

**Adsorption properties and energetic surface heterogeneity
of a $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ sample studied by means
of the thermal analysis and sorptometry techniques**

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This paper presents possible applications of thermal analysis and sorptometric methods to study physicochemical properties $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$. The calculation of the desorption energy distribution by analytical procedure of liquid (n-octane, water) vapour preadsorbed on a solid surface are presented. It is shown that the superconducting Hg-1223 phase is highly sensitive to water vapour. Mechanism of adsorption water molecules depends largely on time activation (t_{act}). When water vapour saturation was $0 < t_{\text{act}} < 90$ minutes, physisorption was observed. In the case of longer water vapour action, $t_{\text{act}} > 90$ min, the chemical decomposition was found.

1. INTRODUCTION

Superconducting oxides are necessary for functioning of many electronic and energetic systems. On one hand, critical temperature (T_c) [1], critical current density (J_c) and critical magnetic field (H_c), on the other hand, surface properties of the high- T_c oxides are likely to limit the scale of their technological application [2-5]. Current leads, MR magnet, power cables, etc. have an active superconductor centre.

A great number of physical and chemical processes take place on the surface bordering phases, while other processes are initiated on them. For this reason the knowledge of the phenomena occurring on the boundary surfaces is of significant importance for the studied processes as in many cases they are responsible for changes of physicochemical properties. The most characteristic properties of solid surface include capability of adsorption of steams and gases.

This phenomenon results in the fact that forces acting within the crystal are only partially saturated on the crystal surface. Therefore, the solid surface can absorb molecules from gas, liquid and even solid phases. Atmospheric gases such as H_2O and CO_2 can influence significantly properties of these materials, which react to their presence in the differential. Literature presents some articles on theme mutual influences of water on the surface of superconducting oxides. Depending on the kind of sample and conditions one can observe different results of the interaction: physical or chemical adsorption.

Studies of the adsorption on semiconducting oxide CuO [6] illustrate different results of the interaction, used as a model for the complex high- T_c superconducting oxides. On CuO , water molecule can chemisorb strongly, at low temperature, and chemisorb by dissociation (between 128 and 158 K). In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, physical and chemical adsorption [7-9] or combinations depending on the temperature of measurements [8] and time of work operation [9] can be observed. Physical adsorption does not change the elementary composition of the surface layer. The chemically adsorbed multilayer of water molecules stimulates the exchange of ions between the surface and the bulk of the crystal lattice with simultaneous decomposition [7]. Water adsorption occurs also on other superconducting materials, for example, chemisorbed on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [10] and physisorbed for $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+x}$ [11].

The studies of adsorption properties and heterogeneous properties of high temperature superconductor presented in literature are rare. For that reason, this paper presents possible applications of thermal analysis and sorptomatic methods to study physicochemical properties of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$. Hg-1223 ($\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$) is the higher member of the Hg-based homologous series [12, 13], $\text{HgBa}_2\text{Ca}_{(n-1)}\text{Cu}_n\text{O}_y$ ($n=1, 2, 3$), with resistance measurements confirm a maximum transition temperature of ~ 133 K [14] and under pressure 150 kbar $T_c=153$ K [15].

Thermodesorption of water and nonpolar liquids on superconducting material grains is studied providing two kinds of information: the influence of saturation time on mechanism of adsorption of water molecules and quantitative description of the energetic heterogeneities of the $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ surface. The first study of numerical procedure for evaluation of desorption energy distribution of liquid vapour preadsorbed on a mesoporous solid surface from the Q-TG and Q-DTG curves measured under the quasi-equilibrium conditions was presented in [16]. The new theory of analytical procedure for evaluation of desorption energy distribution from Q-TG and Q-DTG curves under the quasi-isothermal conditions is discussed in [17].

2. EXPERIMENTAL

The study was carried out on Hg-1223 sample prepared by a solid-state reaction technique using reagent-grade HgO, BaO, CaO and CuO powders, using the method presented by Isawa et al. in paper [18].

