XVIII IMEKO WORLD CONGRESS
Metrology for a Sustainable Development
September, 17 – 22, 2006, Rio de Janeiro, Brazil

SIMPLIFIED EVALUATION OF THE SMALLEST SAMPLE MASS THAT SHOULD BE TAKEN FOR AN ACCURATE CHEMICAL ANALYSIS

Ricardo Rezende Zucchini[(1)]

[(1)] Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A. – IPT, São Paulo, Brazil, zucchini@ipt.br

Abstract: Technology has been developed very much during the last decades. In order to get better materials, with precise chemical composition, electrical properties, thermal properties, etc, it is a must to be capable to accomplish chemical analysis of blends, sometimes dealing with components in very low levels. Today, there are a number of new analytical techniques which allows quantifying extremely low levels of analytes, even employing very small samples. However, using small samples could generate sampling errors. Experimental determination of the minimum sample masses in order to get good accuracy can be a very costly operation, and a time demanding one. In this paper is proposed a simple method to evaluate the minimum sample mass that should be used in chemical analysis, to get low dispersion results

Keywords: Sampling, Sampling Constant, Precision, Particulate Matter.

1. INTRODUCTION

Modern technologies demand many new materials with specific properties, that are only obtained if it is possible to create and analyze compositions very precisely defined, sometimes containing fundamental components in extremely low amounts.

When are analyzed analytes in low concentrations in small particulate samples, the variability in the results can be explained in function of the call sampling error, except when we are near thee quantification of the analytical technique, as shown by Taylor (1987) and Funk & Danmann (1995).

It is common to repeat measurements in order to try avoid this variability problem, using procedures of the type presented in the norm ASTM AND 122 (1999). Sometimes many repetitions are made, being obtained weird results, with unexplainable dispersed values.

It is known that the sampling error increases with the reduction of the mass of the samples, and also with the decreasing of the analyte concentration. An example of this phenomenon was presented by Zucchini (2000) for a case when it was analyzed the sulfur content in mineral coal.

The problem of identifying the smallest sample mass that can be used in order to get some desired precision was studied by several authors. Based in the studies of Gy (1967), Ingamells & Switzer (1973) proposed an experimental procedure that allows the identification of the smallest sample size for the determination of an analyte, using a parameter called sampling constant.

The determination of this constant is so important, that ISO Guide 31 (1987) recommends that if a certified reference material is in granular form, its certificate should present such a constant declared.

The experimental determination of the sampling constant is a difficult procedure that involves the accomplishment of a considerable number of repeated experiments using different sample masses for each analyte concentration. In this work a technique is presented for an approximated and theoretical determination of the smallest possible sample mass needed to achieve a predefined sampling error, using only some physical properties of the solid sample.

2. METHODS

Particulated matter, can be represented approximately by a set of spherical particles. Suppose there is a component A in larger amount (matrix) and a component B in smaller amount (component being analyzed, analyte).

It can be made an analogy between the sampling of that solid, and the drawing of balls from a box, as in the classic model used in the study of the theory of the probabilities, in the following way:

2.1. Properties of the components of a mixture

Suppose that a sample from our material is composed of several little spheres of two components, A and B, with the following properties, presented in the Table 1 :

Table 1. Properties of a sample

Property	Component A (matrix)	Component B (analyte)
Specific gravity (g/cm^3)	ρ_a	ρ_b
Average diameter (cm)	ϕ_a	ϕ_b
Volume of a particle (cm^3)	$v_a = \pi\phi_a^3/6$	$v_b = \pi\phi_b^3/6$
Concentration (%)	c_a	c_b
Mass in the sample (g)	m_a	m_b
Nr of particles in the sample	$n_a = m_a/\rho_a . v_a$	$n_b = m_b/\rho_b . v_b$

Let's call k the relation between the volumes of particles B and A:

$$k = \left(\frac{v_b}{v_a}\right) = \left(\frac{\phi_b}{\phi_a}\right)^3 \qquad (2)$$

2.2. Computing the smallest number of particles

Consider that we have a mixture of spheres A and B, and the proportion of particles type B is ***p***, so that the proportion of particles type A is ***(1-p)***. If we need to know the real proportions from a sample, taking a maximum accepted evaluation error E_p, with a confidence level of $(1-\alpha)$, it is known, from estimation theory, that we need to take at least ***n*** spheres from the mixture, that should be computed in the following way:

$$n \geq \left(\frac{z_{\alpha/2}}{E_p} \right)^2 \cdot p \cdot (1-p) \qquad (3)$$

That equation is valid assuming that: **n . (1-p) > 5** e **n.p > 5**. If we would like to compute the smallest acceptable mass of the sample, we need to convert Equation (3) into another, that stablish a relationship between ***m*** with c_b. So we need the relationship between ***n*** and ***m***, and between ***p*** and c_b, besides another that relates E_p in terms of c_b.

