

---

## LOW-TEMPERATURE GAS ANALYZER FOR SMALL AMOUNTS OF GASES SORBED BY NANOSTRUCTURED AND DISPERSE MATERIALS

A.M. ALEKSANDROVSKII, M.A. VINNIKOV, V.G. GAVRILKO,  
O.V. DOLBIN, V.B. ESEL'SON, V.P. MALETSKII

UDC 536.71  
©2006

B.I. Verkin Institute for Low Temperatures Physics and Engineering,  
Nat. Acad. Sci. of Ukraine  
(47, Lenin Prosp., Kharkiv 61103, Ukraine; e-mail: dolbin@ilt.kharkov.ua)

---

A physical technique for determining the qualitative and quantitative composition of small amounts of gas mixtures is proposed. Based on this technique, the composition of the gas mixture desorbed from a sample of polycrystalline compacted fullerite C<sub>60</sub> heated to 450 °C was analyzed. Recommendations concerning the heating temperature of polycrystalline fullerite C<sub>60</sub> optimal for the maximal elimination of gas admixtures are expressed.

In recent years, the appearance of a new class of substances (nanostructured materials) with internal structure, whose characteristic dimensions amount to unities—tens of nanometers, has opened up the perspectives of development of many new technologies. Rather unusual physical properties of such materials are intensively investigated. It is known that the presence of gas admixtures can essentially influence the properties of such materials [1–3]. That's why, carrying out investigations of various kinds as well as determining the requirements for storage and exploitation of nanostructured materials, it is necessary to know the composition and the amount of gas admixtures sorbed by them. However, due to the complexity and a high cost of production techniques, the real amounts of nanostructured materials, investigators deal with, are often estimated as tenths of gram. Correspondingly, the amount of gases sorbed in such substances is also small. In our experiments, the volume of the investigated samples of fullerite approximated one cubic centimeter. In this case, the rate of inflow of gas into the deaerated volume of the gas analyzer (170 cm<sup>3</sup>) averaged 0.01 Torr per hour. That's why, the determination of the

qualitative and quantitative composition of the gas mixture represents a serious problem.

The principle of operation of the proposed desorption vacuum gas analyzer is the following. Gas admixtures desorbed from a sample condense on a surface cooled with liquid helium. After the completion of the condensation process, the fractions of the gas mixture were successively evaporated by means of the controlled heating of the condensate. Under such evaporation, the temperature dependence of pressure gives information about the composition of the gas mixture, as the saturation vapor pressure that corresponds to a certain value of temperature is different for each of the components. In the process of evaporation, the vapor pressure of each component didn't exceed several tenths of Torr. That's why the vaporization temperature was very low. For example, it amounted to 35 K for nitrogen.

A rather high sensitivity of the given method is conditioned by the fact that, in the low-temperature region, a rise in temperature results in the rapid increase of the saturation vapor pressure of solidified gases. For example, as solidified hydrogen is heated from 5.38 to 8 K, its saturation vapor pressure increases by a factor of 10 000 and so does the vapor pressure of solidified nitrogen heated from 31.4 to 41.7 K. The analysis technique described above gave a possibility not only to determine the qualitative composition of gases desorbed from the fullerite sample but also to establish their specific quantity in the total mass of a desorbent.

The scheme of a gas analyzer is depicted in Fig. 1. Gas desorbed from a sample located in the volume  $V_1$

