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PRODUCTION OF GASEOUS MATRIX-FREE REFERENCE MATERIALS
Application of thermoanalytical techniques

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Reference materials are used in every laboratory in order to assure the appropriate quality of analytical results. The production of reference materials is not an easy task especially in the case of gaseous, toxic and malodorous compounds. Thermal decomposition of immobilized compounds is a convenient way for the generation of those kinds of mixtures. Temperature is an important variable in this process. In this case, thermoanalytical techniques (thermogravimetry and differential scanning calorimetry (TG-DSC)) and scanning electron microscopy (SEM) were used for checking the temperature range which had been previously determined using thermal desorber-gas chromatograph-flame ionization detector (TD-GC-FID) system.

Keywords: *immobilized compounds, reference materials, silica gel, thermal decomposition process*

Introduction

The impact of results of chemical analyses on the quality of life, the state of the environment and the economy is significant. Consequently, it is essential that the analytical results be reliable and could be used as intended. The reliability of instruments and applicability of the procedures used have to be validated [1, 2]. Among the tools employed to facilitate validation, the key role is played by reference materials [3].

Preparation of reference materials is very tedious and time-consuming, which results in their high price. In the analytical practice use is made of a variety of reference materials and their application depends on the objective of analytical work being done [4]. The preparation of reference materials for all analytical measurements is practically impossible due to the variety of matrices and analytes [5].

In case of analysis of gaseous environmental pollutants, standard gaseous mixtures, being an example of matrix-free reference materials, are used for calibration of analytical instruments and validation of analytical procedures. A rapid progress in environmental monitoring and analytics has resulted in increased requirements placed on gaseous standard mixtures. Their preparation poses a number of technical and methodical problems. The development of novel techniques and devices for the generation of standard mixtures has been the subject of numerous studies [6–9].

A significant progress in the area of preparation of standard gaseous mixtures containing analytes at trace and ultratrace concentration levels has been achieved by using thermal decomposition of immobilized compounds. These compounds are formed as a result of chemical modification of the surface of a solid support and upon heating they undergo decomposition or rearrangement yielding a specific analyte. This technique enables easy and convenient generation of gaseous mixtures containing toxic, labile or malodorous compounds. The support, whose surface was chemically modified, may play the role of a reference material for volatile compounds, both organic and inorganic [10].

Experimental

Materials

The available techniques of preparation of gaseous standard mixtures, which can be referred to as ‘reference materials’, have a number of disadvantages and inconveniences in the case of volatile organic compounds. The solution based on using thermal decom-

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position of immobilized compounds for the generation of standard mixtures of toxic, reactive and malodorous analytes seems to be an interesting approach to this problem. So far, this technique has been used for the preparation of standard gaseous mixtures containing the following analytes [11–14]: acetone, acetaldehyde, amines, ammonia, methyl chloride, ethene, thiols, isothiocyanates, carbon monoxide and/or dioxide.

In the preparation of standard gaseous mixtures by thermal decomposition of immobilized compounds, the generation of the analyte is accomplished by heating of a sample of support (e.g. silica gel, porous glass, glass fiber) whose surface had previously undergone chemical modification. In order to change the physical-chemical nature of the support surface, chemical modification based on the reaction of active sites (the –OH groups on the support surface) with modifiers is carried out. The moiety bound to the support surface can in turn be the reactant for a subsequent reaction. Using appropriate sequences of chemical reactions, almost any functional group can be found to the surface of a support.

The chemical compound used for the modification of the support surface undergoes a chemical reaction with the active sites on the surface of a support yielding an immobilized compound. At a suitably high temperature this compound is decomposed or rearranged yielding (preferably) one or several components. The released compounds are removed from the reaction chamber (chromatographic injector, thermal desorber, etc.) by a stream of diluent gas, generating a stream of gaseous standard mixture.

A schematic diagram of chemical modification of the support surface and generation of a specific volatile analyte in the process of thermal decomposition of the immobilized compound is shown in Fig. 1. Thus far, silica gel, porous glass, glass rods coated with silica gel and glass fibers have been as support for immobilized compounds [11, 13–16].

Decomposition of an immobilized compound takes place in a specific temperature range, which is limited by the minimum and maximum temperature.

