SOME CRITERIA FOR STANDARDIZATION IN LASER MICROSPECTRAL ANALYSIS OF MINERALS

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It is well known that microspectral analysis of minerals and rocks has a number of peculiarities that must be taken into account in order to achieve optimum reproducibility of the results [1-5]. In this paper, we investigate the interaction of laser radiation (LR) with minerals in order to select optimum operational regimes for the laser setup and to determine the criteria for standardization in laser local microanalysis.

Microspectral analysis of minerals was performed on the LMA-1 setup manufactured by the Carl Zeiss Company. To investigate different regimes of operation of the laser, an IKT-1m energy meter, a S8-9A storage oscillograph, a FÉU-22 photoelectronic multiplier, and filters were also used.

Up to now, standards made of natural materials are considered to be most preferable, since it is precisely these standards that have the set of physicochemical properties that are most similar to the properties of the specimens being analyzed. Homogeneous pieces of minerals are usually chosen for the standards and their chemical composition and degree of homogeneity are determined. The other most often used form of the standards are tablets [2, 3, 7], prepared from mixtures corresponding to the mineral being analyzed. The relative simplicity of the latter standard lies in the fact that it is not necessary to have a large homogeneous piece of mineral. Powder samples are selected by different methods, so that it is possible to discard "dirty" pieces of mineral and to control strictly the impurity elements. At the same time, both of these standards have a number of characteristic disadvantages, related with the complex structure of natural mineral individuals with syn- and epigenetic elements, having different physical properties and differing by their impurity composition [6] and the explosive nature of the fracture of tablets.

However, in choosing a specific procedure for preparing a standard, it is necessary to take into account not only the correspondence of the chemical composition of the standard to the specimen being analyzed but also the correspondence of a number of physical characteristics (for example, microhardness, thermal conductivity), as well as the correspondence of the interaction of laser radiation with the standard and the specimen being studied. In this case, it is necessary to take into account the dependence of the reproducibility of the results of microspectral analysis on the mutual orientation of the crystallographic axes of the specimen (mineral being studied or standard) and on the parameters of the laser radiation and of the electrical discharge. As experiments show [9], the form and the dimensions of craters differ considerably for different orientations of the specimen (with the remaining parameters of the experiment remaining constant). Tablets do not have anisotropic physical properties, so that when using them as standards, this dependence need not be taken into account.

The interaction of laser radiation with minerals does not easily yield to theoretical calculations, so that in determining the optimum regime for operation of the laser setup, the use of empirical data and some assumptions, related with the specific properties of the object being studied, is justified. This sometimes permits including its properties against one or another topoanatomic background, performing correct comparisons between the data obtained and the genesis of the mineral [9], and improving and searching for new methodological analytical techniques.

In examining the reproducibility of local laser microanalysis, it makes sense to use the concept of specific energy of laser breakdown of minerals L_b together with the latent energy of vaporization and melting L_o. This is due to the fact that for minerals it is dif-

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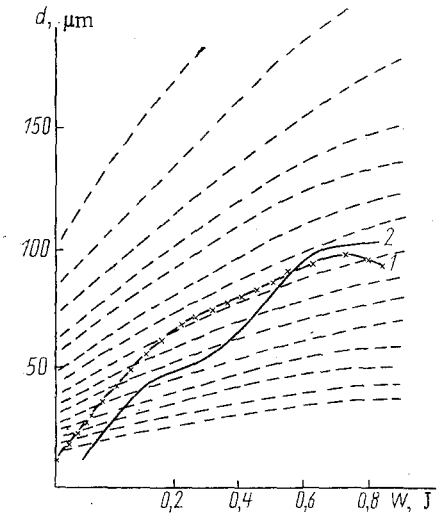

Fig. 1

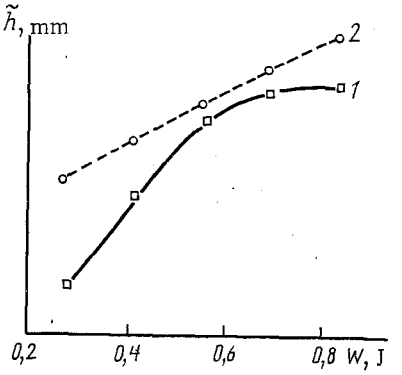

Fig. 2

Fig. 1. Family of characteristic curves showing the dependence of the diameter of the crater as a function of the pulse energy for copper (1) and magnetite (2).