Thickness of the adsorbed liquid layers on the surface can be controlled by the immersion mode of solid sample. The studies of the adsorbed liquid layers were made using simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary). The classical thermogravimetric (DTG) curves of water thermodesorption, which give the dependence of the weight loss of a sample as a function of temperature or time, were measured over a temperature range from 20 to 1000 °C with a furnace-heating rate of 10 °C/min. The TG and DTG curves were registered digitally under the control of the program Derivat running on PC. Specific surface areas, pore size and volume of the high temperature superconductor sample were calculated from the low-temperature nitrogen adsorption isotherms measured by means of the sorptomat apparatus type ASAP 2405 V1.01 (Micrometrics Inc., USA).

The analytical procedure for evaluation of the desorption energy distribution of liquid and/or vapour preadsorbed on a porous solid surface from the Q-TG and Q-DTG curves measured under the quasi-isothermal conditions in the temperature range 20-250 °C at a furnace-heating rate of 6 °C min⁻¹ [7].

3. RESULTS AND DISCUSSION

The experimental differential mass loss Q-DTG curve in relation to temperature for the desorption vapour of n-octane on the Hg-1223 surface is presented in Figure 1. It can be seen that two parts appear in this spectrum: the first one a long wide peak with minimum located near 125 °C and the second part with inflexion at 140-200 °C. In the case of water thermodesorption it appears that there is one larger peak with its minimum located near 100 °C, Figure 2. In the case on the application of analytical method for evaluation of desorption energy distribution from Q-TG and Q-DTG curves, equation of desorption kinetics for the part of surface characterized by the constant value of desorption energy has the form:

$$-\frac{1}{1-\theta_i} \frac{d\theta_i}{dT} = \frac{v_i}{\beta} \exp\left(-\frac{E_i}{RT}\right) \quad (1)$$

where $T=T_0+\beta t$, θ – the degree of surface coverage, v – the entropy factor, E_i – the desorption energy calculated for each temperature, T_0 i T – the initial and given temperatures of desorption, β – the sample heating rate, t – the time, R is the universal gas constant.

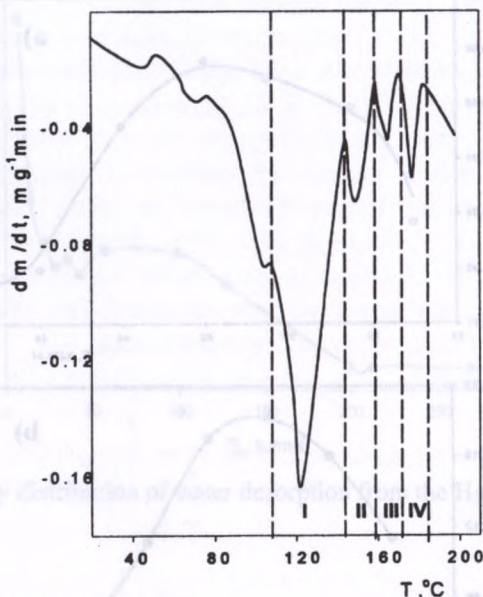


Fig. 1. Q-DTG curve of thermodesorption of n-octane from Hg-1223 surface under the quasi-isothermal condition

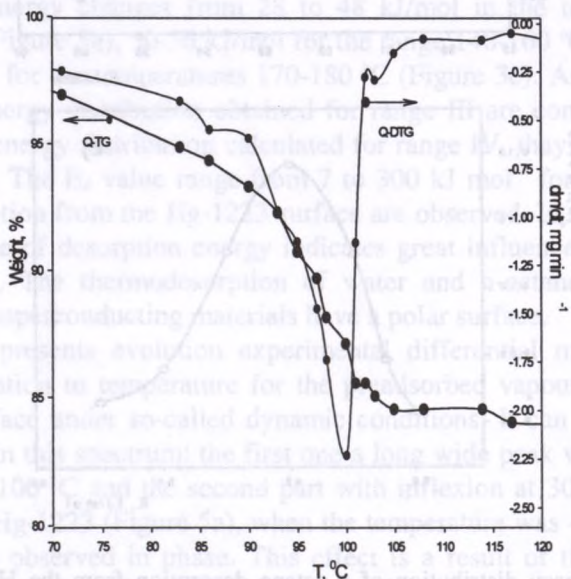


Fig. 2. Q-TG and Q-DTG curves of thermodesorption of water from the Hg-1223 surface, under the quasi-isothermal condition

Equation 2 was used for the approximate desorption energy distribution from the pores for each temperature T_i in the Q-DTG curve Figures 3 and 4.