The minimum temperature is a temperature at which the decomposition or rearrangement of an immobilized compound is initiated. This is accompanied by the liberation of a volatile component, which appears in a stream of eluent gas. The minimum temperature is required to be substantially higher than the ambient temperature. This requirement ensures stability and the possibility of long-term storage of the prepared standard (as samples of modified support) without any losses of the analyte. This is especially important in the case of preparing standards of toxic or malodorous compounds. The high temperature maintained during generation of a standard gaseous mixture prevents adsorption of analytes on the walls of a thermal desorber chamber.

The maximum temperature of decomposition of an immobilized compound is a temperature which, when exceeded, results in uncontrolled degradation of the immobilized compound. The following processes are then observed:

- sudden drop in the amount of analyte released
- appearance in the standard of compounds other than the analyte
- change in color of the modified support, e.g. to brown

The objective of the present investigation was to determine the optimum temperature of decomposition of immobilized compounds, i.e. the temperature at which the largest and most reproducible amount of the analyte is released per unit mass/length of the support.

Methods

Thermal analysis is a group of techniques in which a property of the sample is monitored *vs.* time or temperature while the temperature of the sample, in specific atmosphere, is programmed. The program may involve

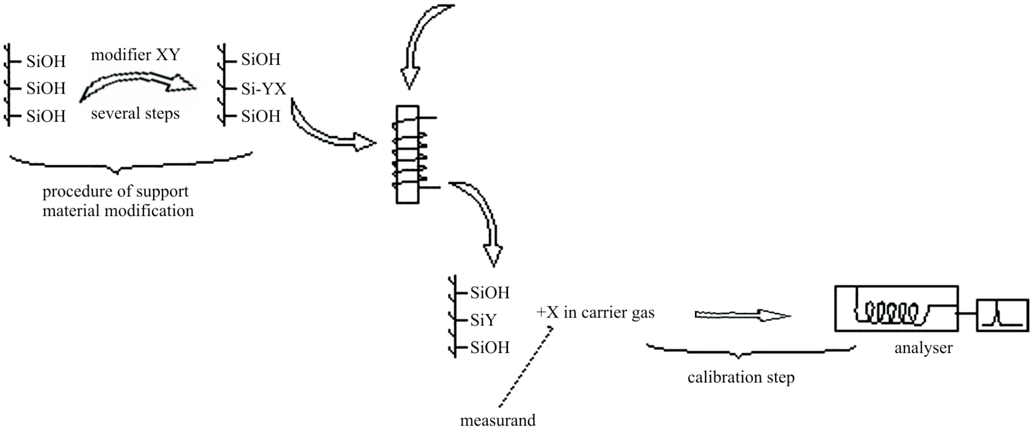

Fig. 1 Preparation of a standard gaseous mixture using thermal decomposition of the immobilized compound formed on the surface of a support

Table 1 Conditions of thermal analyses using TG and DSC

	Thermal analysis	
	TG	DSC
Instrument	OD-103 Derivatograph MOM, Hungary	DSC 120 Seiko Instrument Inc.
Heating	25 to 800°C with a heating rate of 5°C min^{-1} under air atmosphere	80 to over 330°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere
Sample mass	100 mg	15 mg
Reference material	α-aluminum oxide	indium
Container	platinum	silver

heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these. Thermogravimetric analysis was used to check the ranges of decomposition temperatures of specific immobilized compounds because this technique allows the following investigations [17–21]:

- kinetics of decomposition of chemical compounds
- structural changes in solids
- phase transitions (transition temperature, heat effects)
- mechanisms of reactions between solids

DSC is a measurement of the change of the difference in the heat flow rate (dq/dt) to the sample and to the reference sample while they are subjected to a temperature regime. DSC instrument is designed to measure the actual amount of power (rate of heat flow) involved directly with the associated thermal event. The power is then integrated over the time of the thermal event to determine the associated thermal energy. DSC is one of the fundamental methods allowing observation of phase transitions [22–25]. The measurements using DSC are also used for:

- determination of some chemical properties of both low molecular and macromolecular compounds
- determination of melting point, glass transition point and flow temperature
- investigation of crystallization kinetics
- determination of specific heat and degree of crystallinity
- examination of purity of compounds

The conditions used in thermal analyses are listed in Table 1.

