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CONTRIBUTION TO SAMPLING PROCEDURE OF GOLD-BEARING GEOLOGICAL MATERIALS

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If the gold particles in material to be analyzed are distributed homogeneously and follow the Poisson law, the sample weight necessary for analytical work can be easily estimated using the sampling constant according to Ingamells. With gold particles distributed heterogeneously, Visman's equation are used for the same purpose. In the present paper both approaches are described and their practical use is shown on two gold-bearing ores, one with homogeneously and the other with heterogeneously distributed gold particles.

Introduction

Taking a representative analytical sample is easy with homogeneous systems, such as solutions, gas mixtures, glasses or some alloys. Difficulties are encountered when sampling solid materials that consist of heterogeneous mixtures of minerals differing in particle size, density, hardness and chemical reactivity.

In practice, guidelines concerning the weight of the original material in respect to its natural heterogeneity are given, see e.g. Ref [1]. The material is crushed, ground and pulverized to the analytical grain size with concomitant comminution of the bulk. The final step of the processing is the homogenizing of the powdered sample with aim to attain random distribution of the particles of the macro- and microcomponents. The distribution of the particles is then described by the binomial or Poisson law. Such samples are considered to be satisfactorily homogeneous in spite of the fact that individual subsamples may differ somewhat in their composition showing the "remaining heterogeneity" which cannot be removed because of its random character. Practically homogeneous analytical samples can be prepared only if all the mineral phases are finely pulverized. This condition is difficult to fulfil with materials containing particles of gold, platinum metals, metallic iron, droplets of mercury etc. These metals are ductile, and in addition their densities differ greatly from that of the matrix substance. Such materials become segregated, the subsamples show pronounced heterogeneity and the distribution of the particles does not follow the Poisson law.

Theoretical

Error of Analytical Result as Function of the Error of the Analytical Method and the Heterogeneity

The overall variance of the analytical result s^2 has at least two contributions: variance s_{an}^2 caused by the analytical method and variance s_{het}^2 resulting from the heterogeneity of the component to be determined. For s^2 the following equation holds [2]

$$s^2 = s_{an}^2 + s_{het}^2 + 2\operatorname{cov}(x_{an}x_{het}), \tag{1}$$

where $\operatorname{cov}(x_{an}x_{het}) = \sqrt{s_{an}^2 s_{het}^2}$. In most cases the influence of the heterogeneity of the component is negligibly small in comparison with the error of the analytical method ($s_{het}^2 < s_{an}^2$), so the overall variance of the analytical procedure is given practically only by s_{an}^2.

For the quality control of routine analysis of various components the maximum admissible relative standard deviations $v_{\max}$ have been proposed. Thus for the determination of gold in the concentration range from 1 to 10 ppm the following relationship was derived [3]

$$v_{\max,\mathrm{Au}} = 22c^{-\frac{\log c + 2.67}{\log c + 8.42}} \tag{2}$$

In trace analysis the influence of the heterogeneity of the microcomponents may become pronounced to such extent that it is decisive for the overall variance of the procedure. For more precise results of such a procedure the heterogeneity of the material must be improved, i.e. a greater weight of the sample should be taken for analysis or the material should be pulverized to a finer grain size.

If the standard deviation of the heterogeneity of gold is expressed in number of particles ($S_{het,\mathrm{Au}}$, particles), then according to the Poisson law $S_{het,\mathrm{Au}}$ approximately equals the second root of N_{Au}

$$S_{het,\mathrm{Au}} \doteq \sqrt{N_{\mathrm{Au}}} \tag{3}$$

where N_{Au} is the number of gold particles. For the relative standard deviation of the heterogeneity we have

$$v_{het,\mathrm{Au}}(\%) = 100\frac{\sqrt{N_{\mathrm{Au}}}}{N_{\mathrm{Au}}} = \frac{100}{S_{het,\mathrm{Au}}} \tag{4}$$

Sampling Homogeneous Materials

The number N_{Au} of gold particles is directly proportional to the sample weight

$$N_{\mathrm{Au}} = a_{\mathrm{Au}}w \tag{5}$$

where a_{Au} is the number of gold particles in a one-gram sample. Inserting N_{Au} into Eq.. (4) and rearranging it, we obtain

$$v_{het,\mathrm{Au}}^{2}w = \frac{10^4}{a_{\mathrm{Au}}} = const = K_{s,\mathrm{Au}} \tag{6}$$

where $K_{s,\mathrm{Au}}$ is the so-called "sampling constant of Au". For the dependence of $v_{het,\mathrm{Au}}$ on the sample weight w it follows

$$v_{het,\mathrm{Au}} = \frac{\sqrt{K_{s,\mathrm{Au}}}}{w} = \frac{100}{\sqrt{a_{\mathrm{Au}}w}} \tag{7}$$

The concept of the sampling constant was introduced in analytical chemistry by Ingamells et al. [4,5]. For various components of the same sample K_s has different numerical values. For components homogeneously distributed K_s equals tenths of gram, for heterogeneously distributed traces its magnitude may make hundreds of gram.

In Eqs (6) and (7), the validity of the Poisson distribution law is assumed. This assumption must always be verified when K_s is experimentally determined. Various sample weights should be taken, v_{het} computed and the constancy of the product $v_{het}^2 w$ checked.

Sampling Segregated Materials

For the sampling variance s_s^2 of the segregated material the following relationship holds [6–8]

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} \tag{8}$$

where A and B are constants, w is the sample weight in gram and n is the number of subsamples.