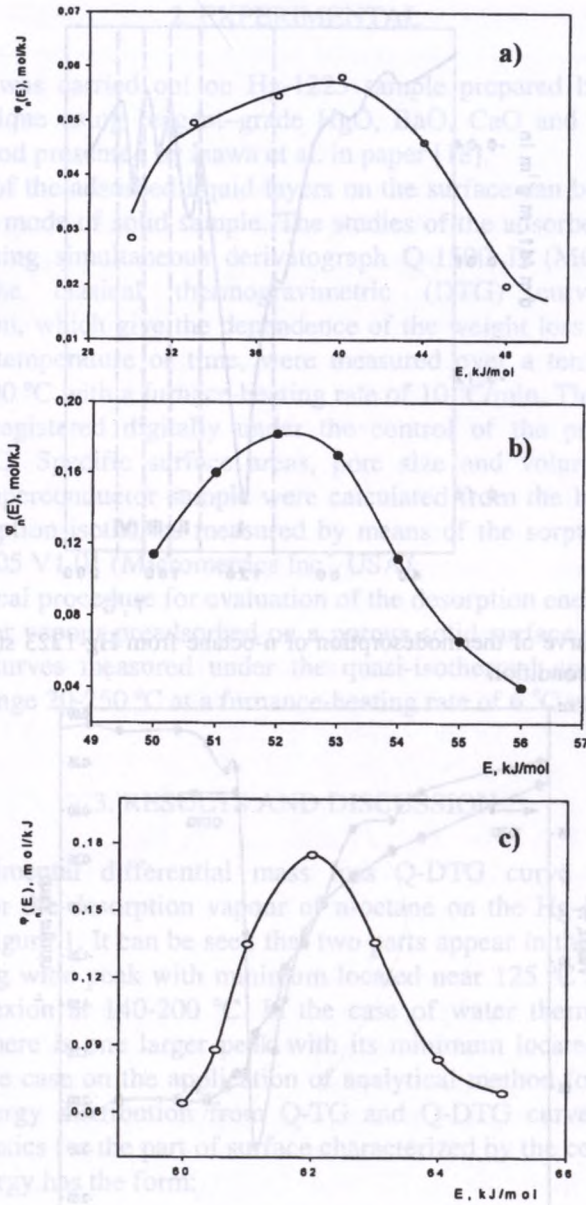


Fig. 3. Plot of energy distribution of n-octane desorption from the Hg-1223 surface calculated for: a) the first part of Q-DTG curve, from 110 to 140 °C, b) calculated for the second part of Q-DTG curve, from 140 to 160 °C, c) the third and fourth parts of Q-DTG curve, from 160 to 170 °C and from 170 to 180 °C [17]

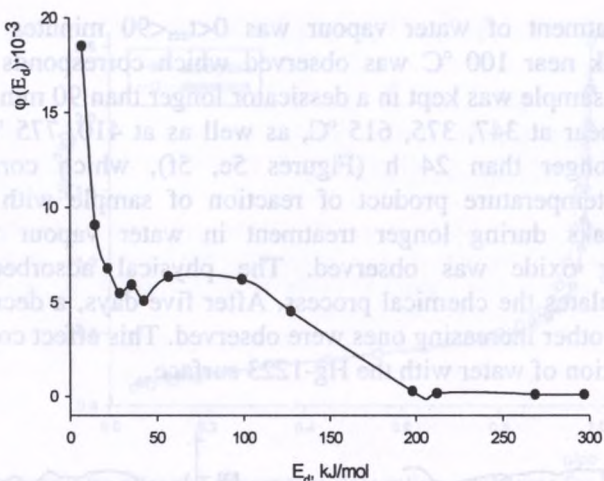
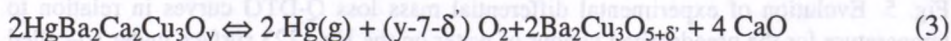


