DYNAMICS OF HEAT AND MASS TRANSFER IN THE SORPTION SENSOR OF A PHOTOCOLORIMETRIC MOISTURE METER

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Results of thermophysical and spectral investigations of the progress in time of sorption processes in a porous sensor of a photocolorimetric gas analyzer are presented. An interpretation of heat and mass transfer processes and of the process of conversion of hydrate complexes in the context of the observed spectral changes is given.

One of the most promising and rapidly developing directions in the field of gas analyzing instrument engineering is the development of gas analyzers including moisture meters of the sorption photocolorimetric type [1, 2]. The sensor, or the primary converter, of this sort of device is in the sorption equilibrium with a gas medium and changes its optical density with changing gas composition. Similar gas analyzers have a number of advantages over some other devices of the same function. However, their wider introduction into practice is hampered to a certain extent by the inherent sluggishness of sorption sensors: the signal time is as much as 1 h or more, whereas speed of response is one of the basic parameters of a gas analyzer. An effective solution of this problem is impossible without thorough investigations of thermophysical and spectrochemical processes in the sorption sensor, and, for that matter they must be conducted together and be considered as a complex.

The basis of the moisture sensor in question is a plane-parallel plate of porous soda-lime glass with cobalt chloride introduced into the pores (II). The procedure for producing this kind of system and some their parameters are given in detail in [3]. It is of fundamental importance that the dimensions of communicating pores be made in such a way (7-8 nm) that the porous plate retains its optical transmission and the filler (cobalt salt) gives absorption in the characteristic visible spectrum.

The sensing element is a plate of porous glass with dimensions 10 × 5 × 1 mm treated in an aqueous solution of cobalt chloride (II) with concentration 1 mole/liter by the procedure described in [3]. Figure 1 gives the absorption spectra of a porous plate with a modifier for two humidities. A change in the ambient air humidity leads to substantial changes in the spectral optical density of the sensor in the wavelength range 620-700 nm.

Thus, for constructing a moisture meter it will suffice to provide the source and the detector of radiation matched to the porous plate in spectral characteristics. The measuring circuit simulating the sensor arrangement is shown in Fig. 2.

As a radiation source 2 we used the AL 307 AM type light-emitting diode having maximum radiation at the wavelength [4] 666 nm. An FD-256 photodiode, whose sensitivity was practically uniform in the spectral region of interest (600-700 nm) served as a photodetector 3. When spectral correction of the radiation from the source 2 is needed, the circuit allows for the installation of a light filter 4. To register the electric signal picked off the photodetector 3, a V7-16 digital voltmeter was used.

For the investigation of thermal effects in sorption we fixed the junction of a differential copper–constantan thermocouple 5 to a porous sensing element of the sensor 1 (electrode diameter 0.1 mm). The second junction of the thermocouple was at the ambient temperature.

For measuring calibration and dynamic characteristics of the sensors we used a humidistat; the relative humidity was prescribed by aqueous solutions of salts which were at equilibrium with the air inside the humidistat [5].

Figure 3 gives the calibration dependence of the sensor obtained in this work as well as, for correlation purposes, the portion of the adsorption isotherm taken from [3] for the analogous porous element. We observe the symmetry of the adsorption and calibration curves, which is due to the very principle of operation of a sorption photocolorimetric sensor. In dry air the spectrum of the porous glass containing cobalt (II) (see Fig. 1) is determined over the operating wavelength range by the formation of tetrahedral ions $[CoCl_4]^{2-}$ on the surface, the main absorption band at 670 nm relates, as has been long established, to the electron transition $A_2 \rightarrow T_1$ in the central cobalt atom (II) of a tetrahedral chloride complex.

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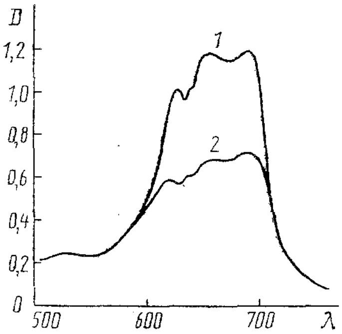

Fig. 1. Absorption spectra of a porous sensing element with cobalt chloride (II) in its pores in the air at relative humidity less than 1% (1) and 50% (2). λ, nm.

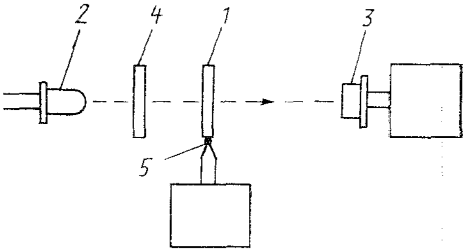

Fig. 2. Scheme of arrangement of a photocolorimetric moisture sensor.

