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High-Sensitivity X-ray Fluorescence Analysis of Solutions with the Use of a Sorption Accumulation Microsystem

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Abstract—A mass-transfer kinetic model is proposed for an embedded sorption accumulation microsystem based on polycapillary structures to be used in the developed X-ray fluorescence analyzer with preconcentration. The model is used to substantiate a kinetic method for high-sensitivity X-ray fluorescence determination of elements in multicomponent solutions. With the use of this model, experimental data on X-ray fluorescence spectra are analyzed and kinetic and equilibrium parameters are found for the sorption of copper, nickel, manganese, iron, and zinc on the selective DETATA sorbent.

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Energy dispersive X-ray fluorescence analysis is a commonly used technique for the determination of metals in various media with relatively high concentrations of target components. The detection limits of this technique in the analysis of solutions are no lower than tens of mg/L. At the same time, current environmental protection regulations and requirements imposed on analytical instrumentation for many technological processes and research works are responsible for the development of commonly accessible instruments with much lower detection limits. A combination of X-ray fluorescence analysis and the preconcentration of test elements with the use of sorption accumulation microsystems (recoverable concentrators), which are arranged in test flows or solutions with limited volumes, seems a promising approach to solve the above problem [1].

In this work, we used a sorption accumulation microsystem embedded in an analytical instrument.

EXPERIMENTAL

Multichannel glass polycapillary structures, which were developed at the Institute of X-ray Optics and manufactured in accordance with a patented process [2, 3], were used to develop a concentrator. Each of the hundreds of thousands or millions of microchannels in polycapillary columns contained a sorbent microgranule [4, 5]. The microgranules were concentrated at an end of the polycapillary tube, and they formed an active sorption layer. Strongly acidic and weakly acidic cation exchangers, Poliorgs sorbents [6], and DETATA sorbent containing diethylenetriaminetetraacetate groups [7] were used as sorption materials.

The instrument developed in cooperation with the Institute of X-ray Optics was an X-ray fluorescence analyzer, which consisted of two units: accumulation and measurement units. In the accumulation unit, the test solution was passed through a flow cell for a specified time with an embedded pump. A concentrator and an ultrasonic activator, which was arranged under the sorption layer, were placed in this cell. Then, the concentrator was transferred to the measurement unit for measuring X-ray fluorescence spectra at a pulse accumulation time of 5 min. Kinetic curves for each particular test component were constructed based on the measurements of the integrated intensities of X-ray fluorescence spectral bands at various sorption accumulation times. After each particular experiment, the accumulation cell was shaken for a few minutes sequentially in a saturated EDTA solution, 1 M HCl, and deionized water for the repeated use of this cell. The model solutions of trace components were prepared with the use of a NaCl solution (0.25 g/L) in deionized water and tap water from the Moskva River.

RESULTS AND DISCUSSION

Figures 1–3 show a photograph of the instrument and the examples of X-ray fluorescence spectra, which demonstrate the possibility of decreasing detection limits in the analysis of solutions by several orders of magnitude.

It was found in previous studies that the kinetics of accumulation of trace components in a sorption layer is

Fig. 1. X-ray fluorescence analyzer with a sorption accumulation microsystem.

described by an external diffusion mass-transfer mechanism [8]. With a good approximation, the kinetics of sorption of the *i*th trace component can be described by the following model:

$$\ln\left(1-\frac{c_i^*}{c_{0,i}}\right) = \ln\left(1-\frac{\bar{c}_{t,i}}{\bar{c}_{\infty,i}}\right) \approx \ln\left(1-\frac{I_{t,i}}{I_{\infty,i}}\right) = f(t), \quad (1)$$

$$I_{t,i} = \alpha_i\Gamma_i c_i^* m = \alpha_i\frac{D_i}{\gamma_i r}c_i^* m = \alpha_i\bar{c}_{t,i}m, \quad (2)$$

at $c_i^* = c_{0,i}$: $\bar{c}_{t,i} = c_{\infty,i}$ and $I_{t,i} = I_{\infty,i}$,

