

Obviously, in such a narrow range of concentrations of insoluble residue (95.0-98.5%) these methods cannot ensure the required accuracy in determining the specified factor (K). At the same time, the method of dielcometry is more sensitive to the ratio of crystalline and glassy phases in fused mullite. As Fig. 3 shows, ϵ falls and $\tan \delta'$ increases with a reduction in the amount of insoluble residue, which completely agrees with the position confirming the rise in $\tan \delta$ with increase in the amount of glass phase in the ceramic.

The greatest expenditure of time in determining the amount of insoluble residue in fused mullite by the dielcometric method is taken on constructing the calibration graph (see Fig. 3). In the presence of such relationships the method can be considered to be a rapid method of determining the amount of residue in the mullite in comparison with x-ray and IR methods.

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QUESTION OF DETERMINATION OF THE DISTRIBUTION OF ERRORS IN X-RAY

FLUORESCENT ANALYSIS OF NONMETALLIFEROUS RAW MATERIAL

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X-ray fluorescent methods of analysis of nonmetalliferrous raw materials are finding increasing use since they possess unquestionable advantages over other methods. They are very rapid and possess relative simplicity in their operations in conducting analyses and sufficiently high accuracy and sensitivity. However, the use of the x-ray fluorescent method in determining the components of a raw material with an atomic number of less than 20 is complicated as a result of increased requirements for identity of the analyzed samples with respect to density, dimensions of the particles of the investigated material, and surface quality. In addition, in making measurements in air, which to a significant degree weakens the characteristic radiation of light elements, there is an increase in the requirements for constancy of the geometric parameters of the measurements. There is also an increase in the requirements for stability of the power supply voltages of the x-ray apparatus.

We have conducted investigations on determination of the distribution of errors in x-ray fluorescent analysis of refractory clays for Al_2O_3 content for a BARS-1 crystalless x-ray analyzer.

The total mean-square deviation of the results of observations may be represented in the form

$$S = \sqrt{S_1^2 + S_2^2 + S_3^2 + S_4^2}, \quad (1)$$

where S_1 , S_2 , S_3 , and S_4 are the mean-square deviations of the results of observations caused by the random process of interaction of the x-ray radiation with the substance and of recording of the photons of the secondary radiation, the geometric factor of the measurements, the instability of the apparatus, and the method of preparation of the samples, respectively.

Depending upon the method of preparation of the samples the analyzed samples differ in density, surface geometry and surface finish, and dimensions of the material particles. In working with a thick emitting layer [1] a change in the thickness of the irradiated sample does not lead to a change in the intensity of the recorded radiation.

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To evaluate the contribution of each of the above factors to the total mean-square deviation of the observation results, N samples are prepared from the same powder. After a certain interval of time t_0 for each sample a single measurement of the intensity of secondary radiation is made. From the equation

$$S = \sqrt{\sum_{i=1}^N \frac{(n_i - \bar{n})^2}{N-1}} \quad (2)$$

(where n_i is the series of pulses for the i -th sample and $\bar{n} = \frac{\sum_{i=1}^N n_i}{N}$) is calculated the mean-square deviation of the results for N samples.

Let us designate $S_1^2 + S_2^2 + S_3^2 = S'^2$ and then

$$S_4 = \sqrt{S^2 - S'^2} = \sqrt{S^2 - \sum_{i=1}^N \frac{(n_i' - \bar{n}')^2}{N-1}} \quad (3)$$

where n_i' is the series of pulses for one of the N samples after the i -th transposition of it

$$\text{and } \bar{n}' = \frac{\sum_{i=1}^N n_i'}{N}.$$

In this case N measurements of the intensity are made for the same sample transposed each time before the measurement. The interval between the measurements is equal to t_0 , as in the preceding case.

To determine the contribution of the geometric factor of the measurements to the total mean-square deviation of the observation results, N measurements were made with the same time interval t_0 between measurements for the same transposed sample. If it is taken that $S_1^2 + S_3^2 = S''^2$, then, obviously,

$$S_2 = \sqrt{S'^2 - S''^2} = \sqrt{S'^2 - \sum_{i=1}^N \frac{(n_i'' - \bar{n}'')^2}{N-1}} \quad (4)$$

where n_i'' is the series of pulses of the i -th measurement of the untransposed sample and

$$\bar{n}'' = \frac{\sum_{i=1}^N n_i''}{N}.$$

The approximate determination of S_1 is calculated from the equation

$$S_1 = \sqrt{\sum_{i=1}^{N-1} \frac{(n_{i+1}''' - n_i''')^2}{2(N-1)}} \quad (5)$$

where n_i''' and n_{i+1}''' are the series of pulses for a fixed sample at the i -th and $(i+1)$ -th measurement, respectively.

In the latter case each successive measurement is made immediately upon completion of the previous one.

