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EFFECT OF WEAR OF THE ATOMIC-ABSORPTION SPECTROMETER GRAPHITE FURNACE ON THE ANALYTICAL ZONE TEMPERATURE

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One mechanism of increase in the heating temperature of the analytical zone of the graphite tube furnace of the atomic-absorption spectrometer as a result of wear is discussed. The influence of the furnace profile on its heating temperature is shown, and the calculated heating temperature of the standard tube is compared to the temperature in the special case where the cross-section area of the analytical zone of the furnace is reduced by half. Experimental proofs of a given temperature excess, as well as of a relation between the change in the tube profile and the decrease in its mass, are given. The dependence of temperature on the furnace mass and the number of measurements has been investigated. The necessity of taking into account the increase in the heating temperature of the furnace in the wear process has been considered.

As experience in working on atomic-absorption spectrometers (AAS) with an electrothermal atomizer (ETA) has shown, in the course of wear (so-called "aging") the mass of the graphite furnace (tube) decreases [1–7]. The authors drew attention to the fact that the geometric parameters of the tube [1] change, and the wall is heated to a somewhat higher temperature than the given one [2, 3].

In most AASs, the furnace is heated by an electric current passed through the material. The value of the power supplied varies depending on the voltage on the contacts of the tubes, the area of their cross-section and length, and the material resistance to the electric current. To hold the temperature constant, a power that suffices to compensate for the loss due to the thermal radiation and the passage through the heated tube is applied. Part of the heat is drawn by the cooled holders which are in close contact with the tube. A small quantity of heat is transferred by the gas screening the surface of the material. As the temperature increases, it is necessary to supply additional energy depending on the given temperature value, as well as on the mass and volume of the system being heated. Each decisive factor for the heating dynamics of the atomizer has unique temperature-dependent properties. As a result, even furnaces similar in shape have different heating dynamics [4, 8, 11]. The aim of the present work is to estimate the influence of the change in the furnace cross-section as a result of wear on the total increase in its temperature upon heating. To this end, we used an AAS with an atomizer having electrical constants (holders) at the furnace's ends.

The KAS-120.1 atomic-absorption complex made by the joint-stock company "SELMI" (Sumy, Ukraine) is a typical specimen of an instrument with contacts at the atomizer ends. The complex is designed to measure traces of chemical elements in liquid samples of various origins and compositions under the conditions of chemico-biological laboratories, research institutions, and industrial enterprises. The complex incorporates an S-115-M1 spectrophotometer, a "Grafit-2" attachment, and a personal computer. The complex is equipped with an A-5 electrothermal atomizer (Massman furnace), whose atomizing cell is an MPG-6-OSCh-7-3 graphite tube of length 28 mm, external diameter 7.6 mm, and internal diameter 6 mm. The working temperature range of the furnace is 313-3343 K. The permissible error of the facility and of holding the atomizing cell temperature constant depends on the temperature range and is 5–15%. The heating-up rate in the fast regime is up to 2000 K/sec [12]. The volume of the measured sample is 5–50 μl. As a characteristic radiation source, a hollow-cathode lamp (HCL) is used. The signal is registered on a photomultiplier (PM). As a shielding gas, argon is used.

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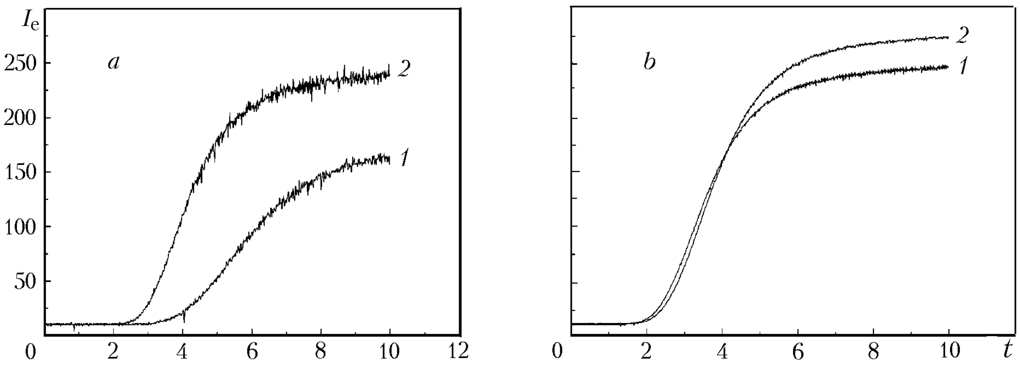

Fig. 1. Emission intensity of new (1) and worn-out (2) furnaces versus the heating time. I_e, arbitrary unit; t, sec.