where c_i^* is the concentration of the *i*th component in solution at the interface with the sorbent (mL/l or mg/mL), c_0 is the initial concentration of the component in solution, $\bar{c}_{t,i}$ is the limiting concentration in the sorbent under equilibrium conditions, $I_{t,i}$ is the integrated intensity of a band due to the *i*th component in the X-ray fluorescence spectrum minus a background (pulse number), $I_{\infty,i}$ is the maximum integrated intensity corresponding to an equilibrium, α_i is a factor for converting the amount of the component in a sorbent phase into integrated intensity unit of the X-ray fluorescence spectrum, $\Gamma_i = \bar{c}_{\infty,i}/c_{0,i}$ is the equilibrium distribution coefficient or the Henry coefficient (mL/g), r is the sorbent grain radius (cm), $\gamma_i = D_i/(\Gamma_i r)$ is the solution to sorbent mass-transfer coefficient (cm/s or cm/h), D_i is the tabulated diffusion coefficient of the component in water (cm^2/s or cm^2/h), and t is time (s or h).

The function *f*(*t*) is a standard solution to the external mass-transfer problem, at which the flow of a test solution around a micrograin or a layer of sorbent microgranules occurs in the presence of an intermediate diffusion layer rather than directly, for example, in the presence of restricting gauze between the flow and the surface of microgranules. This problem is well known as a thermal conductivity model for a finite rod with a heat source (in our case, a substance) at an end and an absorber (sorbent) at the other end:

$$\frac{\partial c_i}{\partial t} = D_i^*\frac{\partial^2 c_i}{\partial x^2} \quad (3)$$

with the following boundary and initial conditions:

$$c_i\big|_{x=0} = c_{0,i}, \quad \frac{\partial c_i^*}{\partial t}\bigg|_{x=x_0} = \gamma_i\frac{\partial c_i^*}{\partial x},$$

$$c_i\big|_{t=0} = c_{0,i}\delta(x=0),$$

where x is the coordinate (mm), $x = 0$ corresponds to the outer boundary of the sorption accumulation cell (between the gauze and the flow), $x = x_0$ corresponds to the boundary between the solution and the sorbent, and

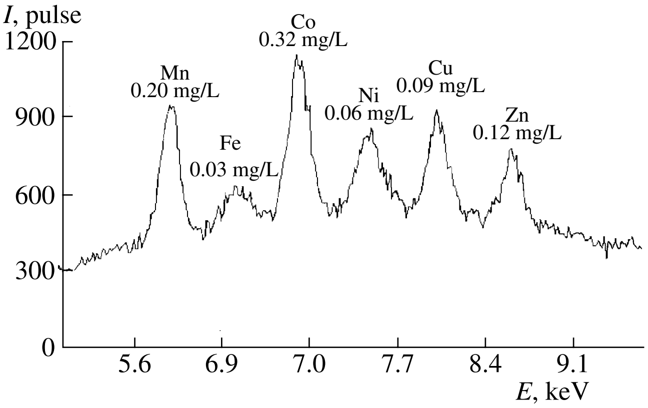

Fig. 2. X-ray fluorescence spectrum of a sorbent phase (KU-2 @ 8) after the accumulation of trace components from a model solution in the presence of 0.25 g/L NaCl.