Fig. 4. Plot of energy distribution of water desorption from the Hg-1223 surface

$$\varphi_n(E) = -\frac{d\theta}{dT} \frac{1}{T} \quad (2)$$

The distribution function $\varphi_n(E)$ of n-octane desorption from the Hg-1223 surface for each temperature range I, II, IV are presented in Figure 3. Desorption energy changes from 28 to 48 kJ/mol in the temperature range 110-140 °C (Figure 3a), 50-56 kJ/mol for the range 140-160 °C (Figure 3b) and 60-65 kJ/mol for the temperatures 170-180 °C (Figure 3c). As the functions of desorption energy distribution obtained for range III are comparable with the functions of energy distribution calculated for range IV, they are not presented in this paper. The E_d value range from 7 to 300 kJ mol⁻¹ for water (Figure 4) thermodesorption from the Hg-1223 surface are observed. In the case of water, the high value of desorption energy indicates great influence of molecules on solid surface. The thermodesorption of water and n-octane shows that the investigated superconducting materials have a polar surface.

Figure 5 presents evolution experimental differential mass loss Q-DTG curves in relation to temperature for the preadsorbed vapour of water on the Hg-1223 surface under so-called dynamic conditions. It can be seen that two parts appear in this spectrum: the first one a long wide peak with the minimum located near 100 °C and the second part with inflexion at 300-850 °C. In the case of pure Hg-1223 (Figure 5a), when the temperature was ~440 °C, a weight decrease was observed in phase. This effect is a result of the decomposition temperature of Hg-1223 [19], schematically according to the following equation:



When a treatment of water vapour was $0 < t_{act} < 90$ minutes (Figure 5b) increase of peak near $100\text{ }^{\circ}\text{C}$ was observed which corresponds to physical sorption. When sample was kept in a dessicator longer than 90 min (Figure 5c), weak peaks appear at $347, 375, 615\text{ }^{\circ}\text{C}$, as well as at $410, 775\text{ }^{\circ}\text{C}$ when the activation is longer than 24 h (Figures 5e, 5f), which corresponds to decomposition temperature product of reaction of sample with water. The increase of peaks during longer treatment in water vapour on mercury superconducting oxide was observed. The physical adsorbed of water molecules stimulates the chemical process. After five days, a decreasing peak near $100\text{ }^{\circ}\text{C}$ but other increasing ones were observed. This effect corresponds to a chemical reaction of water with the Hg-1223 surface.