The regimes of sample evaporation and ashing and of reduction and atomization of the element being determined are given by a control unit (CU). The number of heating stages and the temperatures required at each stage are chosen depending on the element concentration and the composition of the sample matrix. At each stage uniform, fast or accelerated heating can be given.

The tube is heated by electric current supplied from the power unit (PU) of the atomizer. The furnace temperature depends on the power dissipated by it, which is controlled by a triac gate in the primary circuit of the PU power transformer. The rms voltage on the atomizer and, consequently, the power are determined by the opening angle of the triac gate. The sensors located in the atomizer and the PU measure signals proportional to the current intensity and voltage, and their multiplication yields a signal proportional to the power. Its value is matched with the value given by the CU and if they are not equal, then the digital regulator changes the opening angle of the triac gate so that the equality condition is fulfilled. However, the furnace temperature under the same heating conditions increases from cycle to cycle [1–3]. According to Planck's law, a direct evidence of this is the increase in the emission intensity of the tube wall. It can be measured by the same KAS-120.1 spectrometer in the emission regime [3, 12].

The tube (without pyrocoating) was heated under identical conditions (in 10 sec to 2273 K) in two states: "new" (less than 10 heatings) and "worn-out" (more than 300 heatings). The increase in the emission intensity of the worn-out furnace compared to the new one (Fig. 1a) and the temperature increase associated with it can be explained by the fact that the tube loses its mass. Most probably, the mass is lost in a special way, since new and a worn-out tubes with equal mass have different emission intensities (Fig. 1b).

As is seen from Fig. 1a, a new tube was subjected to wear in the following procedure: drying at 353 K (60 sec), pyrolysis at 1273 K (30 sec), atomization at 2673 K (5 sec), cleaning at 2773 (3 sec); as a sample, 20 μl of copper solution (0.1 mg/l) [1] were used. Of the two new tubes, the heavier one was chosen and worn out in a similar way until equality of masses was attained (Fig. 1b).

It should be noted that up to now the tube has been considered as a hollow cylinder whose cross-sectional area is equal along the full length. However, in the middle of the furnace there is a hole of radius 0.9 mm for feeding the sample, and if the emission intensity of the central part of the tube is measured when rotating it by 90^{o} clockwise about its axis, beginning with the position where the holes of the tube and the housing coincide and are directed upward, the portion with the sample-feeding hole (90^{o}) has an emission intensity differing from that in the other portions (Fig. 2). This can cause nonuniform power dissipation by the furnace. In the wear process, because of the destructive influence of the hot vapors of the sample and the mechanical action of the feeder, the radius of the hole increases.

Through the hole a liquid sample is fed, which in the process of preparation for atomization can physically or chemically interact with the tube material. The sample is distributed over no more than one-third of the tube length, and exactly here the graphite "burns out" most actively — it is depleted and pores are formed [13, 14]. The furnace loses its mass, and its cross-section changes along the length. As a result, power redistribution and superheating at the site of a higher resistance occur. This makes the difference between the true and CU-given temperatures more substantial than in taking into account only the power change caused by the above constructional features of the instrument. Using such a model, one can attempt to prove that the temperature of the tube in its central part also increases in the

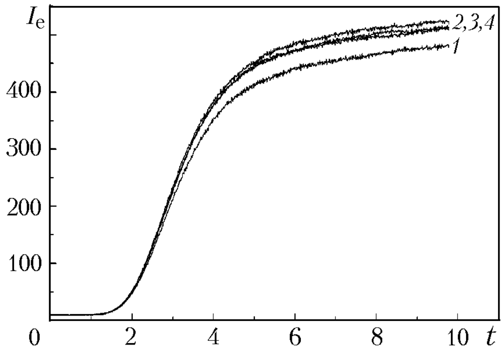

Fig. 2. Emission intensity of the furnace wall versus time at a heating temperature of 2783 K and its rotation about its axis by: 1) 90; 2) 0; 3) 180; 4) 270. I_e, arbitrary unit; t, sec.

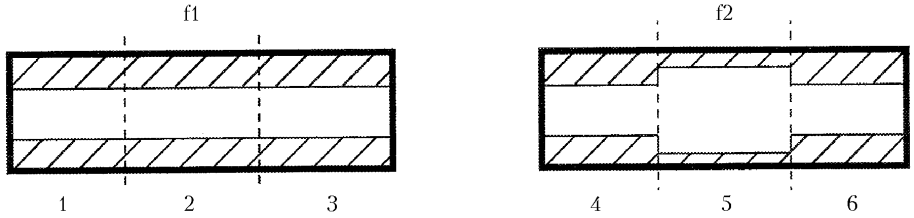

Fig. 3. Schematical longitudinal section of the furnaces.

course of wear under the same given heating conditions. Let us take two furnaces (f1 and f2). Divide each of them arbitrarily into three parts of equal length, with $l_1 = l_2 = l_3 = l_4 = l_5 = l_6$, i.e., $3l_i = l_f$ is the total length of the tube.