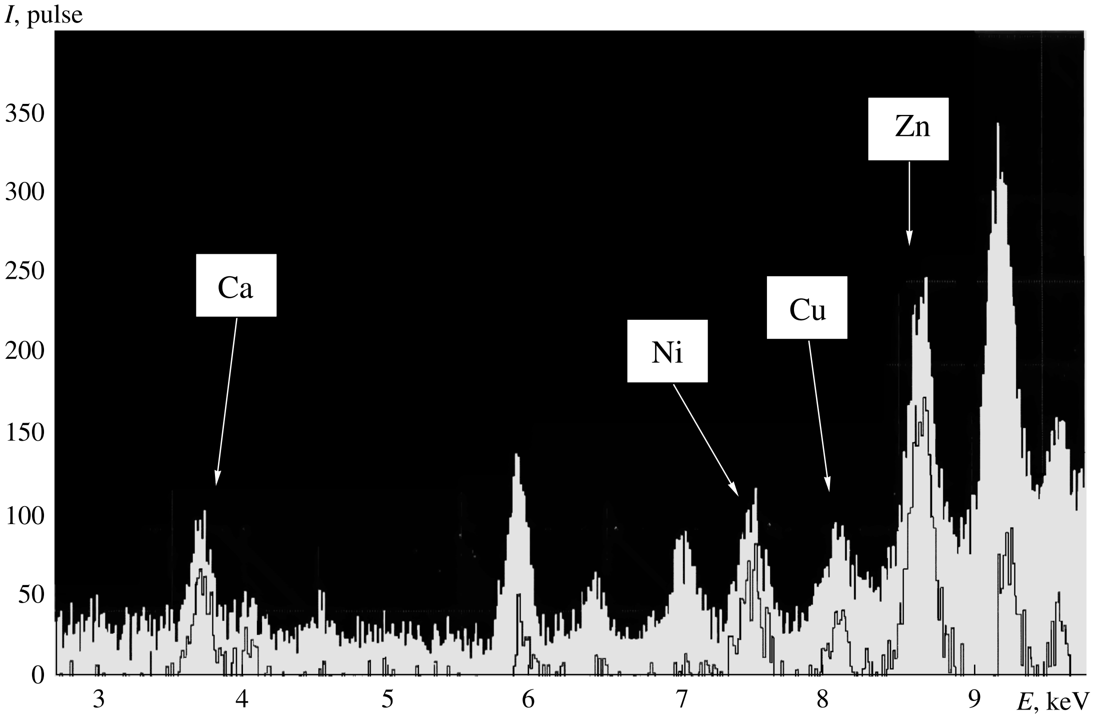

Fig. 3. Fragment of an X-ray fluorescence spectrum after the accumulation of trace components from a model solution in Moscow tap water.

Component concentrations (mg/L): Ni, 0.5; Cu, 0.3, and Zn, 1.0. Sorbent: DETATA. Accumulation time: 120 min. The bottom curve was obtained after subtracting a background spectrum before the accumulation of components.

D_i^* is the apparent diffusion coefficient in an intermediate layer restricted by the coordinates (0; x_0), for example, with consideration for an additional resistance of the gauze. Evidently, the accumulation cell parameter (instrumental parameter) $D_i^*/D_i = D_j^*/D_j = k$ can be introduced for all of the components.

The numerical solution of the described problem can be obtained with no special programming with the use of only the currently available MathCAD software.

Thus, in the general form, the model described by Eqs. (1)–(3) and a corresponding set of boundary conditions implies the following adjusted and known independent parameters: two parameters α_i and γ_i adjusted in solving an inverse problem (in the construction of calibration kinetic curves); instrumental parameter k, which is common for all of the test components; and theknown parameters r, m, and x_0, as well as D_i (tabulated value). All of the other parameters, including the distribution coefficient Γ_i, are the derived quantities of the independent parameters. This also suggests the possibility of using the kinetic method in the analysis of solutions, when calibration kinetic curves are plotted with the use of no less than two solutions with different analyte concentrations. With the use of the X-ray fluorescence spectra of the sorbent measured at several accumulation times, kinetic curves corresponding to Eq. (1) are constructed. In this case, the accumulation processes should not be equilibrated; this is of considerable importance for shortening the analysis time. The examples of the use of the proposed kinetic method for the analysis of solutions by energy dispersive X-ray fluorescence analysis with the use of accumulation microcells with DETATA sorbent are given below.

Analysis of Multicomponent Solutions Containing Cu, Ni, Zn, Fe, and Mn

The results considered below were obtained in the following manner: A large number of model solutions were prepared with various concentrations of copper, nickel, iron, manganese, and zinc in tap water. A portion of these solutions was used to obtain calibration kinetic curves by performing experiments on sorption concentration and the measurement of fluorescence spectra. Figure 4 shows an example of a calibration curve. With the use of a standard program based on the least-squares technique, a theoretical curve specified by a certain set of model parameters was chosen to be the closest to the experimental functions. In this case, the accumulation cell parameters were known: $r = 21 \times 10^{-4}$ cm, $m = 1.6 \times 10^{-2}$ g, $x_0 = 0.1$ cm, and the tabulated value of $D_{Cu} = 7.19 \times 10^{-6}$ cm^3/s.

