

# Influences acting on the distribution of spectrochemical results

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On the basis of the study of experimentally determined distributions of logarithms of analytical spectral line intensity and reference spectral line intensity nearly gaussian distribution of the differences ( $\Delta Y$ ) is obtained also in spite of nonnormal but similar distributions of both original values. As a consequence a lognormal distribution of concentration values determined spectrochemically using an internal reference element is obtained.

Изучение экспериментально найденного распределения значений логарифма интенсивности ( $Y$ ) аналитической спектральной линии и линии внутреннего элемента сравнения показало, что даже в случае, когда их распределение не носит нормальный характер, а некоторый асимметричный, но аналогичный, рассеяние их разницы ( $\Delta Y$ ) приближается к нормальному распределению. Следствием этого обстоятельства является нормальное логарифмическое распределение значений концентраций, которые определены спектрохимическим методом с использованием внутреннего элемента сравнения.

Owing to relatively lower precision of quantitative spectrochemical analytical results as compared with classical analytical procedures, as well as relatively short time necessary for repeated measurements to be performed, the spectrochemical results of the determined concentration represent usually the mean value from results of several times repeated measurements. This situation has led to the circumstance that the statistical evaluation of spectrochemically obtained results has been advantageously performed already for a long time [1—5].

The arithmetical mean of results of several determinations was originally estimated as the most probable value without any particular study of their distribution. *Ahrens* [6] as the first paid attention to the possibility of a better description of spectrochemically determined concentration values taking into account the lognormal distribution. According to *Doerffel* [7], the lognormal distribution must be taken into account in the analysis of very low contents (trace analysis), in observations of a very broad concentration range, at very great random errors and at time measurements. The mentioned author does not give any detailed

explanations of this statement. The given enumeration is to be completed by the statement that lognormal distribution describes better random changes of all quantities (*e.g.* concentration, time) which can accept only positive values. *Mika* and *Török* [5] see the cause for the lognormal distribution of spectrochemically determined concentration values in the Lomakin – Scheibe equation [8, 9]. According to it the logarithm of the relation of the analytical line intensity to the reference line intensity is proportional to the logarithm of the relative concentration of the element to be determined. However, this is only one of conditions for the appearance of experimentally proved [10] lognormal distribution of concentration values obtained by spectrochemical analysis. As a matter of fact, this condition concerns only the linearity of the transformation of the first quantity into the second. A further condition for the lognormal distribution of concentrations is the normal (gaussian) distribution of  $\Delta Y$  values.

*Urusov* [11] finds the appearance of such a distribution in the application of the difference of two similar asymmetric distributions, but he does not give any detailed description of the experimentally obtained distributions. The causes leading to this distribution are dealt more comprehensively in the presented paper.

### Experimental

A mixture of spectrally pure  $MgCO_3$  and  $Li_2CO_3$  in the ratio 3:1 was used as a matrix for the repeated taking of spectra. Carbon powder containing 0.1% Pd and 0.1% Ge in the form of  $(NH_4)_2PdCl_4$  and  $GeO_2$  was mixed with the matrix in the ratio 1.5:1. Spectra were taken under the following conditions:

Spectrograph	PGS-2 (Zeiss, Jena)
Grating	651 lines/mm, blaze 300 nm
Order	first
Spectral range	210–390 nm
Slit width	0.020 mm
Imaging	3 lenses, intermediate diaphragm 3.2 mm
Electrodes	SU-304/SU-201, Elektrokarbon, Topolčany
Electrode gap-length	4 mm
Excitation	D.C. arc, 6 A, anodic polarization of the carrier electrode
Exposure	120 s
Photographic material	ORWO WU-3
Developing	ORWO R 09; 1:20; 5 min, 20°C
Microphotometer	Zeiss, Jena, -4 Dptr., slit 0.2 mm

The taking of spectrum was repeated 95 times. The blackening of the following lines was measured: Pd I 311.404 nm (4.94 eV) and Ge I 265.118 nm (4.85 eV). The blackenings were transformed to  $Y$  values using emulsion calibration curves plotted for the wavelength

range about 260 and 310 nm by means of a preliminary curve [12]. The preliminary curve was constructed from spectra taken through a two-step filter, the filter constant of which was measured at the given wavelengths by the procedure described in [13].

## Results and discussion

The  $Y$  values of the used line of Ge as well as Pd were ordered according to their values in classes and then plotted on histograms presented in Fig. 1 and 2.

As seen an asymmetric distribution having the mode ( $M$ ) greater than the arithmetic mean ( $\bar{Y}$ ) (Table 1) is obtained in both cases.

This type of distribution (for the blackening values which represent a linear function of  $Y$  values only in the linear part of the emulsion calibration curve) is called by *Urusov* [11] antilogarithmic and its origin has been explained by the normal distribution of  $1/a$  values ( $a$  = transmission). The causes of the normality of the last distribution have not been further followed.