Assume that the cross-sectional area of f1 is equal along the full length: $S_1 = S_2 = S_3$, and the cross-sectional area of the central part (S_5) of f2 is equal to 1/2 of the cross-sectional area of f1 and portions 4 and 6 ($S_4 = S_6$). Proceeding from the proposed model, let us find the relative resistance of all parts of the tubes and f2 if the resistance $R_{f1} = R$, where $R = \omega l_f / S_1$. With a series connection of resistors $R_{f1} = R = R_1 + R_2 + R_3$. Then, according to the conditions

$$R_1 = R_2 = R_3 = \frac{\omega \frac{1}{3} l_f}{S_1} = \frac{1}{3}\frac{\omega l_f}{S_1} = \frac{1}{3} R . \tag{1}$$

For f2, portions 4 and 6 have the same parameters as portions 1, 2, and 3. Consequently, $R_4 = R_6 = R/3$, but portion 5 has a different cross-sectional area; therefore

$$R_5 = \frac{\omega \frac{1}{3} l_f}{\frac{1}{2} S_1} = \frac{2}{3} R , \tag{2}$$

and the total resistance $R_{f2} = R_1 + R_2 + R_3 = R/3 + 2R/3 + R/3 = 4R/3$.

If power $P_{f1} = P$, where $P = I_{f2}^2 R$, then in the case of the series connection of resistors $I_{f1} = I_1 + I_2 + I_3 + I_4 + I_5 + I_6 = I_{f2}$ and the power in the portions is

$$P_1 = P_2 = P_3 = \frac{P}{R}\frac{1}{3} R = \frac{1}{3} P , \; P_4 = P_6 = \frac{P}{\frac{4}{3} R}\frac{1}{3} R = \frac{1}{4} P , \; P_5 = I_{f2}^2 R_5 = \frac{P}{R_{f2}} R_5 = \frac{P}{\frac{4}{3} R}\frac{2}{3} R = \frac{1}{2} P . \tag{3}$$

Since at the tube ends, according to the description, the instrument should maintain equal power independent of its other parameters ($P_{f1} = P_{f2}$), one can find the voltage on f1, f2, and on their parts. If $U_{f2}^2 = U^2$, where $U^2 = RP$, then

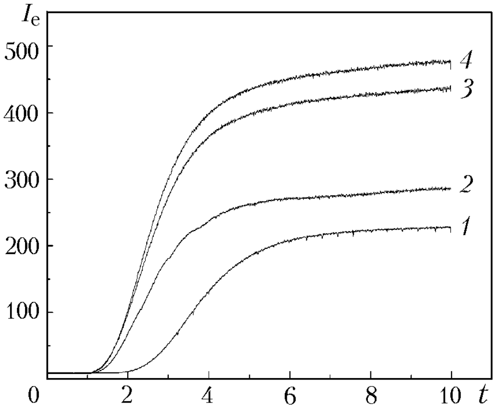

Fig. 4. Time dependence of the emission intensity of the furnace walls at a heating temperature of 2673 K: 1) standard new furnace; 2 and 3) furnaces, from whose surface graphite was removed uniformly and from the center, respectively; 4) worn-out surface. I_e, arbitrary unit; t, sec.

$$U_1^2 = U_2^2 = U_3^2 = \frac{1}{3} R \frac{1}{3} P = \frac{1}{9} U^2 , \quad U_{f2}^2 = R_{f2} P = \frac{4}{3} RP = \frac{4}{3} U^2 , \quad U_5^2 = \frac{2}{3} R \frac{1}{2} P = \frac{1}{3} U^2 ,$$

$$U_4^2 = U_6^2 = \frac{1}{3} R \frac{1}{4} P = \frac{1}{12} U^2 . \tag{4}$$

Because at atomization temperatures the power is largely expended in compensating for the tube emission [3, 15], we have

$$P_i = \frac{U_i^2}{R_i} = \sigma S_f T_i^4 ,$$

whence

$$T_i = \sqrt[4]{\frac{P_i}{\sigma S_f}} = \sqrt[4]{\frac{U_i^2}{\sigma S_f R_i}} . \tag{5}$$