Fig. 2. Flame height for a single crystal (1) and standard tablet (2) of magnetite as a function of the laser radiation energy.

ficult to determine L_0 in a pure form, since natural objects are distinguished by their extreme heterogeneity. The inhomogeneity of minerals is one of the reasons for the dependence of the specific energy of laser breakdown of natural objects on the change in the energy of the laser pulse. For this reason, using the relation in [8] and examining instead of the latent energy of melting and evaporation (L_0), the specific energy of laser breakdown (L_b), it is possible to obtain a relation that determines the diameter of the crater d:

$$d = 2\sqrt[3]{r_0^3 + \frac{3W \operatorname{tg}\gamma}{\pi L_b}},$$

where W is the energy of the radiation in the laser pulse; L_b is the specific energy of breakdown of the mineral, r_0 is the initial radius of the spot; and γ is the angle of the converging beam.

As a rule, $\tan\gamma = 1$, while $r_0 \ll d$, so that we have

$$d \approx 2W^{1/3} \cdot L_b^{-1/3}.$$

This assumption allows us to construct a family of curves (dashed lines in Fig. 1) showing the dependence of the diameter of the crater on the laser radiation energy and different values of the specific energies of breakdown $L_n = \frac{1}{n} L_b$, where n is some number. For L_b, we can take the breakdown energy of natural copper, since its experimental curve practically coincides with the curve from the family of characteristic curves. This coincidence indicates that the breakdown energy of a mineral L_M is constant and equals the value of L_n in the range of variation of the laser energy being examined. The crossing of the computed curves by the experimental curves from bottom to top indicates that the specific energy of breakdown of the mineral decreases with increasing laser pulse energy. This can occur, for example, due to an increase in the fraction of the melt. If, on the other hand, the experimental curve intersects the characteristic curve from top to bottom, then this means that the breakdown energy of the mineral increases. This could be due to the increase in the fraction of evaporation, absorption of laser energy by the plasma cloud, or the appearance of shock waves. Having a family of such curves and knowing the real diameter of the crater, for well-defined energy of the laser radiation, it is possible to estimate the relative energy of breakdown of the mineral and the relative magnitude of the density of the plasma formed. Such an analysis of the experimental curve showing the dependence of the diameter of the crater for the mineral against the background of the computed curves permits determining the range of values of laser energies (or pumping intensity) for performing the analysis. Thus, curve 1 (Fig. 1)

shows that the specific breakdown energy of copper begins to increase at a pulse energy of 0.7 J, which naturally affects the amount of evaporating material. This means that the optimum pulse energy for microanalysis of natural copper may be taken as 0.65-0.75 J, where absorption of laser radiation by the plasma is apparently still absent.

A more complicated picture of the dependence of the dimensions of the crater on the laser energy is observed in magnetite (Fe_3O_4) (Fig. 1). The curve for this mineral can be arbitrarily separated into four sections, which, apparently, correspond to the following:

surface breakdown;

volume breakdown with insignificant melting, when L_M is constant;

volume breakdown with a large amount of melt displaced with decreasing specific breakdown energy;

increasing L_M.