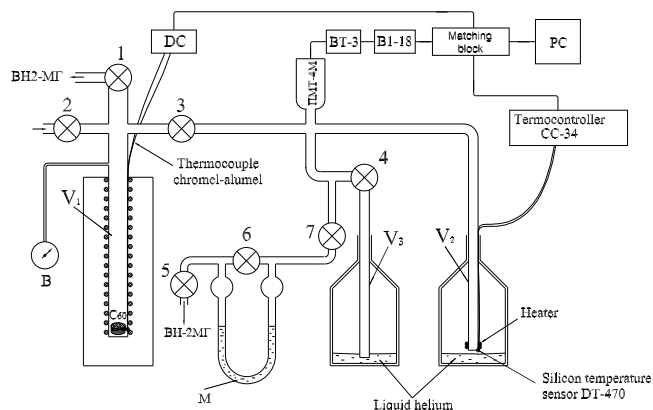


Fig. 1. Diagram of a gas analyzer.  $C_{60}$  — fullerite sample of  $1 \text{ cm}^3$  in volume;  $V_1$  — the volume with a sample located inside the furnace;  $V_2, V_3$  — small volumes (capillars); VT-3 — thermocouple vacuum-gauge;  $B$  — sample vacuum-gauge; PMT-4M — thermocouple transducer; DC — analog-to-digital converter; V1-18 — digital voltmeter; CC34 — temperature controller Crio-Con model 34; VN2-MG — forepump; 1–7 — valves;  $M$  — differential oil circulation gage; PC — computer

was condensed in a small volume  $V_2$  on the surface cooled up to the liquid helium temperature. After the completion of the condensation procedure, the volume  $V_1$  was disconnected from the measuring system and the temperature of the volume  $V_2$  was slowly increased. As the components of the gas mixture were evaporated at various temperatures, the slow heating gave a possibility to evaporate them in turn. Naturally, one can separate in such a way only those components, whose evaporation temperatures at the same pressure differ by more than several degrees (for example, it is practically impossible to separate nitrogen, oxygen, and carbon oxide). The accuracy of separation depends on the rate of increase of the temperature of the volume  $V_2$ . After the evaporation of a certain component, it was condensed into the volume  $V_3$ . During recondensation, the pressure in the system of the volumes  $V_2$ – $V_3$  amounted to  $10^{-4}$  –  $10^{-1}$  Torr. The process of temporal variation of the pressure was registered with the help of a PMT-4M thermocouple transducer. As a result, the gas mixture evaporated from the volume  $V_2$  was decomposed into components, each of which was registered in the form of a peak on the temperature dependence of the pressure in the system (see Fig. 2). The qualitative composition of the gas mixture was determined by the location of a pressure peak of either component on the temperature scale [4]. The quantitative composition of the gas mixture was determined in the following way. The gas mixture was

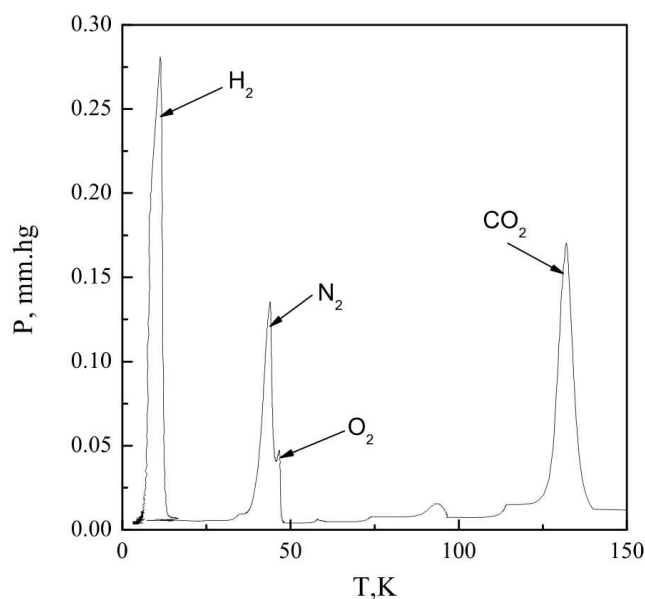


Fig. 2. Temperature dependence of the pressure variation in the volume of a gas analyzer under recondensation of the gas mixture