Equation (8) has two terms: The first one describes the random distribution of the particles, the second their segregation. If the values of A and B are known, the optimum weight of the segregated material to be taken for analysis may be computed and the error of the sampling estimated.

The constants A and B are computed in the following manner: In the first step, n subsamples of the larger weight w_{lg} are analyzed and from the scatter of the results the variance s_{lg}^2 is computed. In the second step, n subsamples of smaller weight w_{sm} ($w_{sm} \leq 0.5\, w_{lg}$) are analyzed and the variance s_{sm}^2 is again computed. According to Visman [6] we have for A and B

$$A = \frac{w_{lg} w_{sm}}{w_{lg} - w_{sm}} \left(s_{sm}^2 - s_{lg}^2 \right) \tag{9}$$

For totally segregated material $s_{sm}^2 = s_{lg}^2$. In this case the constant A in Eq. (9) equals zero and the sampling variance $s_s^2 = B/n$, which means that s_s^2 is given by segregation only. If we want to obtain a smaller value of s_s^2, n should be increased.

$$B = s_{lg}^2 - \frac{A}{w_{lg}} = s_{sm}^2 - \frac{A}{w_{sm}} \tag{10}$$

For materials without segregation the constant $B = 0$. From Eq. (8) it follows: $s_{lg}^2 : s_{sm}^2 = w_{sm} : w_{lg}$ and further $v_{lg}^2 w_{lg} = v_{sm}^2 w_{sm}$, i.e. the sampling constant, a relationship derived as an important characteristic of randomly distributed particles.

For partly segregated material ($s_{lg}^2 < s_{sm}^2$) both A and B are involved in the magnitude of s_s^2. The optimum sample weight w_{opt} can be derived from the requirement that the random and segregation terms in Eq. (8) be equal.

$$\frac{A}{w_{opt} n} = \frac{B}{n} \tag{11}$$

$$w_{opt} = \frac{A}{B} \tag{12}$$

Inserting w_{opt} into Eq. (8) for sampling variance of partly segregated materials we have

$$s_s^2 = 2\frac{B}{n} \tag{13}$$

Experimental

Two gold-bearing ores Au 1 and Au 2 were analyzed on gold concentration in the following manner: The sample weights 50, 25 and 10 g of each ore were mixed with ammonium nitrate and heated at the temperature of about 800 °C for two hours. After the thermal treatment the samples were leached with aqua regia, the solution evaporated to dryness and the residue dissolved in 2 mol l^{-1} hydrochloric acid. Gold chloride was extracted by means of 5 ml 0.1 mol l^{-1} dibuthylsulphide in toluene. The amount of gold was determined by flameless atomic absorption spectrometry using the graphite atomiser GRA 90. An aliquot of 5 μl was used for analysis. The calibration line was constructed using pure gold solutions.

Results and Discussion

From the analytical data the arithmetic mean, standard deviation, relative standard deviation and sampling constant were calculated. The results are given in Table I.

Tab. I Analytical results and statistical parameters obtained on two gold-bearing ores Au 1 and Au 2

Gold ore	Weight of sample w, gram	Number of determinat., n	c ppm	s_{het} ppm	v_{het} %	K_s gram
Au 1	50	20	8.06	0.59	7.29	2656
	25	20	7.81	0.82	10.50	2756
	10	20	8.07	1.32	16.38	2683
Au 2	50	20	6.12	1.23	20.18	20356
	25	20	6.07	1.42	23.46	13764
	10	20	6.46	1.86	28.81	8300

The gold particles in the ore Au 1 are randomly distributed and obey Poisson law. The ore can be considered homogeneous on gold and its sampling constant can be computed.

The minimum sample weight necessary for analysis can be estimated by the following reasoning. The ore Au 1 contains 8 ppm Au. For this concentration the maximum relative standard deviation computed from Eq. (2) is $v_{\max,\mathrm{Au}} = 9.9\,\%$. Consequently, $v_{het,\mathrm{Au}}$ must be smaller than 9.9 %. Using the sampling constant $K_s = 2700$ g the sample weight should be

$$w \geq \frac{2700}{9.9^2} \geq 27.5 \text{ g ore Au 1} .$$

The number of the gold particles in one-gram sample can be estimated from Eq. (6). There are $10^4/2700 = 3.7037$ particles in a 1 gram sample and 102 particles in a 27.5 gram sample. Supposing Poisson's distribution of the particles, $v_{het,\mathrm{Au}}$ in a 27.5 g sample is: $v_{het,\mathrm{Au}} = 100\sqrt{102}/102 = 9.9\,\%$ rel.

The gold particles in the ore Au 2 are segregated which is evident from the dependence of the K_s values on the sample weight. This ore is heterogeneous in gold content, and for its sampling Visman's equations are appropriate.

The computation of the constants A and B from the sample weights 50 – 25 g, 25 – 10 g and 50 – 10 g gives the following mean values

$$A = 24.52 \quad \text{and} \quad B = 1.03$$

The optimum sample weight is

$$w_{opt} = \frac{24.52}{1.03} = 23.8 \text{ g}$$

The sampling variance $s_s^2 = 2.06/n$. For $n = 1$, $s_s = 1.4353$ and the relative sampling standard deviation $v_s = 143.53/6.06 = 23.6\%$. It is clear that the overall error of the gold determination in the ore Au 2 is primarily affected by the heterogeneity of the gold particles, and that it is meaningless to use an excessively precise analytical method for the gold determination of this sample.

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