Using expression (5), one can find the temperature of the central parts of f1 and f2:

$$T_2 = \sqrt[4]{\frac{\frac{1}{3} P}{\sigma \frac{1}{3} S_f}} = T , \quad T_5 = \sqrt[4]{\frac{\frac{1}{2} P}{\sigma \frac{1}{3} S_f}} = \sqrt[4]{\frac{3}{2}}\, T . \tag{6}$$

From expressions (6) it is seen that in the central part of the old tube the temperature is higher than in the new one by some value depending on the cross-sectional area of the portion. To confirm this, we conducted an experiment, in which we measured the emission intensity of a standard new tube and a worn-out one, as well as of new tubes in which the graphite was removed from the outer surface in different ways with the help of a fine-grained abrasive paper until the same mass as in the worn-out tube was attained (Fig. 4). In one case, removal was carried out uniformly along the full length, and in the other — at the center, on one-third of the length (analogously to the model). As is seen from Fig. 4, the emission intensity curve of the ground-off tube passes closer to the curve of the new tube, and the tube ground-off at the center emits like the worn-out one, i.e., this experiment validates the proposed model.

A similar result can be obtained with the use of the furnace mass in the calculations. Let us calculate the relative masses of the portions and tubes if the mass of f1 is m_{f1}:

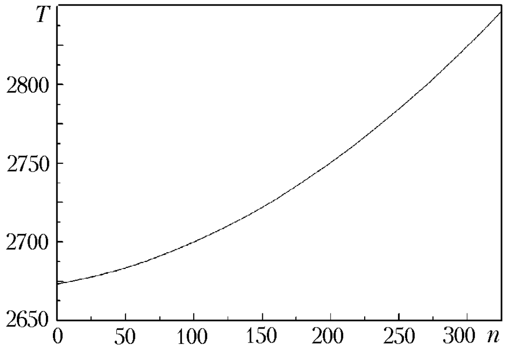

Fig. 5. Calculated dependence of temperature on the furnace mass. T, K; m_f, kg.

TABLE 1. Relations between Various Parameters of Furnaces f1 and f2 and Parts of These Furnaces Depending on $k = (S_2 - S_5)/S_2$

k	R_5/R_{f1}	R_{f2}/R_{f1}	U_5^2/U_{f1}^2	U_{f2}^2/U_{f1}^2	P_5/P_{f1}	m_5/m_{f1}	m_{f2}/m_{f1}	T_5/T_{f1}
1/10	10/27	28/27	25/189	28/27	5/14	3/10	29/30	1.017
1/5	5/12	13/12	25/156	13/12	5/13	4/15	14/15	1.036
3/10	10/21	24/21	25/126	24/21	5/12	7/30	9/10	1.057
2/5	5/9	11/9	25/99	11/9	5/11	1/5	13/15	1.081
1/2	2/3	4/3	1/3	4/3	1/2	1/6	5/6	1.107
3/5	5/6	3/2	25/54	3/2	5/9	2/15	4/5	1.136
7/10	10/9	16/9	25/36	16/9	5/8	1/10	23/30	1.170
4/5	5/3	7/3	25/21	7/3	5/7	1/5	11/15	1.210
9/10	10/3	4	25/9	4	5/6	1/30	7/10	1.257

$$m_1 = m_2 = m_3 = m_{f1}/3\ ;\quad m_4 = m_6 = m_{f1}/3\ .$$

The mass can be given as $m_{f1} = \rho V_f = \rho S_1 l_f$. Hence $m_5 = \rho \frac{1}{2} S_1 \frac{1}{3} l_f = \frac{1}{6} m_{f1}$ and $m_{f2} = m_{f1}/3 + m_{f1}/6 + m_{f1}/3 = 5m_{f1}/6$.

Compare now the temperatures of the central portions of the tubes. Taking into account that $T_i = \sqrt[4]{\frac{m_{f1} U_i^2}{\omega\rho l_f^2 \sigma S_f}}$, we obtain

$$T_2 = \sqrt[4]{\frac{\frac{1}{3} m_{f1} \frac{1}{9} U^2}{\omega\rho \frac{1}{9} l_f^2 \sigma \frac{1}{3} S_f}} = T\,,\quad T_5 = \sqrt[4]{\frac{\frac{1}{6} m_{f1} \frac{1}{3} U^2}{\omega\rho \frac{1}{9} l_f^2 \sigma \frac{1}{3} S_f}} = \sqrt[4]{\frac{3}{2}}\, T\,.$$

More tedious operations permit obtaining the furnace material porosity according to GOST 25281-82 and conductivity [3, 15, 16] and more correct calculations of the temperature differences, but in our case it suffices to show that with decreasing mass of the tube in the process of its operation its temperature increases and the above model is quite good for judging the change (Fig. 5).