When the ambient air is humidified, both the adsorption of water molecules on a free pore surface in glass and the addition of water molecules to the chloride complex take place, and in the latter case the splitting parameter of the d-electron energy states changes and the absorption band intensity decreases (curve 2, Fig. 1). The approach to saturation is accompanied within the limit by formation of the hydrate complex $[Co \cdot 6H_2O]^{2+}$ with an octahedral coordination. The formation enthalpy of this complex r^* from the reference data [7] is $\approx 3 \cdot 10^3$ kJ/mole while the adsorption of moisture by a clean porous glass is estimated by the value of about 50 kJ/mole [8]. Both types of adsorption take place simultaneously; however, it is the first one which is accompanied by spectral changes and considerable heat liberation. In this connection, from here on we will not consider the second type of adsorption.

Figure 4 shows the time dependences of the optical glass and temperature obtained by us on a measuring unit (see Fig. 2). It is obvious that the sorption equilibrium of the sensor with the ambient air only comes 90 min later. According to the optical data, the temperature dependence takes a more complicated form characterized by the appearance of a temperature "splash" in the first minutes after placing the sensor into a damp atmosphere. It is determined by the thermal effect of sorption [9]. It is evident that the settling time for the optical signal is related to the settling time of the thermal equilibrium of the sensing element.

For analyzing the processes of heat and mass transfer and for optimizing the fast-response parameters of a moisture sensor it is necessary to use a mathematical model of moisture sorption by porous glass, allowing for the accompanying thermal effects. The solution of the stated problem for the mean-volume temperature is given in general form as [9]:

$$t_c - \bar{t}(\tau) = \frac{r^* (c_{\text{н}} - c_{\text{p}})}{c} \frac{R_V}{R} \frac{\text{Lu}}{\text{Bi}} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} B_n \mu_n B_m \times \frac{\mu_m^2}{\mu_n^2 - \text{Lu}\mu_m} \{\exp(-\mu_m^2 \text{Lu Fo}) - \exp(-\mu_n^2 \text{Fo})\}. \quad (1)$$

The solution (1) is obtained on the assumption of an instantaneous settling of local sorption equilibrium, the constancy of the mass conductivity k, a constant distribution coefficient of the equilibrium function A_{eq} – the slope of the curve of the sorption isotherm, the absence of a thermodiffusive flow, and the presence of phase transformations only on the body surface. Correctness of the two latter assumptions is substantiated in [10, 11]. The assumption of a constant A_{eq} is validated by the data from [3]. Analysis of the behavior of k in sorption based on its estimation procedure $k \sim \partial c_c'/\partial c_a$ has shown that the assumption of its constancy is also correct. As a first approximation we obtained calculations by formula (1) for the conditions of experiments with reference data from [3] on r^* and A_{eq}, and data from [12] on k. In [12] gas permeability of porous glasses in the Knudsen regime of gas flow was studied. It is easily shown that in this case gas permeability can be considered the mass conductivity k.

Comparison of the results of calculations and experiments (Fig. 4) has shown their substantial discordance. In this connection an agreement was carried out of the calculated curves of changing porous glass temperature in sorption with the experimental data. This was performed by varying the initial reference data (A_{eq}, k, r^*) at fixed conditions of the external heat and mass transfer (the heat transfer coefficient α and the mass transfer coefficient β_c).

In connection with the fact that temperature splashes in sorption are of a complicated form the agreement of the results of the calculations and experiments was performed by two criteria: the abscissa of the curve maximum and the cooling rate of porous glass. Thus, we managed to fit the coefficients and to obtain the calculated curves of the heating-up dynamics for porous glass, checking with the experimental ones within the measurement error of the temperature drop ΔT. Analysis of the obtained combination of initial data has shown that the mass conductivity k is in the data range of [12], the heat of sorption is $\approx 10\%$ more than that from the data of [3] (this may be connected with increasing r^* in the porous material [13]), the distribution coefficient of equilibrium function A_{eq} decreases by nearly a factor of 2 as compared with [3]. Such behavior of A_{eq} is probably a result of deactivation of a portion of chemical reagent molecules during the operation of a porous indicator in free air. Thus, since so far as we have managed to obtain a physically noncontradictory combination of initial parameters, permitting a mathematical description of experimental data on heating-up porous glass in sorption, the mathematical model [8] can be considered adequate. This permits us, on the basis of experimental data on temperature "splashes" in sorption, to determine the strength characteristics of porous glass as a sensing element. They include the mass conductivity k, characterizing the transmission rate of adsorbed gas in porous glass, the distribution coefficient of equilibrium function A_{eq}, characterizing the sorption capacity of porous glass, and the sorption heat r^*, characterizing the heat liberation rate and ultimately the dynamics of sorption.