2.2.1. Relationship between m and n

If ***m*** is the sample mass: $m = m_a + m_b$
Assuming the particle volumes equal, we have the following approximated relationships:

$$m = m_a + m_b = (1-p) \cdot n \cdot \rho_a \cdot v_a + p \cdot n \cdot \rho_b \cdot k \cdot v_a$$

$$\therefore \qquad m = n \cdot v_a \cdot [\rho_a + p(k \cdot \rho_b - \rho_a)] \qquad (4)$$

2.2.2. Relationship between *p* and c_b

By definition, the proportion of particle type B in the mixture is:

$$p = \frac{n_b}{n_a + n_b} = \frac{\frac{m_b}{\rho_b . v_b}}{\frac{m_a}{\rho_a . v_a} + \frac{m_b}{\rho_b . v_b}} = \frac{\frac{m_b}{k . \rho_b . v_a}}{\frac{m_a}{\rho_a . v_a} + \frac{m_b}{k . \rho_b . v_a}} =$$

$$= \frac{m_b}{k . \rho_b . v_a} \cdot \frac{1}{\frac{k . \rho_b . m_a + \rho_a . m_b}{k . \rho_a . \rho_b . v_a}} = \frac{1}{1 + \left(\frac{k . \rho_b . m_a}{\rho_a . m_b} \right)}$$

being :

$$\frac{m_a}{m_b} = \frac{m}{m_b} - 1 = \frac{100}{c_b} - 1$$

$$p = \frac{1}{1 + \left[\frac{k . \rho_b}{\rho_a} . \left(\frac{m}{m_b} - 1 \right) \right]} = \frac{1}{1 + \left[\frac{k . \rho_b}{\rho_a} . \left(\frac{100}{c_b} - 1 \right) \right]} \qquad (5)$$

2.2.3. An alternative to E_p

E_p represents the maximum accepted error in terms of proportions in the Equation (3). We need to find an alternative relationship for E_p, in terms of maximum accepted error in c_b. We have the following:

$$E_p = p_{encontrada} - p_{real} = \Delta p$$
$$E_{cb} = c_{b\,encontrada} - c_{b\,real} = \Delta c_b$$

Then:

$$\frac{E_p}{E_{C_b}} = \frac{\Delta p}{\Delta c_b} \qquad (6)$$

The relationship between Δp and Δc_b can be obtained computing the integral the following expression:

$$\frac{dp}{dc_b} = \frac{d}{dc_b} \left[\frac{1}{1 + \left[\frac{k . \rho_b}{\rho_a} . \left(\frac{100}{c_b} - 1 \right) \right]} \right] \qquad (7)$$

Using: $\varphi = k . \rho_b / \rho_a$,

$$\frac{dp}{dc_b} = \frac{d}{dc_b} \left[\frac{1}{1 + \left[\varphi . \left(\frac{100}{c_b} - 1 \right) \right]} \right] \qquad (7)$$

$$\frac{dp}{dc_b} = \frac{100\ \varphi}{c_b^{\,2} [1 + \varphi \cdot (\frac{100}{c_b} - 1)]^2}$$

$$dp = \frac{100\ \varphi}{c_b^{\,2} \left[1 + \varphi \cdot \left(\frac{100}{c_b} - 1 \right) \right]^2} dc_b$$

$$\int_{p_i}^{p_f} dp = \int_{c_{b_i}}^{c_{b_f}} \frac{100\ \varphi}{c_b^{\,2} \left[1 + \varphi \cdot \left(\frac{100}{c_b} - 1 \right) \right]^2} dc_b$$

$$\Delta p = - \frac{100\ \varphi}{\left[c_{b_f} (\varphi - 1) - 100\ \varphi \right] (\varphi - 1)} +$$

$$\frac{100\ \varphi}{\left[c_{b_i} (\varphi - 1) - 100\ \varphi \right] (\varphi - 1)}$$

$$\Delta p = \frac{100\ \varphi (c_{b_f} - c_{b_i})}{\left[c_{b_f} (\varphi - 1) - 100\ \varphi \right] \left[c_{b_i} (\varphi - 1) - 100\ \varphi \right]}$$