From the calculated data (see Table 1) for the average statistical mass of the tube (0.9 g) and the given heating temperature of 2673 K it is seen that a decrease in the cross-sectional area of the central part of the tube to 1/10 of the initial cross section leads to a temperature change within the limits of 700 K. This is a considerable value, but according to the model, in the course of the experiment the cross-sectional area (S_5) of the tube changed by less than 2/5 of the initial one, which is equivalent to about 200 K. However, under the conditions of research laboratories, even where measurements are automatic and an automatic feeder is used, one rarely manages to take more than 100

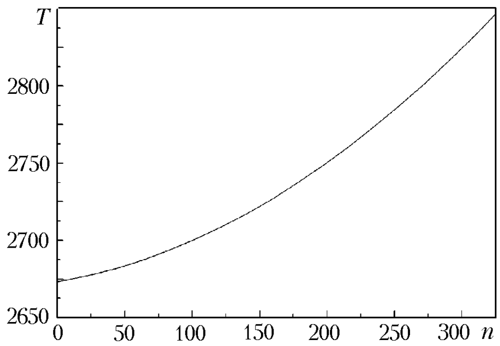

Fig. 6. Dependence of the calculated furnace heating temperature on the number of measurements. T, K.

measurements a day, taking into account the necessity to prepare and dilute samples and calibration and process solutions, adjust the instrument (tune to another analytical wavelength, change the lamp, set up a new program for heating the atomizer, etc.), the duration of an individual measurement cycle, and the current processing of the data obtained. Consequently, in one day of measurements the tube heating temperature under the same given conditions increased by no more than 50 K, and this value can be neglected in practice even taking into account the fact that the higher the degree of wear of the tube, the faster the process of temperature increase (Fig. 6). Besides, if instrument recalibration is carried out in good time, then the increase in the heating temperature of the tube in the wear process will be of no practical importance in routine measurements.

However, in studying the mechanisms of atomization of an element [17, 18], it is necessary to take into account the above temperature increase. As under the conditions of industrial production, where, e.g., the content of one and the same element is controlled by the given method for eight hours (maximum time of continuous operation of the instrument according to the description), an increase in the tube temperature can affect the measurement data. For example, at a high ashing temperature the element volatilizes or, vice versa, the spectrometer will show an increase in the element concentration with increasing atomization temperature if the concentration is calculated by the maximum of the atomization peak. Therefore, to avoid such a situation, according to our calculation, it is necessary to recalibrate the instrument at least twice in the above time interval so that the measurement data remain correct.

Summarizing the foregoing, it may be noted that when simple conditions (a small number of heatings or recalibration) are fulfilled on the KAS-120.1 complex, then the influence of an increase in the heating temperature in the process of tube wear on the final results of analytical measurements is immaterial. The exclusion is the investigation of the kinetic and thermochemical processes proceeding during atomization of elements.

NOTATION

I_{f1}, I_{f2}, current strength in respective furnaces, A; I_1–I_6, current strength in respective parts of furnaces, A; I_e, emission intensity of the furnace, arbitrary unit; k, coefficient defining the degree of reduction of the cross-section area; l_f, total length of the tube furnace, m; l_i, length of the ith part of furnaces, m; l_1–l_6, lengths of respective parts of furnaces, m; m_f, mass of a standard furnace, kg; m_{f1}, m_{f2}, mass of respective furnaces; m_1–m_6, mass of the respective part of furnaces, kg; n, number of measurements; P_i, power consumed by the ith part of furnaces, W; P_{f1}, P_{f2}, power consumed by respective furnaces, W; P_1–P_6, power consumed by respective parts of furnaces; W; R_i, electrical resistance of the ith part of furnaces, ohm; R_{f1}, R_{f2}, electrical resistance of respective furnaces, ohm; R_1–R_6, electrical resistance of respective parts of furnaces, ohm; S_f, area of the emitting surface of the furnace, m^2; S_1–S_6, cross-sectional area of respective parts of the furnace walls, m^2; t, time, sec; T, temperature, K; T_f, furnace temperature, K; T_i, temperature of the ith part of furnaces, K; T_2, T_5, temperature of respective parts of furnaces, K; V_f, volume of the furnace material, m^3; U_i, voltage of the ith part of furnaces, V; U_{f1}, U_{f2}, voltage applied to respective furnaces, V; U_1–U_6, voltage applied to respective parts of furnaces, V; ρ, density of the furnace material, kg/m^3; σ, Stefan constant, V/(m^2·K^4); ω, specific resistance of graphite, ohm·m. Subscripts: e, emission; f, furnace.

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