, 100 nm, 300 nm averaged pore diameter) saturated with distilled water

Wettability Assessment

Wettability is the major factor controlling the location, flow, and distribution of fluids in an oil reservoir [5]. Amott, Amott-Harvey, USBM (US Bureau of Mines) method or a combination of them are considered as industry standards for wettability estimation in core analysis [6]. Wettability is determined by the physicochemical interactions of reservoir fluids with each other and with the heterogeneous surface of the formation. Due to the complexity of investigation of surface interactions no universal method for wettability determination exists up to date, which drives continuous research on this theme.

Immersion calorimetry experiments are of interest in this part of the manuscript. Immersion experiments are commonly conducted with the use of sealed ampules containing the samples. The ampules are immersed in the wetting liquid situated inside the calorimeter cell and are broken during the experiment thus ensuring wetting of the sample. From immersion calorimetry, it is possible to get the variation of state functions like internal energy U (at constant volume) or enthalpy H (constant pressure experiments) related to the wetting process. They cannot be used directly to predict wetting properties because only free energy G variations are able to do that. The change of the enthalpy of the system is related to the change of the Gibbs free energy of the system:

$\Delta H = \Delta G - \frac{T\partial\Delta G}{\partial T}$. In the immersion process the variation of the Gibbs energy is equal to the variation of the surface energies of the system. If the solid is immersed from the vacuum conditions: $\Delta G = \gamma^S - \gamma^{SL}$, where γ^S – is the solid-vacuum interface surface tension and γ^{SL} – is the solid-liquid interface surface tension (Figure 4, left part), and:

$$\Delta H = A(\Delta\gamma - T\partial\Delta\gamma/\partial T) = A[(\gamma^S - \gamma^{SL}) - T\partial(\gamma^S - \gamma^{SL})/\partial T] \quad (3)$$

where A – is the solid phase surface area. Taking the Young equation ($\gamma^{L1L2} \cos\theta = \gamma^{SL1} \gamma^{SL2}$) into consideration one may obtain from (3):

$$\cos\Theta = (k_1 \Delta H_{imm}^1 - k_2 \Delta H_{imm}^2) / A \gamma^{L1L2}, \quad (4)$$

where k_1 and k_2 – are the ratios of the first to second term in (3) for first and second wetting liquids. It was shown by direct experiments [7] that for many solids and liquids:

$$k = [\gamma^S - \gamma^{SL}] / [(\gamma^S - \gamma^{SL}) - T \partial(\gamma^S - \gamma^{SL}) / \partial T] \approx \gamma^{LV} / (\gamma^{LV} - T \partial \gamma^{LV} / \partial T). \quad (5)$$

Consequently k parameters for different liquids can be obtained from the measurements of the surface tensions of these liquids at different temperatures, which are easily obtained with commercially available equipment. The surface area of the sample should be determined separately either by some other method, such as e.g. BET gas adsorption method [8], or again, with the use of the DSC by the modified Harkins-Jura method [9].

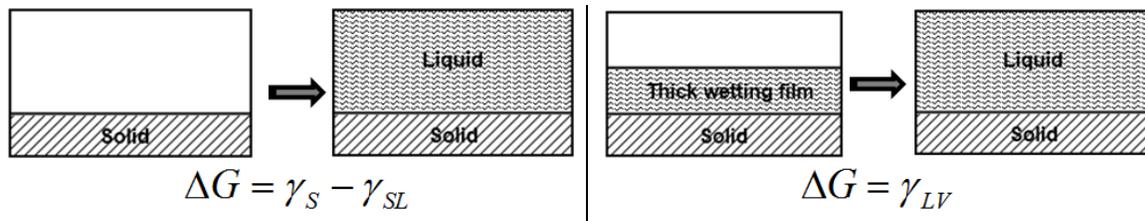


Figure 4. To the determination of immersional wetting

Surface Area Measurements

The idea of the modified Harkins-Jura method is to make an immersion experiment with the sample that is precovered with a thick liquid layer prior to immersion. In this case $\Delta G = \gamma^{LV}$ (Figure 4, right part) and the measured enthalpy is:

$$H = A(\Delta \gamma^{LV} - T \partial \Delta \gamma^{LV} / \partial T) \quad (6)$$

Thus the surface area of a given sample can be measured by immersion calorimetry if the liquid-vapor interfacial tension and its variation with the temperature are known. Water is commonly used with hydrophilic surfaces, while pure hydrocarbons can be used with both the hydrophilic and hydrophobic ones for the surface area measurements [9].

CONCLUSIONS

Differential scanning calorimetry is a powerful technique that is widely implemented in many modern industries. The utilization of DSC measurements for core analysis may provide a lot of valuable core properties with unprecedented accuracy. Some of the common applications may include: core samples specific heat capacity, pore size distribution, surface area and wettability measurements.

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