The contribution of instability in the power supply conditions of the x-ray equipment to the total mean-square deviation of the observation results is determined from the equation

$$S_3 = \sqrt{S''^2 - S_1^2} \quad (6)$$

Since complete separation of the mean-square deviations caused by instability in the power supply conditions of the analyzer and the statistical error is not possible, the value of S_1 calculated according to Eq. (5) will be somewhat too high and the value of S_3 too low.

Using the method given above we determined the distribution of errors in analyzing clay for Al_2O_3 content for two cases. In the first case the investigated material, first worn to a maximum particle size of 74 μm , was poured into 37-mm-diam. containers and smoothed out with a glass plate. In the second case the worn material was pressed with a force of 10^5 N into preforms of the same diameter. The length of a single measurement was 40 sec and the interval t_0 between measurements 10 sec.

Table 1 shows the distribution of the mean-square deviations of the observation results expressed in percentages of the total mean-square deviation, which is taken as 100%.

TABLE 1. The Distribution of the Mean-Square Deviations of Results of Observations of Refractory Clay Samples in Determination of Al_2O_3 *

Method of sample preparation	$S_1, \%$	$S_2, \%$	$S_3, \%$	$S_4, \%$	$S_5, \%$
Unpressed powder	4,3	13,8	15,1	66,8	100
Pressed powder	9,1	27,4	34,0	29,5	100

*BARS-1 analyzer, N = 10.

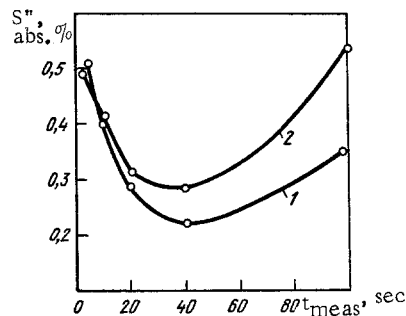


Fig. 1. The relationship of the error S'' to the measuring time t_{meas} : 1) N = 5; 2) N = 15. BARS-1 analyzer.

From the data presented it may be seen that in analyzing for light elements the primary source of errors is the quality of preparation of the samples and lack of identity of the geometric conditions of the measurements. The latter make a contribution to the total mean-square deviation of 55-80% depending upon the method of preparation of the samples. At the same time, while the total mean-square deviation for the unpressed samples is 1.3-1.5 abs.% with 15-40 wt.% Al_2O_3 in the clay, pressing makes it possible to reduce this deviation to 0.5-0.7 abs.%.

The mean-square deviation caused by the quality of preparation was 1.1 abs.% for unpressed samples but 0.2 abs.% for pressed ones.

The significant influence of sample preparation quality and measurement geometric conditions on analyzing for Al_2O_3 content in refractory clays may be explained by a number of reasons:

1. The measurements in air are made at short (2-5 mm) distances between the surface of the sample and the detector. In this case a change in density of the investigated material and also in the geometric conditions of the measurements (misalignment of the samples, change in distance between the sample and the detector) have a significant influence.
2. In air the characteristic radiation of light elements is strongly absorbed and even an insignificant change in the distance between the sample and the detector leads to a change in intensity of recorded radiation.
3. The requirements for surface quality of the analyzed samples are increased (roughness, uniformity in density and particle dimensions).
4. The working layer of the sample is 20-40 μm , and therefore even an insignificant amount of dust on its surface leads to a substantial distortion of the analysis results.

With pressing of a powder material better identity of the investigated samples with respect to density and surface quality is obtained as the result of pulverization of the powder in the surface layer of the particles.

A reduction in analysis errors for light elements is possible in making measurements in a strongly evacuated medium or in vacuum. In this case the measurements may be made with a greater distance between the sample and the detector, which leads to a reduction in errors caused by differences in the density and measurement geometric conditions of the samples.

Measurements for the purpose of determination of the light element content are characterized by a low increment of the intensity of the recorded radiation for the corresponding increment in concentration, as the result of which there is an increase in the requirements for stability of the power supply voltages and currents for the analyzer. The mean-square deviation caused by instability of the equipment and the random process of emission and recording of the radiation is 43.1% of the total mean-square deviation for pressed samples. Consequently, a further reduction in analysis error may be obtained with greater stabilization of the power supply voltages and currents of the analyzer or with the use of special methods making it possible to take a change in them into consideration.

Important parameters significantly determining the accuracy of the measurements are the length of a single measurement and the interval of time after which it is necessary to correct the power supply conditions of the analyzer.

The optimum measurement time is selected based on the requirements of the minimum mean-square deviation as the result of instability of the equipment with respect to time and the random process of emission and recording of the x-ray radiation.

Measurements were made on a single fixed sample with a constant interval of time between the measurements (Fig. 1).

The increase in the error with $t < 40$ sec and $t > 40$ sec may be explained by the increase in the statistical error and the error caused by instability in the equipment, respectively. The increase in the error with $N = 15$ is related to the increase in the range of changes in the power supply conditions of the analyzer for a specified interval of time. In practice the optimum time of measurements for each sample to correct the power supply conditions of the analyzer is selected based on relationships 1 and 2 (Fig. 1).

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