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THE DESCRIPTION OF DISTRIBUTION OF MICROELEMENTS WHEN A PART OF RESULTS LIES BELOW THE LIMIT OF DETERMINATION

(Fig. 1—2)

Abstract: The knowledge of average content and its dispersion for characteristic trace elements in a set of samples is necessary for the geochemical characterization of a given type of geological material. The content of elements to be analysed lies usually in a part of samples below the detection limit of the applied analytical method. This makes impossible a direct calculation of the mean value, as well as of the dispersion of the investigated contents. The problem has been till now approached more or less conventionally. The present work gives an axact method how to estimate these parameters. The method is based on the lognormal distribution of trace elemens in geological materials.

Резюме: Для геохимической характеристики совокупности образцов данного типа надо знать среднее значение и рассеяние содержаний типичных микроэлементов. Содержание определяемых элементов находится обычно в части образцов ниже уровня определения данного аналитического метода. Это препятствует прямому исчислению среднего значения и рассеяния исследованных содержаний. До настоящего времени употребляемые решения этой проблемы, более или менее конвенциональны. В предлагаемой работе описан экзактный метод определения этих параметров выходящий из логарифмически нормального распределения микроэлементов в геологических материалах.

Reliable analytical results describing the content of both, macro and microelements form the basic condition for the geochemical study of distribution of elements in geological materials.

These values obtained in a given set of samples serve for the calculation of parameters like the arithmetic, resp. the geometric mean corresponding standard deviations, correlation and regession coefficients, histograms of frequency distribution etc. used in the statistical analysis. Whereas the statistical informations and parameters describing the distribution of macroelements can be gained without any considerable problems, at the mathematical statistical description of the data for the microelements, it is necessary to take in account in the studied set of samples also the presence of results lying below the limit of determination of the used analytical method. In this case we have to do with analytical results currently signified as "not detected", or "less than".

These results are in the statistical treatment often replaced by a conventionally choosen real number corresponding to a given part of the limit of determination. In spite of the fact that this procedure is not correct from the point of view of statistical analysis it has been currently used especially in the treatment of analytical results for geochemical purposes, where it can provide informations which do not correspond to the real concentration distribution of elements in the considered set of samples, as well as it provides less reliable

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informations concerning the arithmetic and geometric mean. J. A. Tkachev and J. E. Yudovich (1975) made notice of this problem and proposed its solution under the condition of normal (gaussian) distribution of concentrations of the studied elements.

Similar problems emerged in the treatment of analytical data, a part of which laid below the limit of determination of the used analytical method. The study of magnesites of different genetic types from West Carpathians (E. Martiny, I. Rojkovič, 1977). The contents of following elements: B, Ba, Co, Cr, Cu, Mn, Ni, Sr, Ti and V were determined in the studied types of magnesites spectrochemically using the method described by J. Medveď, J. Kubová, E. Plško (1979).

The distribution of microelements can be sufficiently described by the logarithmic normal distribution, as it was showed by L. H. Ahrens (1954) and confirmed also by other authors (S. Ďurovič, 1959; E. Plško, 1973). From the mentionned reason, the procedure by J. A. Tkachev and J. E. Yudovich (1975) cannot be directly used.

The calculation of arithmetic and geometric mean on the basis of logarithmic normal distribution from not complete histograms of the frequency of the content of cobalt in magnesite samples from the locality Bankov can serve as exemple for the application of the proposed procedure.

As it can be seen from Fig. 1a, the content of cobalt lies in a considerable part of samples below the limit of determination of the used method i. e. below 4 ppm (log 4 = 0,6). The frequency of these values is presented in the hatched open interval. It is clear that the mean value and deviation cannot be determined directly from such a set of results. For the determination of the needed parameters it is therefore necessary to proceede as follows.

The cumulative normalized frequency distribution Φ (*t*) of a randomly distributed value (*x*) can be described in the range from $-\infty$ to *t* by the following equation:

$$\Phi\,(\mathrm{t}) = \frac{1}{\sqrt{2\,\pi}} \int_{-\infty}^{\mathrm{t}} \hat{\mathrm{e}} - \frac{\mathrm{x}^2}{2}\ .\ \mathrm{dx} \tag{1}$$

The solutions of the equation (1) for different values of parameters are tabulated. The values of the inverse function Ψ (*x*) are tabulated, too (Van der Waerden, 1965).

In the case of a logarithmic normal distribution, instead of the standard deviation "σ", the parameter "λ" is used (E. Plško, 1973). To determine the interval in which the corresponding percentage of all results occurs, the geometric mean is multiplied, resp. divided by λ. As the input the "*x*" — value serves then the logarithm of the value of concentration. For the sake of simplicity, in the following text only: logarithm of concentration.

For the processed set of results the percentage of results lying below the limit of determination corresponds to the cumulative frequency for the intervall from the $-\infty$ (the logarithm of the zero concentration) up to the limit of determination. For this frequency the corresponding t_0 value is obtained from the tables of inverse function Ψ (*x*) in relative standard deviation units.

The remaining numerically described logarithms of concentration above the limit of determination are classified in classs with equal intervall $\Delta log\ C$ so that the logarithm of the limit of determination is taken as the beginning of the first class. The intervall of classes is chosen in a manner that the total amount of classes (i. e. also with classes containing the results characterised as "less than") does not exceed the value equal to $2. \sqrt[3]{n}$, where n is the amount of samples. The amount of results (the frequency) in the first class is added to the amount of results ("frequency") characterised as "less than" and the corresponding cumulative frequency (percentage) of samples is calculated. The t_l value for the cumulative frequency in the interval from $-\infty$ up to the logarithm of the concentration of the upper limit of the first class is determined from the tables of the function $\Psi\ (x)$. For the following classes it is proceeded in similar way.