Scanning electron microscope (SEM) is now an indispensable instrument in a wide variety of applied fields [26]. Scanning a specimen surface with finely focused electron beam (several nanometers), information (signal) will be emitted from each point of the scanning. The emitted information is converted into an electric signal, amplified and then fed into an observation CRT. SEM combined with energy dispersive X-ray spectrometer (EDS) is used primarily for structural studies of surfaces of specimens. This allows the determination of chemical composition of a sample with the simultaneous visual inspection of its surface. In case of determination of the surface structure of chemically modified silica gel, the analysis of gel samples was carried out at different temperatures (ambient, optimum and maximum). Prior to the analysis, samples of chemically modified silica gel were coated with gold to give the specimen electrical conductivity. This decreases the specimen's capacity to acquire an electrostatic charge and increases the yield of secondary electrons.

Table 2 Characteristics of SEM

Instrument	JSM-5800LV (Jeol Ltd.)
Resolution	3.5 mm
Sample size	max. 8 inch
Imaging memory	1280×960 elements
Option	low vacuum observation

Table 3 Characteristics of EDS

Instrument	JED-2100 (Jeol Ltd.)
Area to be analyzed	max. 10×10 mm
Energy resolution	144 eV (^{55}Fe, 1000 cps)
Elements to be analyzed	B~U
X-ray take off angle	52.5°
Option	color mapping

The characteristics of SEM and EDS instruments are listed in Tables 2 and 3.

Results and discussion

The range of decomposition temperatures of an immobilized compound formed on the surface of silica gel is determined from the results of investigations of the amount of released analyte at different decomposition temperatures for successive samples of modified silica gel. The investigations begin at ambient temperature, followed by an increase every 10 or 20°C up to 200 or 330°C and checking whether degradation of the examined sample took place [13]. The amounts of released analyte are converted to the per unit mass basis, which is necessary as a result of using different masses of silica gel samples.

The dependence of the amount of analyte released per unit mass of chemically modified silica gel on the

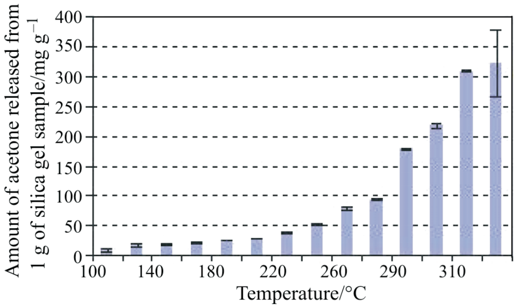

Fig. 2 Dependence of the amount of acetone liberated per gram of silica gel on the temperature of thermal decomposition of the immobilized compound

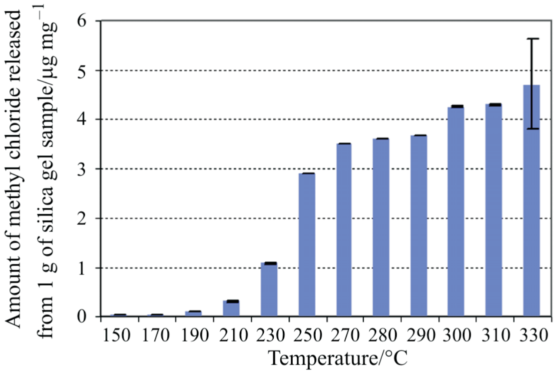

Fig. 3 Dependence of the amount of methyl chloride liberated per gram of silica gel on the temperature of thermal decomposition of the immobilized compound

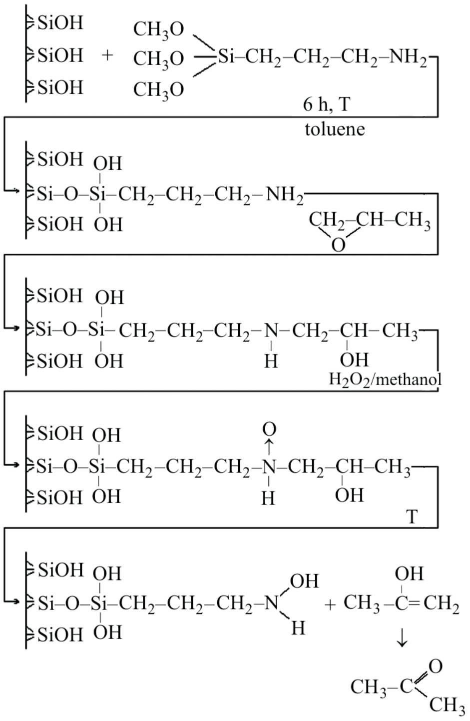

Fig. 4 Synthesis of an immobilized compound on the surface of silica gel and its thermal decomposition yielding acetone

