INCREASING THE ACCURACY OF
ATOMIC-FLUORESCENCE ANALYSIS

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Allowance for scattered light using an additional continuous-spectrum source is considered. The effect of light-pulse rise and fall time on analysis accuracy is evaluated. An atomic-fluorescence analyzer is proposed.

Atomic-fluorescence analysis (AFA) is a method for determining the concentration of impurity atoms in a specimen by measuring the fluorescence intensities of the atoms or ions of the elements to be determined [1].

The AFA method has a high detection capacity that often reaches limiting values, which allows individual atoms in the gas phase to be recorded [1]. Atomic-absorption analysis is closest to AFA; the detection possibilities of both methods differ by not more than an order of magnitude. As a rule, when modern methods for excitation and recording of fluorescence are employed, AFA has advantages in this regard [1].

AFA is successfully used to solve many analytic problems in the determination of trace amounts of metals in solutions. However, analysis accuracy is reduced due to scattered radiation produced in the excitation of fluorescence. The effect of scattered radiation is especially strong in AFA of products with a complex composition. Various methods of allowing for scattered radiation in AFA allow complicated analytic problems to be solved – for example, determination of gold in ore on the order of 1 g/t or less [2].

One of the most effective methods of substantial attenuation of the effect of scattered radiation is the alternate excitation of the analytic cell by radiation sources with continuous and line spectra. A diagram of an atomic-fluorescence analyzer with two excitation sources is presented in Fig. 1.

The line-spectrum source 1 (an LK or LS lamp) is powered by a pulse supply 2. The continuous-spectrum source 9 is a DKsEL-1000 xenon lamp. The light from the lamps is sent to a flame atomizer 13 by quartz lenses 10, 12, and 14 and a flat mirror 11. The radiation is collected by a quartz lens 16 at the entrance slit of a monochromator 3. Spherical mirrors 15 and 16 redirect the luminous flux through the atomizer. The light from the continuous-spectrum source is modulated by a shutter disk 6, which is rotated by a motor 8. A shutter sensor 7 synchronizes the light pulses of the line-spectrum source with the light pulses of the continuous-spectrum source. The radiation is registered by an FÉU-39A photomultiplier (PM) 4. Subsequent signal processing and recording are performed by an electronic recorder 5.

The method of allowance for and suppression of the effect of scattered radiation on analysis results is explained by the timing diagram of the photomultiplier signal in Fig. 2. When the continuous source is covered by the shutter disk and the line source is disabled (see sections d, f, and k in Fig. 2), the random output signal $\xi(t)$ of the PM is chiefly a result of flame noise. With the line source enabled (sections e and h), the PM output signal

$$U_{PM} = U_{l1} + U_{s1} + \xi(t),$$

and when the continuous source is open (sections b and h),

$$U_{PM} = U_{c2} + U_{s2} + \xi(t),$$

where $U_{l1}$ and $U_{c2}$ are the fluorescence signals excited by the line and continuous sources, respectively; and $U_{s1}$ and $U_{s2}$ are the scattered-radiation signals produced by the same sources.

Fig. 1. Diagram of atomic-fluorescence analyzer: 1) line-spectrum source; 2) pulse supply; 3) monochromator; 4) photomultiplier; 5) electronic recorder; 6–8) disk, shutter sensor, and motor; 9) continuous-spectrum source; 10, 12, 14, 16) quartz lenses; 11) flat mirror; 13) flame atomizer; 15, 17) spherical mirrors.

The fluorescence signal is discriminated step by step as follows. At first, the PM signal is integrated over the time interval $\tau_0$ with passage of the radiation from the continuous source through the atomizer. After time interval $\tau_1$, the signal is integrated over time $\tau_0$ with the continuous source covered by the shutter disk. The difference $J_1$ between the integrals is determined and then is multiplied by a factor of $K_1$. Then, provided that $U_{\Omega} \ll U_{s1}$,

$$J_1 = K_1 \left\{ \frac{1}{\tau_0} \int_{0}^{\tau_0} [U_{s2} + \xi(t)] dt - \frac{1}{\tau_0} \int_{\tau_0}^{\tau_0+\tau_1} \xi(t) dt \right\}.$$  

Assuming that $\xi(t)$ is a continuous stationary random process, we have

$$M[J_1] = K_1 U_{s2},$$

where $M[J_1]$ is the mathematical expectation of the difference signal $J_1$.

Then the PM output signal is integrated over time $\tau_0$ with a radiation pulse emitted by the line source, the output signal is integrated over time $\tau_0$ after the luminescence of the line source has ended, and the difference between the integrals is determined:

$$J_2 = \frac{1}{\tau_0} \int_{0}^{\tau_0} [U_{s2} + U_{s1} + \xi(t)] dt - \frac{1}{\tau_0} \int_{\tau_0}^{\tau_0+\tau_1} \xi(t) dt.$$  

where $M[J_2] = U_{\Omega} + U_{s1}$. Then the difference $J_1 - J_2$ is measured, the factor $K_1$ is determined with a dummy solution introduced into the atomizer from the condition $M[J_1 - J_2] = 0$, and, finally, $M[J_1 - J_3] = U_{\Omega}$ is measured.

The proposed method for fluorescence-signal measurement with correction of the scattered radiation of the continuous source is based on the assumption of the possibility of substantial reduction of the effect of the low-frequency noise of the flame in steps c and d (see Fig. 2). It is natural to assume that fluorescence measurement will be optimal when $\tau_1 = 0$, but the design of the shutter that modulates the radiation of the continuous source does not permit a decay time $\tau_1$ of nearly zero to be obtained. In addition, minimization of $\tau_1$ considerably complicates the apparatus. Thus, in the proposed method, it is important to evaluate the dependence of the error of desired-signal measurement on the decay time $\tau_1$. We use the dispersion of the random signal $J_1$.  

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