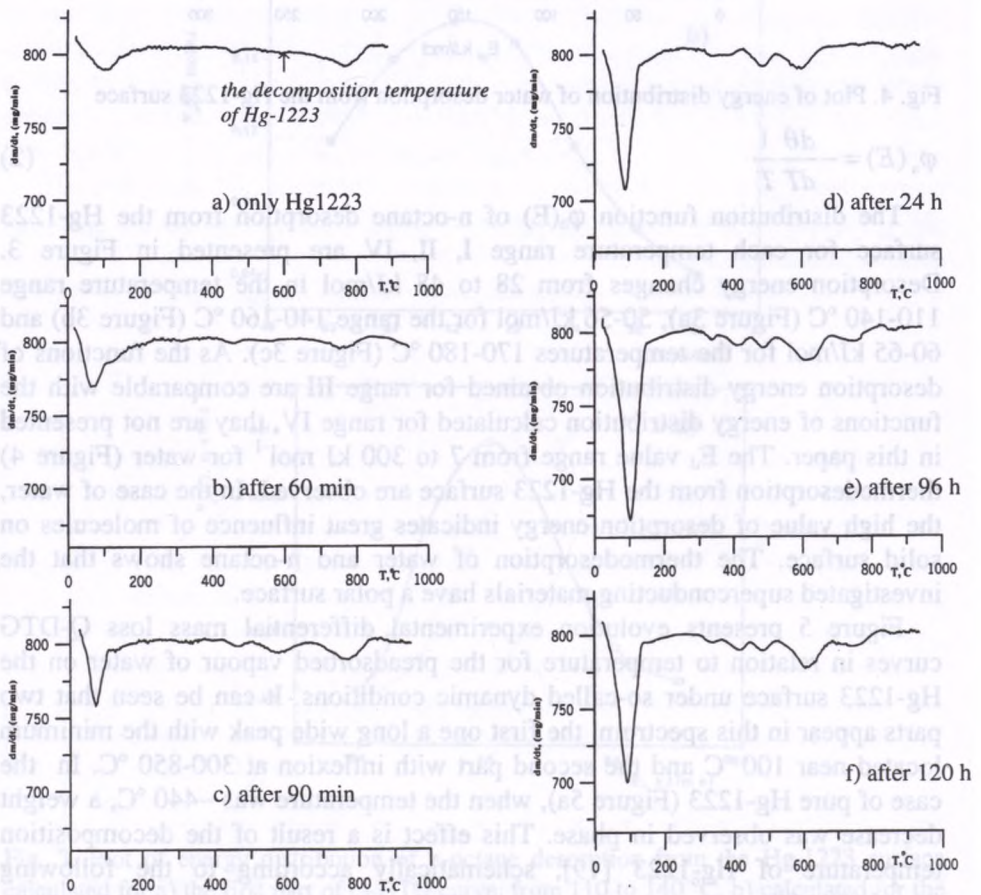


Fig. 5. Evolution of experimental differential mass loss Q-DTG curves in relation to temperature for the preadsorbed vapour of water on the Hg-1223 surface under so-called dynamic conditions. The initial mass was 100 mg

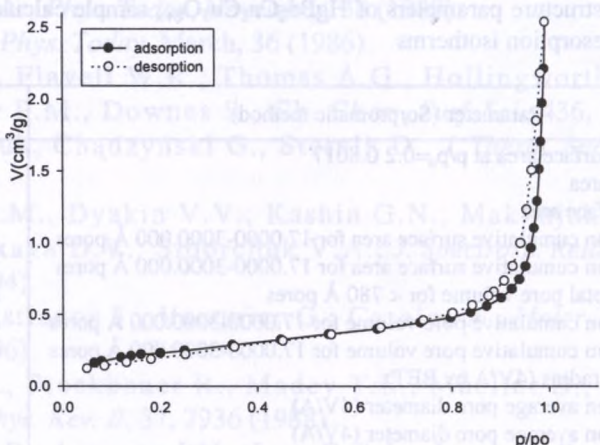


Fig. 6. Low-temperature nitrogen adsorption-desorption isotherms for Hg-1223

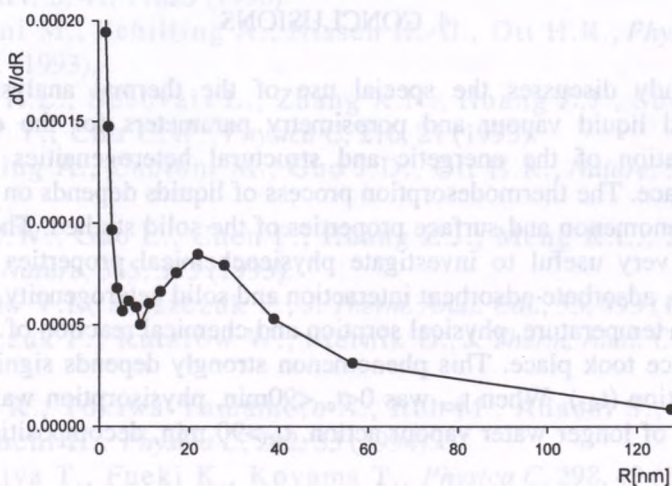


Fig. 7. Pore volume distribution function for Hg-1223

The porosimetry measurements showed that the mean pore radius and the pore volume of the superconducting sample were calculated from the BJH desorption isotherms to be 128.7 Å and 0.0039 cm³ g⁻¹, respectively (Table 1). The BET specific surface area of the fresh ceramic material (Hg-1223) was 0.89 m²/g.