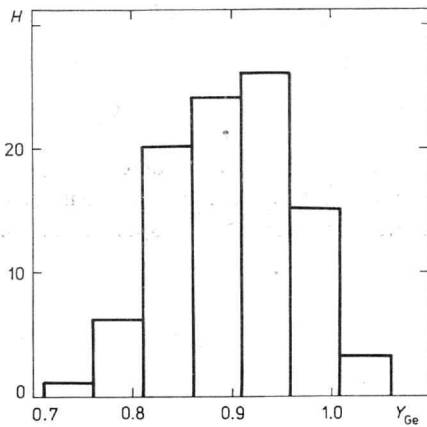


Fig. 1. Histogram of the distribution of  $Y_{Ge}$  values.

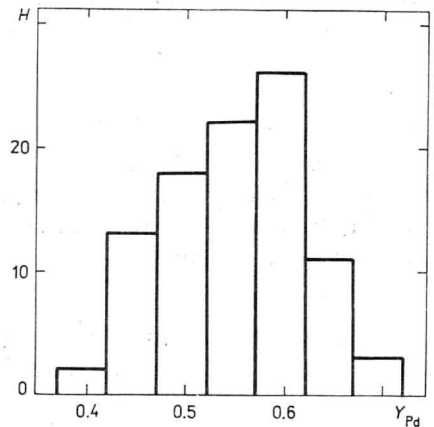


Fig. 2. Histogram of the distribution of  $Y_{Pd}$  values.

Table 1

Parameters of the individual distributions

	$M$	$\bar{Y}$	$s_Y$	$q$
$Y_{Ge}$	0.935	0.901	0.064	-9.02
$Y_{Pd}$	0.595	0.549	0.070	-8.00
$\Delta Y_{Ge-Pd}$	0.352	0.349	0.039	+1.36

$M$  — modulus,  $\bar{Y}$  — arithmetical mean,  $s_Y$  — standard deviation,  $q$  — skewness.

We studied comprehensively the distribution of blackening values of spectral lines [14, 15] and proved that the origin of the distribution having the mode greater than the arithmetic mean had to be seen in the radial wandering of the discharge. As a consequence of that effect the higher intensity values (and so also of blackenings) of spectral lines corresponding to the burning of the discharge in the proximity of the optical axis occur more often, whereas smaller values occur at the rarer sidewise burning of the discharge. This effect was proved by the placement of the discharge into the Ulbricht's sphere, where the influence of the radial wandering of the discharge was eliminated [16]. The microphotometric measurement of the blackening of spectral lines can additionally contribute to the nonnormal distribution having the mode greater than the arithmetic mean [17]. Therefore it is correct to consider the last distribution instead of the antilogarithmic one.

In accordance with the logarithmic presentation of the Lomakin—Scheibe equation ( $A$ ,  $b$  are constants)

$$Y = A + b \log c \quad (1)$$

a similar asymmetric distribution of  $\log c$  values having the mode greater than the arithmetic mean is obtained if the evaluation is made by using  $Y$  values. An exact mathematical description of this distribution is rather difficult. Under the given conditions no reliable conclusions can be therefore drawn concerning the type of the distribution of concentration values.

The method of internal reference element represents the case when the difference of logarithms of analytical spectral line intensity and reference spectral line intensity is used as experimental entrance value. Let us now follow this method which is practically exclusively used in spectrochemical analysis. In our case  $\Delta Y = Y_{\text{Ge}} - Y_{\text{Pd}}$ .

The difference of two randomly chosen elements from one population of any (also unsymmetric) frequency distribution will obey the normal (gaussian) distribution, as it follows from its statistical mathematical analysis. As a matter of fact it means that the frequency distribution of  $\Delta Y$  values will be as near to the gaussian as much the distribution of  $Y_{\text{Ge}}$  values will be near to the distribution of  $Y_{\text{Pd}}$  values.

The analogy of the type of a distribution — in both cases we have to do with an asymmetric distribution the mode of which is higher than the arithmetic mean — can be judged according to their standard deviation ( $s$ ) and skewness ( $\rho$ ) estimated by means of the following formulas

$$s = \pm \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (2a)$$

$$Q = \frac{\sum_{i=1}^n (x_i - \bar{x})^3}{nS^3} \quad (2b)$$

The obtained results are in Table 1.