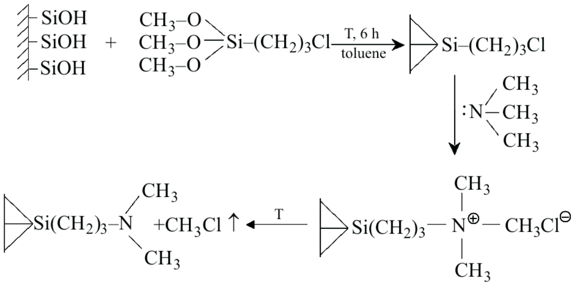

Fig. 5 Synthesis of an immobilized compound on the surface of silica gel and its thermal decomposition yielding methyl chloride

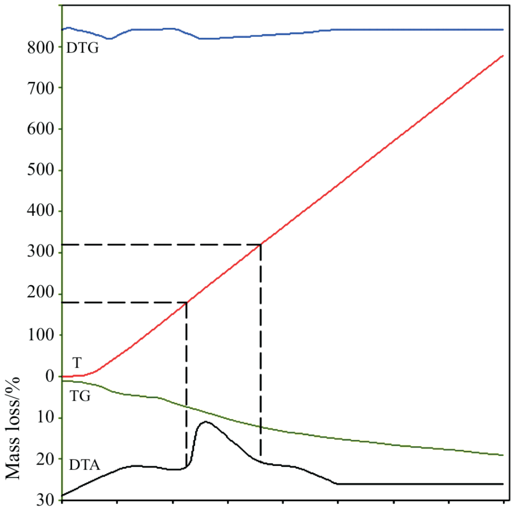

Fig. 6 Thermogravimetric curve obtained during the heating of chemically modified silica gel sample (acetone as the analyte)

temperature of thermal decomposition at constant flow rates of the diluent gas and time of the process are shown in Figs 2 and 3. On the basis of the obtained results, the temperature ranges over which thermal decomposition of the immobilized compounds yielding acetone and methyl chloride took place were found to be 100–320 and 150–330°C, respectively. The optimum temperatures of decomposition of the immobilized compounds used for the generation of gaseous mixtures containing acetone and methyl chloride as the analytes were 310 and 280°C, respectively.

Thermogravimetric and calorimetric curves obtained for samples of silica gel chemically modified via the reactions shown in Figs 4 and 5 are depicted in Figs 6–9.

Inspection of the above curves reveals that the ranges of decomposition temperature of the immobilized compounds are close to the values determined by thermal decomposition of these compounds obtained by using TD-GC-FID. The nature of the obtained peaks demonstrates that in these temperature ranges exothermic reactions (e.g. release of the

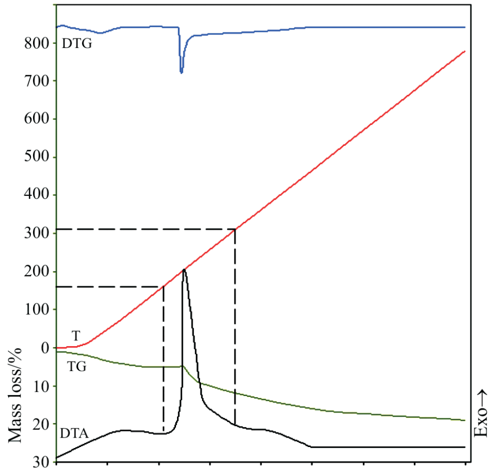

Fig. 7 Thermogravimetric curve obtained during the heating of chemically modified silica gel sample (methyl chloride as the analyte)

analytes) take place. Shifts of the temperature ranges observed in thermogravimetric techniques can be explained by the fact that the differences in the amounts of analytes released at lower temperatures are too small to be detected by the detectors used.