Tab. 1. Pore structure parameters of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ sample calculated from nitrogen adsorption-desorption isotherms

| Parameter (Sorptomatic method) | Unit | Value |
|---|------------------------|----------|
| Single point surface area at $p/p_0=0.2$ 0.8017 | m^2/g | 0.8888 |
| BET surface area | m^2/g | 1.2773 |
| Langmuir surface area | m^2/g | 0.9183 |
| BJH adsorption cumulative surface area for 17.0000-3000.000 Å pores | m^2/g | 0.9398 |
| BJH desorption cumulative surface area for 17.0000-3000.000 Å pores | m^2/g | 0.002860 |
| Single point total pore volume for < 780 Å pores | cm^3/g | 0.003471 |
| BJH adsorption cumulative pore volume for 17.0000-3000.000 Å pores | cm^3/g | 0.003884 |
| BJH desorption cumulative pore volume for 17.0000-3000.000 Å pores | cm^3/g | 128.72 |
| Average pore radius (4V/A by BET) | Å | 151.21 |
| BJH adsorption average pore diameter (4V/A) | Å | 165.31 |
| BJH desorption average pore diameter (4V/A) | Å | |

4. CONCLUSIONS

This study discusses the special use of the thermal analysis data on preadsorbed liquid vapour and porosimetry parameters for the quantitative characterization of the energetic and structural heterogeneities of high- T_c oxides surface. The thermodesorption process of liquids depends on the surface wetting phenomenon and surface properties of the solid studied. The presented method is very useful to investigate physicochemical properties of surface liquid films, adsorbate-adsorbent interaction and solid heterogeneity.

At room temperature, physical sorption and chemical reaction of H_2O on the oxide surface took place. This phenomenon strongly depends significantly on time activation (t_{act}). When t_{act} was $0 < t_{\text{act}} < 90$ min, physisorption was observed. In the case of longer water vapour action, $t_{\text{act}} > 90$ min, decomposition reaction was found.

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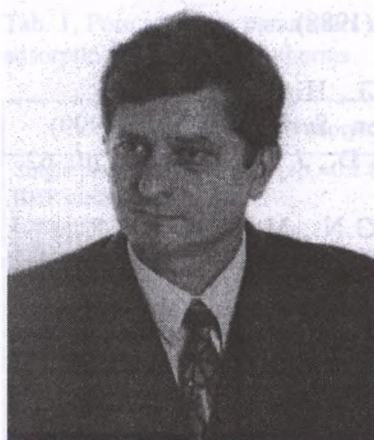
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CURRICULA VITAE

Piotr Staszczuk was born in Poland on May 17, 1949. He studied chemistry at the Maria Curie-Skłodowska University, graduated in 1972, received Ph.D. in 1980 and Sc.D. in 1987. He received the professor position at the Maria Curie-Skłodowska University in 1995 and the full professor title in 2001. In 1990-1992 he was the vice-Dean for education of the Faculty of Chemistry and in 1991-1992 he was the supervisor (protector) of the Department of Stereo- and Spectrochemistry. In 1989 he organized his research Thermal Analysis



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Main research interests: applications of thermal analysis and other methods for studies of adsorbed liquid films (especially water), liquid/solid interactions, adsorption properties and total heterogeneity of new generation and modern advanced technology materials, e.g.: adsorbents, zeolites, MCM-41 molecular sieves, high-temperature superconductors, *smart* surfaces, chemically modified new adsorbents, natural and thermally treated dolomite samples (so-called *dolomitic* sorbents), preparation of inorganic and organic magnesium compounds from domestic dolomite.

Representative publications:

1. P. Staszczuk, Guest Editor, Conference Issue (Proceedings): 27th *International Vacuum Microbalance Techniques Conference*, UMCS Lublin, Poland, 16-18 July, 1997, *J. Thermal Anal. Cal.*, vol. 55, no 2, 1999, 331-711.
2. P. Staszczuk, D. Głazewski, *Studies of heterogeneity properties of solids by means of a special thermal analysis technique*, *J. Thermal Anal. Cal.*, 55, 1999, 467-481.
3. V.I. Bogillo, P. Staszczuk, *Characterisation of the structural and energetic heterogeneity of mesoporous solid surface from Q-DTG data*, *J. Thermal Anal. Cal.*, 55, 1999, 493-510.

4. P. Staszczuk, *Study of the liquid/solid systems using thermal analysis*, American Lab., **28**(12),1996, 21-24.
5. P. Staszczuk, *Studies of the adsorbed water layers on solid surfaces by means of the thermal analysis special technique*, Thermochim. Acta, **308**, 1998, 147-157



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