Thus the optimum laser pulse energy for microspectral analysis of magnetite may be taken as 0.60-0.65 J, where L_M is constant for magnetite. The dimensions and form of the crater determine the parameters of the plasma forming with laser evaporation of the mineral, on whose characteristics the quality of the microspectral analysis, in its turn, depends. Investigations showed that the height of the flame depends approximately in the same way on the laser radiation energy as the diameter of the crater. Thus, for magnetite, the height of the flame reaches its maximum value at a pulse energy of 0.65 J (Fig. 2), which coincides with the maximum diameter of the crater. Thus the laser radiation energy 0.6-0.65 J can be determined from two indicators: constancy of the crater and the height of the flame.

The reproducibility of the local analysis, as practice shows, also depends considerably on the zone of circumcrater breakdown and changes which are apparently determined by the dimensions of the individual elements of the anatomical structure of the mineral individual: sectors, subindividuals, sections of recrystallization, etc. [8, 9]. We include in the concept of a breakdown zone the change in the mechanical properties, chemical composition, and electrical and other properties of the mineral. To determine the localizability of the method, it makes sense to introduce the concept of coefficients of surface (K_S) and volume (K_V) breakdown. These coefficients show the number of times by which the area (volume) with the altered properties S_{max} (V_{max}) exceeds the area of the orifice of the crater S_{cr} (volume V_{cr}):

$$K_S = S_{max}/S_{cr};\ K_V = V_{max}/V_{cr}.$$

Investigations of the dependence of these coefficients on the magnitude of the laser radiation energy show that they are constant over a wide range of radiation energies. It was found in the experiments that for natural copper K_S = 16, K_V = 50; for sphalerite K_S = 11, K_V = 35. The value of the crater parameter and of the coefficient of breakdown permit determining the dimensions of the circumcrater halo of changes and thereby the actual localizability of the microspectral analysis of the given mineral. If the dimensions of the grains investigated or of the homogeneous sections are less than S_{max} and V_{max}, then it is difficult to achieve reproducibility of the forms and dimensions of craters, and thereby also reproducibility of the spectral line intensities. It is especially important to take these coefficients into account in analyzing natural objects, which are distinguished by their exceptional heterogeneity.

Investigations of the morphological properties of craters [9] against an established topoanatomic background and a comparison of the results of spectral analysis show that there are elements of the anatomical structure which, under the action of laser radiation, produce a plasma with high and low density. The first group of anatomical elements includes recrystallized and little-deformed sections, zones of growth with low porosity, regions where habits change, regions of regeneration, etc. The second group includes porous zones, sections of leaching porosity, boundaries of growth pyramids, twins, subindividuals, regions of development of plastic deformation, etc.

The results of the local analysis also depend on the crystallographic orientation of grains and the nature of the section of the anatomical elements of the individual and their orientation relative to the direction of the pulsed discharge or the optic axis of the spectral instrument. To obtain a large signal, porous zones must be oriented perpendicular to the discharge. All of this complicates the microspectral analysis of minerals, and at the same time makes the results much more informative.

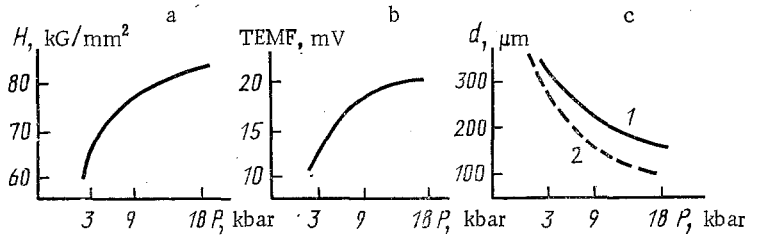

Fig. 3. Nature of the changes in the hardness (a), thermoelectromotive force (TEMF) (b), and the diameter of the crater (c) as a function of the pressure applied to the tablet: 1) PbS, 2) Fe_3O_4.

Thus the effect of physical inhomogeneities and anatomical peculiarities of crystals and aggregates on the reproducibility of spectral line intensities makes it inadvisable to use natural materials as standards.

As standard, it is possible to use tablets prepared from the powder of the pure mineral with appropriate additives. Such tablets must have minimum porosity, the dimensions of the grains of the powder, from which they are prepared, must not exceed several micrometers, the tablets must be mechanically strong and, in this case, adhesive fillers cannot be used.