The results of determination of selected components for two samples of chemically modified silica gel yielding acetone and methyl chloride using SEM are compiled in Table 4. A plot of the content of selected elements in the examined silica gel sample is shown in Fig. 10.

An inspection of the data in Table 4 reveals a decrease in the content of the selected elements in samples of chemically modified silica gel with an increase in temperature. This is additional evidence that at a specific temperature specific analytes are liberated as a result of decomposition of the immobilized compound.

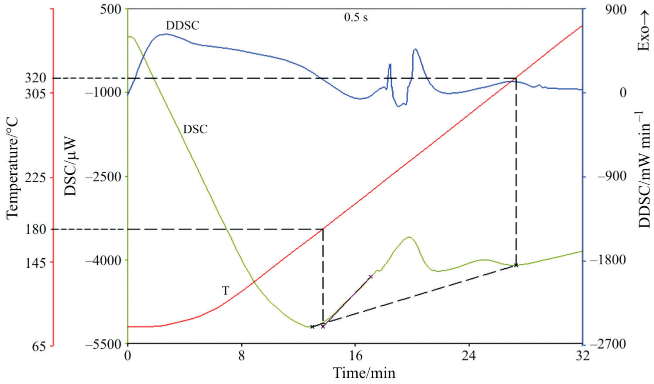

Fig. 8 Calorimetric curve obtained during the heating of chemically modified silica gel sample (acetone as the analyte)

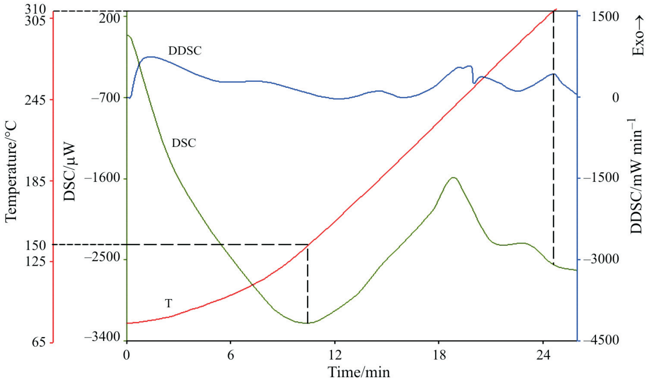

Fig. 9 Calorimetric curve obtained during the heating of chemically modified silica gel sample (methyl chloride as the analyte)

Table 4 The results of determination of selected elements in samples of chemically modified silica gel yielding specific analytes

Element	Analyte/%					
	acetone			methyl chloride		
	25°C	310°C	350°C	25°C	280°C	320°C
C	1.14	1.06	0.98	2.34	1.31	0.95
O	0.87	0.76	0.73	–	–	–
Cl	–	–	–	0.20	0.09	0.01

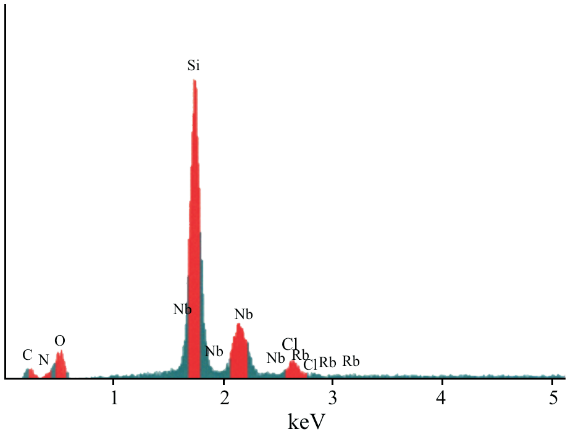

Fig. 10 The plot of content of selected elements present in a sample of chemically modified silica gel yielding methyl chloride

Conclusions

Temperature is an important parameter in thermal decomposition of immobilized compounds used for the preparation of reference materials of volatile analytes. Heating a chemically modified support to a suitably high temperature yields reliable and reproducible results. Proper adjustment of temperature makes a convenient way of preparation of matrix-free reference materials containing analytes at a desired concentration level. It should be remembered that an incorrectly determined temperature range of decomposition of immobilized compounds characteristic of each analyte can lead to incorrect results and thus to negative health, economic and social effects. Consequently, other techniques capable of determination of the range of decomposition temperatures of a specific immobilized compound are also used. A vital role in this area is played by thermogravimetric analysis, and particularly by differential thermal analysis and differential scanning calorimetry. The measurements carried out by these two techniques provide information on the nature of chemical reactions taking place (endothermic or exothermic) and the temperature range over which these reactions occur. The present study also made use of scanning electron microscopy which enabled the investigation of the surface structure of chemically modified silica gel heated to different temperatures.