recondensed from the volume  $V_3$  into the volume  $V_2$  cooled up to the liquid helium temperature. After that, the volume  $V_3$  was disconnected and the volume  $V_2$  was attached to a differential oil (dibutyl phthalate) circulation gage. The volume  $V_2$  was slowly heated, so that the components of a gas mixture were successively evaporated. After the completion of the evaporation of each component, we measured the change of the pressure in the system consisting of a differential manometer and the volume  $V_2$ . Based on the change of pressure in the system and its volume, the amount of gas for each component of the gas mixture was calculated. Under the rather slow evaporation, the amount of a certain component of the gas mixture is proportional to the area of the corresponding peak on the curve of the temporal pressure dependence  $P(t)$ . Thus, after determining the proportionality coefficient for each component, one can approximately estimate the amount of gas by evaluating the areas of the peaks on the  $P(t)$  dependence under the condition that the heating regime of the volume  $V_2$  remains invariable during the measurements.

The inaccuracy of the determination of the quantitative composition of a gas mixture using the given technique approximates 6%. An essential part of the inaccuracy is conditioned by the temperature gradient along the volume  $V_2$ . In order to decrease the value of this error, the volumes  $V_2$  and  $V_3$  were prepared in the form of capillars of 1 mm in diameter. The

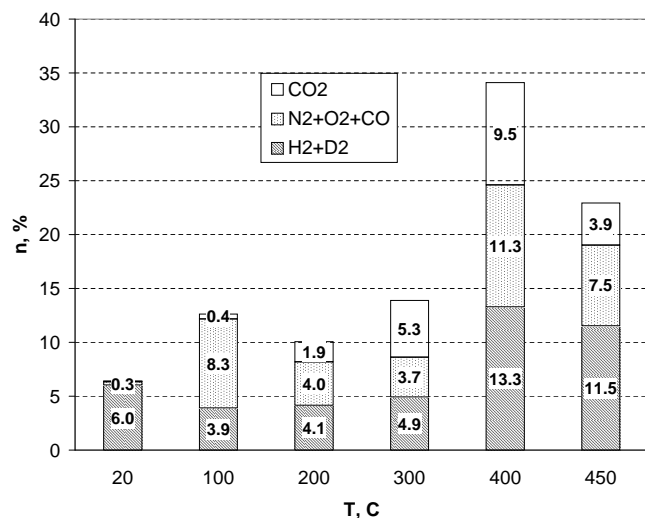


Fig. 3. Composition of the gas mixture (in volume percents) desorbed from the sample of C<sub>60</sub> fullerite heated to 450 °C

proposed technique was tested with the help of a gas mixture of the known composition.

The described technique was used for the qualitative and quantitative analyses of the composition of the gas mixture desorbed from a sample of polycrystalline compacted fullerite C<sub>60</sub>.

As is known, the crystal lattice of fullerite has intersite cavities. Moreover, each C<sub>60</sub> molecule accounts for one cavity of octahedral form and two cavities of tetrahedral one. The size of octahedral cavities (4.14 Å [5]) is sufficient for the penetration of the molecules of gas admixtures into them. The sample of C<sub>60</sub> fullerite was compacted at the Umea University (Sweden) of a fullerite powder of high purity (99.99% by weight) produced by the Term company, USA, Berkeley. The initial sample weighed 1.22 g. In the process of preparation and storage, fullerite was in various gas media under various conditions. Before carrying out the experiment, the sample was placed for several days to hydrogen medium at room temperature and atmospheric pressure. In order to determine the amount and the composition of gas admixtures sorbed by the sample in the process of preparation, storage, and transport, the following experiment was fulfilled. After the sample was placed into the volume V<sub>1</sub>, the latter was evacuated up to a residual pressure of 10<sup>-2</sup> Torr reached in 1 min.