Moreover, using the mathematical model [9] allows us to analyze the influence of various factors on the response time of a porous indicator, for example, of heat liberations in sorption. Calculations performed for the case of sorption of water vapor by 1-mm-thick porous glass (relative humidity 75%) from a quiet atmosphere (the porous glass temperature is 20°C and equals the ambient temperature) show that the transient time (reaching 95% of the stationary state) is $\approx$13 min without reference to the thermal effects in sorption, $\approx$20-23 min allowing for thermal effects. Experimental results under analogous conditions show that heat liberation in a porous element is finished in 30-35 min, whereas a variation in the optical density persists up to 60 min with no longer pronounced heat liberation. Consequently, the response time of a porous indicator is not limited only by thermal effects. A delay in the onset of sorption equilibrium from the results of spectral measurements is likely to be determined by the fact that the reconstruction of the configuration of complex ions containing Co, from tetrahedral to octahedral, does not happen in a moment. This process, as with any chemical reaction, must have a finite rate which is probably limited by the close disposition of neighboring complex ions and by the influence of potential fields of the pore walls. In this connection, by raising the porous indicator temperature and thus increasing the reaction rate, we can reduce the transient time. Experimental investigations of the dynamics of sorption of water vapor by porous glass at a temperature of 313 K (Fig. 4) confirm the reduction of the settling time for sorption equilibrium down to 30 min. However, a further increase of the operation temperature must be analyzed separately, since with increasing temperature the amount of the sorbed gas decreases, which results in a decrease of the indicator sensitivity.

Calculations by formula (1) show that a variation in the porous glass thickness and in the conditions of the external heat and mass transfer leads to a roughly multiple variation in the sorption transient time.

Thus, on the basis of experimental investigations and calculations we can propose the following recommendations for improving the dynamic properties (the response time) of a porous photocolorimetric indicator:

– decrease the porous glass thickness;

– provide the removal of liberated heat of sorption from the porous glass, i.e., exert active or passive control of the temperature thereof;

– increase the external heat and mass transfer of the porous glass with the analyzed gas, i.e., carry out the air blow thereof; in case this is impossible or undesirable one must use a construction of fixation for a porous indicator which will not hamper the access of the analyzed gas to the porous glass surface;

– carry out the heating-up of the porous glass with the porous plate in this case being placed vertically; this will contribute to the formation of intensive convective flows by increasing the heat and mass transfer.

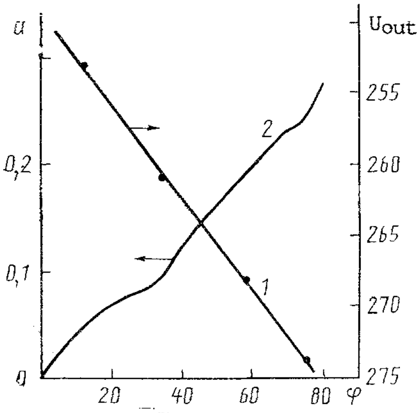

Fig. 3

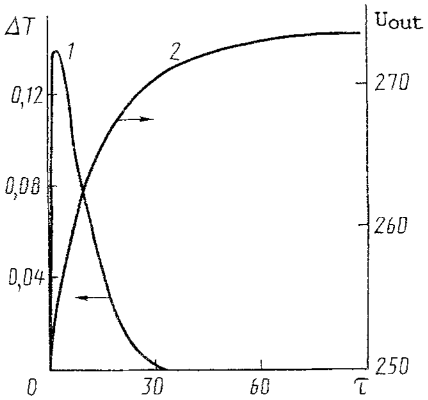

Fig. 4

Fig. 3. Calibration dependence of a moisture sensor (1) and adsorption isotherm of a porous sensing element (2). a, g/cm^3; U_{out}, mV; φ, %.

Fig. 4. Time dependences of the porous sensing element temperature (1) and the moisture sensor output signal (2). ΔT, K; τ, min.

Thus, the response time of a porous photocolorimetric indicator can be minimized to a few minutes or less. This will enable the developed indicators [1-3] to take up a position among currently available ones and to find their application.

The specific features of dynamics of sorption of water vapor by porous glass are dealt with in this work. However, the estimates of the response time and recommendations on the reduction thereof can be applied to the other indicators as well – to CO and CO_2 indicators [2, 3] – as an upper estimate. This is on account of the fact that the heat of sorption released by $CoCl_2$ during the interaction with water molecules is much greater than the heat released when the corresponding chemical reagents interact with CO and CO_2.

NOTATION

t_m, temperature of medium, K; $\bar{t}(\tau)$, running mean-volume temperature of porous glass, K; r^*, heat of sorption, kJ/kg; c_{in}, c_{eq}, relative mass fractions per unit mass of porous glass – the initial fraction and the final (equilibrium) one, respectively, kg/kg; c, specific heat of porous glass, kJ/(kg·K); R_v, ratio of the volume of a porous glass plate to its surface, m; R, characteristic dimension of a porous glass plate (half the thickness), m; Lu, Luikov number; Bi, Bi_m, thermal Biot number and mass transfer Biot number; Fo, thermal Fourier number; $B_n = 2Bi^2/\mu_n^2\,(Bi^2 + \mu_n^2 + Bi)$; $B_m = 2Bi_m^2/\mu_m^2(Bi_m^2 + \mu_m^2 + Bi_m)$; μ_n, roots of the characteristic equation $\cot\mu_n = \mu_n/Bi$; μ_m, roots of the characteristic equation $\cot\mu_m = \mu_m/Bi_m$.

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