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USING THE TGA-DSC-IR-GCMS COMBINED SYSTEM AND TL-9000 TRANSFER LINE FOR THE ANALYSIS OF ORGANIC OBJECTS

The use of combined system of thermal gravimetric analysis, differential scanning calorimetry, IR-Fourier spectroscopy, gas chromatography, and mass spectrometry allows the researchers both to identify and to separate various components of organic objects. The installation makes it possible to carry out comprehensive complementary express analysis of objects at the temperature up to 1000 °C.

Key words: express analysis, thermal gravimetric analysis, differential scanning calorimetry, gas chromatography, and mass spectrometry.

For the analysis of samples of various organic compounds, polymers, composites, alloys, etc., there are frequently used the methods of thermal analysis, such as the thermal gravimetric analysis (TGA), the differential scanning calorimetry (DSC), and the differential thermal analysis (DTA).

For the rapid analysis it is convenient to use the simultaneous thermal analysis when TGA, DSC, and DTA are combined in one instrument TGA/DSC (Fig. 1). At the same time, the TGA allows the users to determine the change in sample mass under the influence of temperature, the sample temperature stability, and the number of stages of decomposition, as well as to conduct thermo-kinetic analysis and to determine the corrosion resistance. The DSC gives an opportunity to determine the temperature and heat of phase transition, crystallinity, presence or absence of contaminants, and glass transition temperature. The advantage of synchronous thermal analysis is the identical test conditions for the thermal gravimetric and the calorimetric measurements.

Fig. 2 shows the results of thermal analysis of granular polystyrene. The sample was heated in thermo-analyzer STA6000 (*Perkin Elmer*) at a heating rate of 20 °C/min, in nitrogen environment. The TG curve shows that polystyrene is thermally stable up to 350 °C. As the temperature increases further, an intense weight loss is observed. The material is completely decomposed at 470 °C, with the weight loss being accompanied with an endothermic peak on the DSC curve.

However, the TGA/DSC does not give any information about the molecular structure of material. The combination of these two or more instruments gives complementary information about the material, which cannot be provided if only one method is used. The molecular structure information can be obtained, for example, using the infrared (IR) spectroscopy or the Raman spectroscopy (RS) method because both them are sensitive to the molecules functional groups.

The combination of TGA/DSC with IR spectrometer (TGA/DSC-IR) is the most widely used method for the analysis of gases released during the material decomposition, since being heated in

TGA/DSC the sample begins to decompose, which, at a certain temperature, is accompanied with the releasing gases (volatile decomposition products). If the decomposition products are analyzed in the gas cell of infrared spectrometer they can be identified through the analysis of vibrational spectra.

The TGA/DSC-IR method is informative for the identification of released gases and decomposition products when the sample is heated (e.g. for identification of residual solvents in pharmaceuticals, the components of polymers, plastics, and rubber products, as well as for the analysis of decomposition products during pyrolysis).

Fig. 3 shows an IR spectrum of polystyrene decomposition products fixed at a temperature of 370 °C. This spectrum was recorded with the help of *Frontier* FTIR spectrometer (*Perkin Elmer*) using a gas cell and a TL-9000 transfer line allowing for the transport of gaseous products from the thermo-analyzer to the IR spectrometer.

The search in the IR spectra library has showed that the experimental spectrum corresponds to polystyrene with convergence of 0.911.

Hence, the IR spectroscopy allows the researchers to reliably identify the major components of materials of unknown composition.

Another good method for obtaining the information on the chemical structure of organic matter is mass spectrometry. The combination of TGA/DSC with mass spectrometer (MS) becomes increasingly popular due to its ability to detect very low content of impurities (as opposed to the IR spectroscopy).

Both the TG/DSC-IR and TG/DSC-MS methods allow for conducting the real-time (i.e. during the record of TG curve) analysis, but in this case, these methods have disadvantages. Since both methods are real-time they detect the substances extracted from the sample at a certain time and temperature. In the most cases, the mixture of components rather than the single one releases during the thermal decomposition of material. This can complicate the identification because of overlapping peaks of ions having the same mass or because of aliasing IR spectra of components. In this case, there can be some problems related to detecting the low concentration compounds in mixture.