#### Molar and mass concentrations of the gas admixtures desorbed from a sample of C<sub>60</sub> fullerite

Gas admixture	$n_{mol}$	$n_m \times 10^{-3}$
H <sub>2</sub>	0.12	0.51
N <sub>2</sub> +O <sub>2</sub> +CO	0.1	4.0
CO <sub>2</sub>	0.06	3.6

After that, the volume was disconnected from the forepump and attached to the measuring system (see Fig. 1). The desorption of gases from the sample first took place at room temperature of the volume V<sub>1</sub>. Then its temperature was increased stepwise up to 450 °C. In this case, the gases desorbed from the sample were analyzed at each step. The heating temperature was limited to 450 °C, because higher temperatures induce the process of sublimation of fullerite [6]. Figure 3 shows the diagram composed on the basis of the experimental determination of the qualitative and quantitative compositions of the desorbed gases. The total volume of the desorbed gas mixture recalculated for normal conditions amounted to 4.86 cm<sup>3</sup>. The concentration of molecules of the gas admixture per one fullerite molecule  $n_{mol}$  as well as the ratio of the mass of the desorbed gas admixtures to that of the sample  $n_m$  are given in the Table.

As one can see from the diagram (Fig. 3), the sample released not only hydrogen and gases, which represented the basic part of air (nitrogen, oxygen) and could be sorbed by the sample in the process of its storage and transport, but also carbonic acid CO<sub>2</sub>, whose amount appeared to be much higher than its content in air. The presence of a large amount of CO<sub>2</sub> can be explained by the decomposition of carboxylic groups [7] formed in C<sub>60</sub> under the influence of temperature, as it was in air. The diagram also demonstrates that the maximum total amount of gas admixtures released from the sample at a temperature of 400 °C. This temperature can be recommended as the optimal one for the heating of fullerite aimed at the elimination of gas admixtures sorbed in it. For the elimination of gas admixtures from some other nanostructured materials, they can be heated to higher temperatures. For example, in order to degas and to increase the sorption ability of nanotubes, it is appropriate to heat them in vacuum to 1073 K [8].

The authors express their thanks to Academician of NASU V.G. Manzhelii for the fruitful discussion.

The work is performed with support of the Scientific and Technology Center in Ukraine (STCU), project contract Uzb-116(j).

1. A.N. Aleksandrovskii, A.S. Bakai, A.V. Dolbin et al., *Fiz. Nizk. Temp.* **29**, 324–332 (2003).
2. A.N. Aleksandrovskii, A.S. Bakai, D. Cassidy et al., *Ibid.* **31**, 565 (2005).

3. P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, *Science*, **287**, 1801 (2000).
4. R. Honing, H. Hook, *RCA Rev.* 360–368 (1960).
5. M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
6. M. Haluska, H. Kuzmany, M. Vybornov et al., *Appl. Phys. A.* **56**, 161 (1993).
7. A. Kuznetsova, D.B. Mawhinney, V. Naumenko et al., *J. Chem. Phys. Lett.* **321**, 292 (2000).
8. A. Kuznetsova, J.T. Yates, Jr., J. Liu, R.E. Smalley, *J. Chem. Phys.* **112**, 9590 (2000).

Received 30.01.06.

Translated from Ukrainian by H.G. Kalyuzhna

НИЗЬКОТЕМПЕРАТУРНИЙ ГАЗОАНАЛІЗАТОР  
ДЛЯ МАЛИХ КІЛЬКОСТЕЙ ГАЗІВ, СОРБОВАНИХ  
НАНОСТРУКТУРНИМИ ТА ДИСПЕРСНИМИ  
МАТЕРІАЛАМИ

А.М. Александровський, М.А. Вінніков, В.Г. Гаврилко,  
О.В. Долбин, В.Б. Єсельсон, В.П. Малецький

Р е з ю м е

Запропоновано фізичну методику визначення якісного та кількісного складу малих кількостей сумішей газів. За допомогою цієї методики було зроблено аналіз складу газової суміші, яка була десорбована зі зразка полікристалічного компактованого фулериту  $C_{60}$  при нагріванні зразка до  $450\text{ }^\circ\text{C}$ . Висловлено рекомендації щодо оптимальної температури нагрівання полікристалічного фулериту  $C_{60}$  для максимального видалення газових домішок.