We fixed the found parameters $\alpha = 3.68 \times 10^7$ pulse/mol, $\gamma_{Cu} = 8.82 \times 10^{-6}$ g s^{-1} cm^{-2}, and the common parameter $k = 0.55$, which led to a satisfactory set

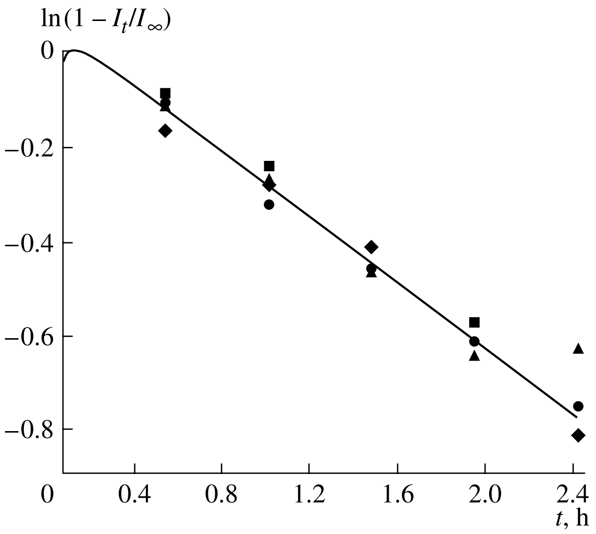

Fig. 4. Calibration kinetic curve for multicomponent solutions with various copper concentrations in tap water.

Experimental points correspond to the following concentrations ($c_{0,\,\mathrm{Cu}}$, mg/L): (■) 0.5, (◆) 0.75, (●) 1.6, and (▲) 2.0. (—) refers to the theoretical line determined by the least-squares technique.

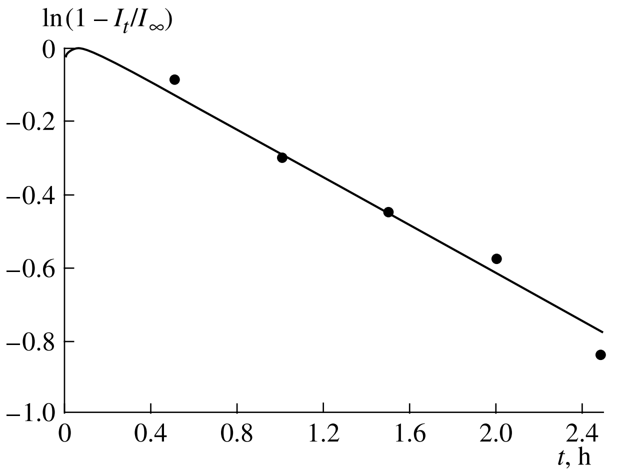

Fig. 5. Kinetic curve for the test solution.

Cu added, 0.4 mg/L. The line shows a theoretical (calibration) curve, and the points show experimental data.

of results. Note that the value of the dependent parameter, the distribution coefficient $\Gamma_{\mathrm{Cu}} = 3.68 \times 10^2$ cm^3/g, also followed from the above independent parameters of the model.

The other solutions were used to perform independent experiments on the determination of target component concentrations in these solutions. The X-ray fluorescence spectra obtained at this stage were processed for each of the test solutions with the use of the above kinetic method with model parameters fixed in the course of calibration. Figure 5 shows an example of the kinetic curve used in the analysis of a solution, and Table 1 summarizes the results of analysis. In this procedure, a theoretical curve was fixed, and it corresponded to the calibration curve in Fig. 4. The determination of the analyte concentration $c_{o,\,\mathrm{Cu}}$ consisted in choosing the parameter $I_{\infty,\,\mathrm{Cu}} = \varphi(c_{o,\,\mathrm{Cu}})$ at which the sum of squares of the deviations of points ln $(1 - I_t/I_\infty)$ corresponding to the experimental values of $I_{t,\,\mathrm{Cu}}$ with respect to the theoretical calibration function reached a minimum. Additionally, the same procedure was performed individually for each particular point. The required value of $c_{o,\,\mathrm{Cu}}$ was determined using Eq. (2) at

Table 1. Results of the determination of copper in multicomponent solutions (mg/L)