The optimal solution of this problem is to use the gas chromatography (GC) technique which allows the researchers to separate the mixture of gaseous products. This means that after TGA/

Fig. 1. General view of installation

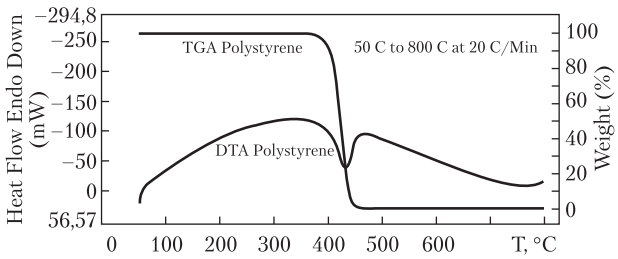

Fig. 2. Polystyrene thermal analysis results: curve 1: thermal gravimetric analysis (TGA); curve 2: differential scanning calorimetry (DSC)

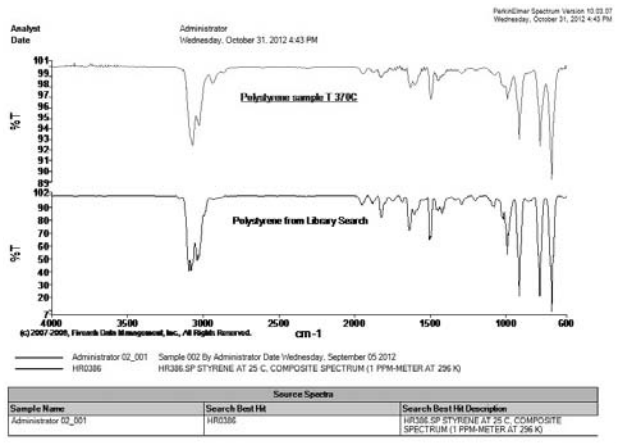

Fig. 3. Results of FTIR spectroscopy. The spectrum of polystyrene pyrolysis products fixed at a temperature of 370 °C: curve 1: the experimental spectrum; curve 2: library spectrum; convergence is 0.911

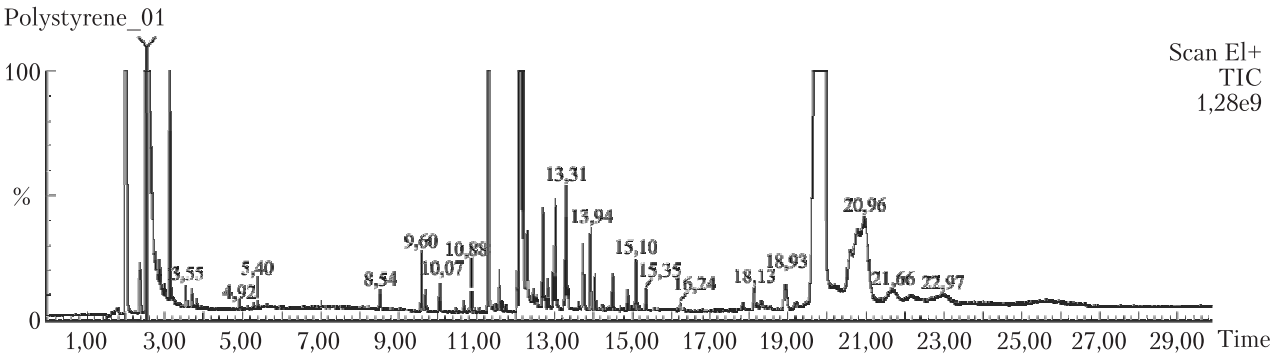

Fig. 4. Complete chromatogram of polystyrene pyrolysis products fixed at a temperature of 370 °C