The equality of standard deviations for  $Y_{Ge}$  and  $Y_{Pd}$  can be proved by the  $F$  test. The experimental  $F$  value is

$$F_{\text{exp}} = \frac{7.00^2}{6.45^2} = 1.18 \quad (3)$$

The theoretical value for the significance level of 95% and 95 repeated measurements in the numerator as well as in the denominator is equal to  $F = 1.40$  [18]. The experimental value is smaller than the theoretical one. It means that the one deviation agrees significantly with the other also in the case of stochastic independence of both populations. In accordance with a considerable negative  $Q$  value (Table 1), the skewness of both distributions has a similar character with the mode higher than the arithmetic mean. The  $\Delta Y$  values are, however, distributed

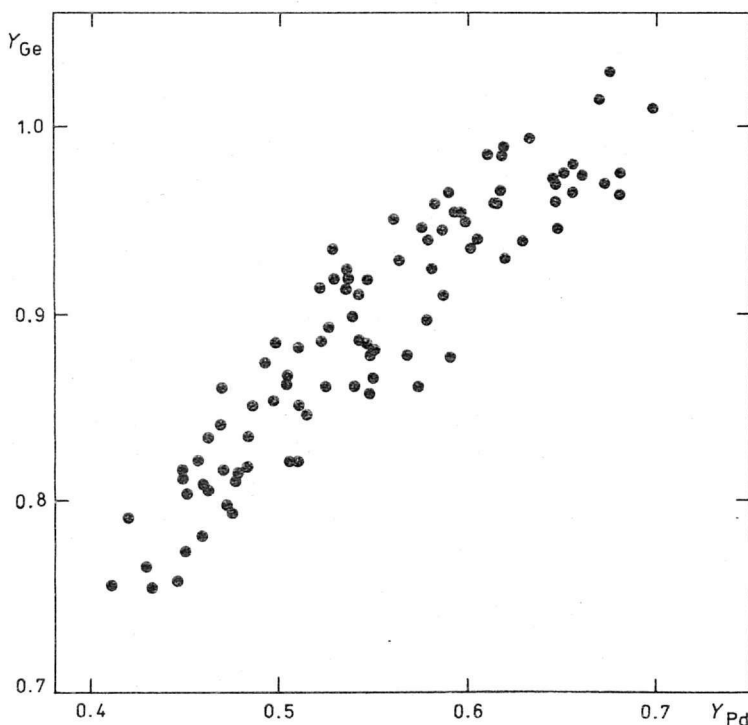


Fig. 3. Scatter diagram of  $Y_{Ge}/Y_{Pd}$  values.

practically symmetrically, as it follows from the small  $g$  value. Their distribution can be accepted with sufficient accuracy as normal.

Beside that the  $Y_{Ge}$  and  $Y_{Pd}$  values show a correlation as it can be seen from the scatter diagram [19, 20] in Fig. 3. The orthogonal regression coefficient of the scatter diagram is near to unity. It is in agreement also with the above-mentioned equality of the standard deviations. It means that the  $\Delta Y$  values have to be practically normally distributed [21] and their standard deviation will be small. The histogram of the distribution of  $\Delta Y$  values in Fig. 4 proves the expected result. The mode of the  $\Delta Y$  values distribution equals practically their arithmetic mean. The corresponding parameters of the  $\Delta Y$  distribution are listed in Table 1, too.

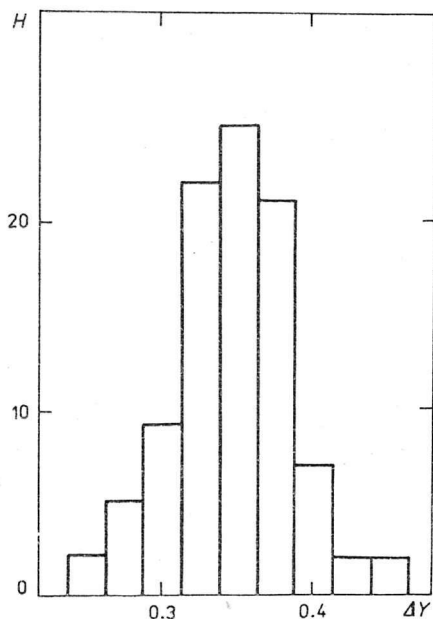


Fig. 4. Histogram of the distribution of  $\Delta Y_{Ge-Pd}$  values.

According to eqn (1) written for the case of the application of an internal reference element, the  $\log c$  values will be distributed equally as the  $\Delta Y$  values, *i.e.* normally. The concentration values will be then distributed lognormally. It means that the geometrical mean has to be calculated as the most accurate from parallel spectrochemical results.

On the basis of the performed study the lognormal distribution of spectrochemically determined concentrations is then a consequence of the normal distribution of  $\Delta Y$  values. As a matter of fact the differences can principally accept values in the whole range of negative as well as positive figures. At the same time each of the  $Y$  values in question can be distributed nonnormally (unsymmetrically) but the character of both distributions has to be similar, which condition is fulfilled in the majority of practical cases.

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