These requirements are met by tablets prepared under adequate pressure, which can be determined from the changes of some physical properties of the minerals. For example, the magnitude of the hardness and the thermoelectromotive force of galena tablets increase with increasing pressure applied to the prepared tablet (Figs. 3a and b). The diameter of the crater, in this case, decreases and attains dimensions that are characteristic of the natural specimen (Fig. 3c). The compressibility of the tablet varies analogously to the hardness and the thermoelectromotive force [10]. Investigations showed that for minerals such as galena, sphalerite, and magnetite, an adequate pressure is 17-20 kbar.

The presence of laser melting is the criterion for the applicability of tablets as standards. Melting to some extent nullifies the lack of correspondence between the tablet and the mineral. If the composition of the tablet is chosen so as to correspond to the composition of the mineral being analyzed, i.e., a large difference in their chemical compositions is not permitted and an adhesive is not introduced, then the properties of the melts formed by the tablet and by the mineral will be identical. At high temperatures, adhesive components separate out in the form of gases, thereby destroying the identity between the fusion and evaporation processes in the tablet and in the mineral.

Standard tablets, prepared taking into account these requirements, were used to analyze magnetite. Relatively pure magnetite, not containing vanadium and nickel, was first ground into a powder. Vanadium and nickel oxides were added to the powder. After this, the mixture obtained was ground in an agate mortar until the dimensions of the grains reached 1-3 μm. Subsequent dilution was used to obtain mixtures with composition 1, 0.6, 0.3, 0.1, 0.06, 0.03, and 0.01%. These mixtures were then compressed under a pressure of 20 kbar. The thickness of the tablets in our case equaled 0.5-1 mm. The reproducibility of the diameters of the craters for such tablets was 3-4%. It should be noted that the iron line intensities in the analysis of the tablet are 10% higher than the intensities obtained in analyzing the mineral.

In the analysis of magnetite, the spectra were recorded on type 22 aerial photography film with a light sensitivity of 1500 GOST units. We determined the laser radiation energy required for the analysis from the dependence of the crater diameter in magnetite on the changes in the laser radiation energy. A range of energies was chosen on the background of the family of curves (Fig. 1) with minimum dependence of the diameter on variations of the laser radiation energy. In our case, this equaled 0.65 J. The slit width of the spectrograph was 30 μm, the distance between the electrodes was l = 1 mm, the height of the electrodes above the specimen was 0.6 mm, and the voltage on the carbon electrodes was 3.2 kV. These operating conditions permitted successful quantitative determination of the content of vanadium in the range 0.01-0.6% and of nickel in the range 0.03-0.7%, which is almost an order of magnitude greater than the results obtained in [4]. The errors in determining the nickel and vanadium content were w = 13 and 9%, respectively.

Experiments on the microspectral analysis of minerals with laser sampling of the specimens show that when using natural specimens as standards, it is necessary to take into account an extensive range of characteristics of the interaction of the laser radiation:

effect of the anatomical peculiarities of the crystal of the mineral,

mutual orientation of the elements of inhomogeneity of the crystal and of the laser radiation;

inclusion of inhomogeneities of a higher order than the localizability of the method.

The identity of craters, of the morphology of circumcrater damage and of the pyrogenic substances of the standard and of the specimen being studied can be viewed as a criterion for the suitability of the natural specimen for use as a standard in laser microspectral analysis.

The dependence of the results of microspectral analysis on the influence of the physical inhomogeneities and anatomical peculiarities of crystals and their aggregates make widespread use of natural minerals as standards inadvisable.

Tablets, prepared from the powder of the pure mineral with appropriate additives under a pressure of the order of 20 kbar, can be used as standards in laser microspectral analysis of minerals. Tablets do not exhibit physicochemical anisotropy, which decreases the errors due to the analysis of the standard itself.

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