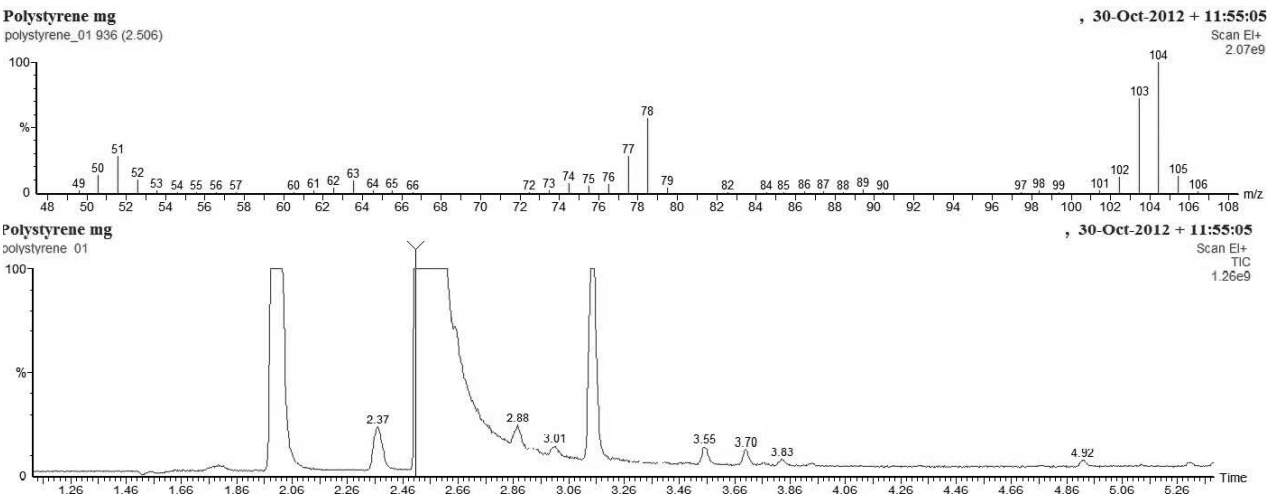

Fig. 5. a) Chromatogram of pyrolysis products for the retention time from 1.26 to 5.26 min; b) mass spectrum corresponding to chromatogram peak at 2.506 min

Fig. 6. Comparison of the experimental spectrum (t = 2.506 s) with the literature data

DSC or TGA/DSC-IR the gaseous decomposition products fall into the mass spectrometer through gas chromatograph, not directly. Such combined use of TGA/DSC (IR) and GCMS makes it possible to identify the trace amounts of material in complex mixture.

Fig. 4 features a chromatogram of polystyrene pyrolysis at a temperature of 370 °C obtained using a *Clarus* 580 (*PerkinElmer*) chromatograph with SQ8S (*PerkinElmer*) mass spectroscopic detector. The figure shows that, on the chromatogram, there are many peaks corresponding to different fragments and different lengths of polystyrene polymer chains. Obviously, the minimum retention time corresponds to the most lightweight components. In our case the most lightweight fragments of polystyrene are desorbed at the beginning of heating process. Fig. 5 (a) shows the chromatogram for retention times from 1.26 to 5.26 minutes. For a retention time of 2.506 minutes the mass spectrum has an intense peak (Fig. 5b). In this mass spectrum the largest peak corresponds to the molecular ion with a mass of 104 amu.

The results of search in the NIST mass spectra base show that this peak corresponds to styrene (S_8H_8) with convergence of 0.951 (Fig. 6).

The analysis of other peaks in the chromatogram shows that the polystyrene test sample does not contain any fillers or impurities, with the rest of peaks corresponding to the polystyrene fragments of different length.

The combined use of different methods of analysis (TGA/DSC (IR), TGA/DSC (IR) GCMS) provides an opportunity to identify and to separate the different components of material. It allows the users to analyze the materials with complex chemical composition and unknown history of their preparation and use. Also, the combinations of several methods give complementary information about materials in a relatively short time.

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ОСОБЛИВОСТІ ВЖИВАННЯ ПОЄДНАНОЇ СИСТЕМИ ТГА-ДСК-ІК-ГХМС ТА ТРАНСФЕРНОЇ ЛІНІЇ Tl-9000 ДЛЯ АНАЛІЗУ ОРГАНІЧНИХ ОБ'ЄКТІВ

Використання поєднаної системи термогравіметричного аналізу, диференціальної скануючої калориметрії, ІК-Фур'є-спектроскопії, газової хроматографії і мас-спектрометрії дає можливість здійснювати як ідентифікацію, так і розділення різних компонент органічних об'єктів. Установка дозволяє здійснювати комплексний взаємодоповнюючий експрес-аналіз об'єктів при температурах до 1000 °С.

Ключові слова: експрес-аналіз, термогравіметричний аналіз, диференціальна скануюча калориметрія, спектроскопія, газова хроматографія, мас-спектрометрія.

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ОСОБЕННОСТИ ПРИМЕНЕНИЯ СОВМЕЩЕННОЙ СИСТЕМЫ ТГА-ДСК-ИК-ГХМС И ТРАНСФЕРНОЙ ЛИНИИ TL-9000 ДЛЯ АНАЛИЗА ОРГАНИЧЕСКИХ ОБЪЕКТОВ

Использование совмещенной системы термогравиметрического анализа, дифференциальной сканирующей калориметрии, ИК-Фурье-спектроскопии, газовой хроматографии и масс-спектрометрии дает возможность осуществлять как идентификацию, так и разделение различных компонент органических объектов. Установка позволяет осуществлять комплексный взаимодополняющий экспресс-анализ объектов при температурах до 1000 °С.

Ключевые слова: экспресс-анализ, термогравиметрический анализ, дифференциальная сканирующая калориметрия, спектроскопия, газовая хроматография, масс-спектрометрия.

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