Added	Found (least-squares technique)	Deviation, %	Found ($P = 0.95, n = 5$)
0.40 ± 0.01	0.44	11	0.45 ± 0.02
0.50 ± 0.02	0.44	11	0.43 ± 0.06
0.75 ± 0.02	0.87	16	0.92 ± 0.20
0.90 ± 0.03	1.06	17	0.94 ± 0.03
1.00 ± 0.03	0.84	16	0.82 ± 0.06
1.10 ± 0.03	1.26	15	1.4 ± 0.2
1.30 ± 0.04	1.34	3	1.5 ± 0.3
1.60 ± 0.05	1.64	2	1.6 ± 0.1
2.00 ± 0.06	1.96	2	2.0 ± 0.2

Table 2. Results of the determination of nickel in multicomponent solutions (mg/L)

Added	Found (least-squares technique)	Deviation, %	Found ($P = 0.95, n = 5$)
0.40 ± 0.01	0.46	15	0.45 ± 0.06
0.50 ± 0.02	0.54	9	0.53 ± 0.05
0.75 ± 0.02	0.75	0	0.68 ± 0.04
0.90 ± 0.03	1.06	18	1.1 ± 0.3
1.00 ± 0.03	0.86	14	0.87 ± 0.07
1.10 ± 0.03	1.14	3	1.2 ± 0.2
1.30 ± 0.04	1.23	5	1.3 ± 0.2
1.60 ± 0.05	1.70	6	1.7 ± 0.2
2.00 ± 0.06	2.10	5	2.0 ± 0.2

Table 3. Results of the determination of zinc in multicomponent solutions (mg/L)

Added	Found (least-squares technique)	Deviation, %	Found ($P = 0.95, n = 5$)
0.75 ± 0.02	0.78	5	0.82 ± 0.14
1.00 ± 0.03	1.13	13	0.95 ± 0.22
1.00 ± 0.03	0.84	16	0.88 ± 0.08
1.50 ± 0.05	1.44	4	1.4 ± 0.3
1.50 ± 0.05	1.34	11	1.4 ± 0.4
2.00 ± 0.06	2.11	6	2.1 ± 0.2

Table 4. Results of the determination of manganese in multicomponent solutions (mg/L)

Added	Found (least-squares technique)	Deviation, %	Found ($P = 0.95, n = 5$)
0.50 ± 0.02	0.64	28.7	0.66 ± 0.20
0.60 ± 0.02	0.56	6.4	0.47 ± 0.10
0.75 ± 0.02	0.84	12.6	0.76 ± 0.19
1.50 ± 0.05	1.50	0.3	1.5 ± 0.3
1.75 ± 0.05	1.75	0.2	1.7 ± 0.4

Table 5. Results of the determination of iron in multicomponent solutions (mg/L)

Added	Found (least-squares technique)	Deviation, %	Found ($P = 0.95, n = 5$)
0.50 ± 0.02	0.54	9	0.56 ± 0.04
1.00 ± 0.03	1.08	8	1.0 ± 0.3
1.50 ± 0.05	1.70	13	1.6 ± 0.4
1.50 ± 0.05	1.79	19	1.8 ± 0.5
2.00 ± 0.06	2.28	14	2.3 ± 0.3

$c_i^* = c_{o,i}$ and model parameters fixed at the stage of calibration. All of the procedures related to the direct use of the mathematical model were performed in the automated mode.

Analogously, the following parameters for nickel were obtained: $D_{\mathrm{Ni}} = 7.53 \times 10^{-6}$ cm^2/s, $\alpha = 4.26 \times 10^7$ pulse/mol, and $\gamma_{\mathrm{Ni}} = 9.31 \times 10^{-6}$ g s^{-1} cm^{-2}. The dependent parameter, the distribution coefficient $\Gamma_{\mathrm{Ni}} = 3.85 \times 10^2$ cm^3/g, was also derived from the above independent model parameters.

Tables 2–5 summarize data obtained in a chemicoanalytical test of the proposed kinetic method for the determination of nickel, manganese, iron, and zinc in multicomponent solutions with the use of energy dispersive X-ray fluorescence analysis with the sorption accumulation microsystem.

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