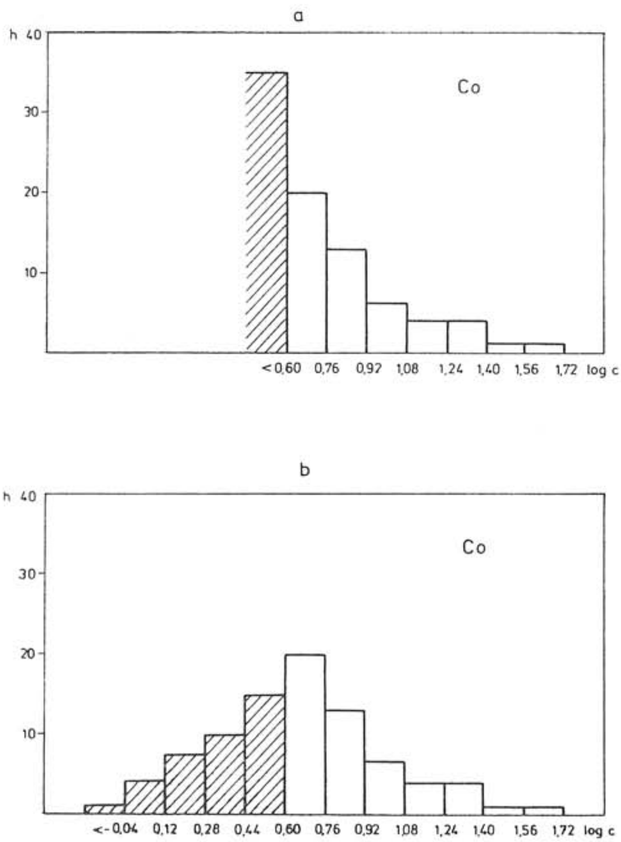

Fig. 1a. Observed frequency (h) distribution of cobalt concentration (ppm). The results lying below the limit of determination are presented in an open intervall. — 1b. Frequency (h) distribution of cobalt concentration (ppm) containing values calculated from the results lying below the limit of determination.

The obtained t – values are plotted graphically in the dependence on the logarithms of concentrations corresponding to the limits of the classes. The graphical representation of this dependence is shown for the mentionned case of Co – concentration in magnesites in Fig. 2. Apart from the described numerical – graphical procedure, the mentioned dependence can be constructed advantageously also using the so called probability papers.

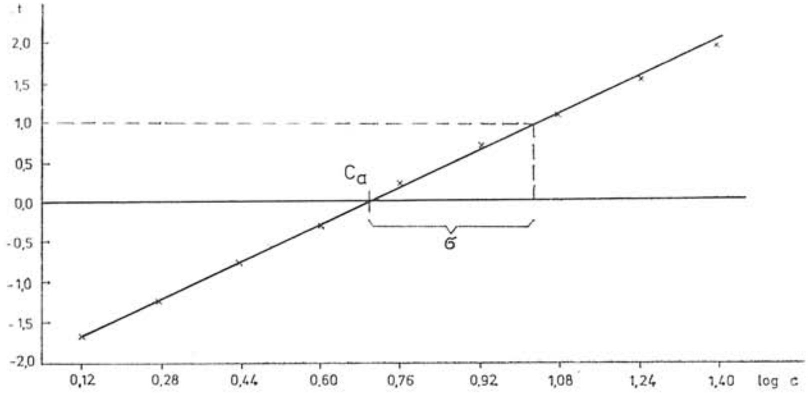

Fig. 2. The dependence of the multiple *(t)* of standard deviation on the logarithm of the concentration.

The linear course of the dependence of t on the logarithm of the concentration proves the applicability of the logarithmic normal model to the frequency distribution of the cobalt content in the stutied type of magnesite.

From the definition of t – value, representing the relative standard deviation, the mean value of log c can be determined at the value $t = 0$ and the $log\ C \pm \sigma$ at the value $t = \pm 1$ (resp. $log\ C \pm 2\sigma$ at $t = \pm 2$, etc.). This anables to determine the parameters of the given logarithmic – normal distribution, where C_g is the geometrical mean of the concentration in question and is the standard deviation.

The arithmetic mean of concentration C_a can then be calculated using the formula:

$$log\,(C_a) = \frac{ln\ 10}{2}\,\sigma^2 + log\,(C_g)$$

The determined mean value of the logarithm of the concentration and the standard deviation enable then the estimation of the distribution also for the samples contained in the open interval ("less than") as it is shown in Fig. 1b. For the sake of objectivity, this figure is placed below the original histogram. The histogram calculated in the described manner proves the lognormal concentration distribution of the studied element. This statement is important in the geochemical study for the evaluation of the uniform genesis of the given set of samples.

The concentrations of other elements analysed in magnesites from different localities were evaluated in similar way. On the basis of the obtained results, the classification of element associations characteristic for individual genetic types of the studied magnesites was possible (E. Martiny, J. Rojkovič, 1977).

Apart from the mentionned application, the proposed statistical procedure can be used also for the calculation of clark values, as well as for the solution of different practical questions e. g. in the exploitation of mines, when sometimes the deposit of rare elements, contained only in very small concentrations in the ore must be estimated.

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