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References

1 J. Namieśnik and T. Górecki, Rev. Roum. Chim., 46 (2001) 953.
2 A. Świtaj-Zawadka, P. Konieczka, E. Przyk and J. Namieśnik, Anal. Lett., 38 (2005) 29.
3 S. D. Rasberry and J. Fresenius, Anal. Chem., 360 (1998) 277.
4 B. Jerzak, Analityka, 4 (2003) 40.
5 B. Zygmunt, E. Kremer, M. Rompa, P. Konieczka and J. Namieśnik, Chem. Inż. Ekol., 10 (2003) 655.
6 D. Fenyö, W. Zhang, B. T. Chait and R. C. Beavis, Anal. Chem., 68 (1996) 721A.
7 J. Namieśnik, Crit. Rev. Anal. Chem., 30 (2000) 221.
8 I. R. Pereiro, A. Wasik and R. Łobiński, Fresenius J. Anal. Chem., 363 (1999) 460.
9 R. Łobiński, V. Sidelnikov, Y. Patrusher, I. R. Pereiro and A. Wasik, Trends Anal. Chem., 18 (1999) 449.
10 A. Świtaj-Zawadka, P. Konieczka, J. F. Biernat, J. Wójcik and J. Namieśnik, Anal. Chem., 77 (2005) 3018.
11 A. Świtaj, E. Przyk, J. Szczygelska-Tao, J. Wójcik, J. F. Biernat and J. Namieśnik, J. Sep. Sci., 26 (2003) 1057.
12 E. Przyk, A. Świtaj-Zawadka, P. Konieczka, J. Szczygelska-Tao, J. F. Biernat and J. Namieśnik, Anal. Chim. Acta, 488 (2003) 89.
13 A. Świtaj-Zawadka, P. Konieczka, J. Szczygelska-Tao, J. F. Biernat and J. Namieśnik, J. Chromatogr. A, 1033 (2004) 145.
14 M. Prokopowicz, A. Przyjazny, J. F. Biernat and J. Namieśnik, Microchem. J., 59 (1998) 437.
15 M. Prokopowicz, K. Lewandowska, E. Luboch, J. Namieśnik, A. Przyjazny and J. F. Biernat, JHRC, 21 (1998) 303.
16 E. Przyk, A. Świtaj-Zawadka, J. Szczygielska-Tao, A. Przyjazny, J. F. Biernat and J. Namieśnik, Crit. Rev. Anal. Chem., 33 (2003) 249.
17 M. Kamruddin, P. K. Ajikumar, S. Dash, A. K. Tyagi and B. Raj, Bull. Mater. Sci., 4 (2003) 449.
18 M. Lalia-Kantouri and Ch. Papadopoulos, J. Therm. Anal. Cal., 81 (2005) 375.
19 D. Minic, N. Strbac, I. Mihajlovic and Z. Zivkovic, J. Therm. Anal. Cal., 82 (2005) 383.
20 V. A. Drebushchak, L. N. Mylnikova, T. N. Drebushchak and V. V. Boldyrev, J. Therm. Anal. Cal., 82 (2005) 617.
21 J. Dweck and C. M. S. Sampaio, J. Therm. Anal. Cal., 75 (2004) 385.
22 I. M. Vitéz, J. Therm. Anal. Cal., 78 (2004) 33.
23 S. S. Das and P. Singh, J. Therm. Anal. Cal., 78 (2004) 731.
24 J. Pak, W. Qiu, M. Pyda, E. Nowak-Pyda and B. Wunderlich, J. Therm. Anal. Cal., 82 (2005) 565.
25 D. Ishii, T. Yamado, M. Nakagawa, T. Iyoda and H. Yoshida, J. Therm. Anal. Cal., 81 (2005) 569.
26 G. Della Gatta, E. Badea, R. Ceccarelli, T. Usacheva, A. Masi and S. Coluccia, J. Therm. Anal. Cal., 82 (2005) 637.

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