As usually we desire to have very similar concentrations, we can do the following aproximation :

$$\Delta p \cong \frac{100\varphi(c_{b_f} - c_{b_i})}{[c_b(\varphi-1)-100\varphi]^2} = \frac{100\varphi}{[c_b(\varphi-1)-100\varphi]^2}\cdot \Delta c_b$$

$$\therefore \frac{\Delta p}{\Delta c_b} \cong \frac{100\varphi}{[c_b(\varphi-1)-100\varphi]^2}$$

Otherwise, considering the square:

$$\frac{\Delta p}{\Delta c_b} = \left[\frac{100\varphi}{[100\varphi + c_b(1-\varphi)]^2}\right]$$

$$\therefore \qquad E_p = E_{c_b}\left[\frac{100\varphi}{[100\varphi + c_b(1-\varphi)]^2}\right] \qquad (8)$$

2.2.4 Computing the smallest sample mass

Substituting Equations (4), (5) e (8) in Equation (3) we have the theoretical smallest sample mass:

$$m_{\min} = \frac{\pi\phi_a^3}{6}\cdot\left(\frac{Z_{\alpha/2}}{E_P}\right)^2 \cdot p(1-p)[\rho_a + p(k\rho_b - \rho_a)] \quad (9)$$

Mass m_{min} computed from Equation (9), is the smallest sample mass (in grams), from what we can determine a concentration result of the analyte B, c_b *(%)* with a maximum error E_{cb} *(%)*, with confidence level ***(1- α)***. Equation (9) despite of its size is not complex. In item 4 it is presented a step-by-step method for that computation.
In order to use this method, we need to know a bit about geometry of the particles, their specific gravities, and also we need to have na idea of the concentration of analyte B.
The method gives an approximated result of the smallest sample, due to the simplifications adopted. The main goal of this method is to help the analyst to find results with better precision.

3. STEP-BY-STEP METHOD

Tables 2 and 3 present a step-by-step stategy for the calculation of the smallest sample mass in chemical analysis of particulated solids.

Table 2. Informations needed

Símbolo	Descrição
ρ_a	Specific gravity component A (matrix) (g/cm^3)
ρ_b	Specific gravity component B (analyte) (g/cm^3)
ϕ_a	Mean diameter of component A, *(cm)*
ϕ_b	Mean diameter of component B, *(cm)*
c_b	Concentration of the analyte, *(%)*
E_c	Maximum allowable error in the evaluation of concentration of the analyte, *(%)*
α	Significance level, *(%)* *(usually α = 0,05 =5%)*
$Z_{\alpha/2}$	Value from the Stadardized Normal Distribution to $\alpha/2$ *(if □ =0,05 then Zα/2=1,96)*

Table 3. Compute as follows:

Compute *k*	$k = \left(\frac{\phi_b}{\phi_a}\right)^3$
Compute φ	$\varphi = k\left(\frac{\rho_b}{\rho_a}\right)$
Compute *p*	$p = \frac{1}{1+\left[\varphi\left(\frac{100}{c_b}-1\right)\right]}$
Compute *E*	$E = E_c\frac{100\varphi}{[100\varphi + c_b(1-\varphi)]^2}$

Compute smallest sample mass, m_{min}	$m_{\min} = \frac{\pi\phi_a^3}{6}\left(\frac{Z_{\alpha/2}}{E}\right)^2 p(1-p)[\rho_a + p(k\rho_b - \rho_a)]$

4. RESULTS

To illustrate the use of this method, it is presented in the Figure 1, the results of the evaluations of the smallest sample masses needed to have an evaluation error, for the concentration of Fe_2O_3 in a mixture of hematite and quartz, not larger than 1% at 95% of confidence level. In the x-axis we have the bulk concentration of Fe_2O_3, in the y-axis we have the smallest mass to be taken as a sample, and the curves represent the behaviour of several samples with diferent average particles sizes.

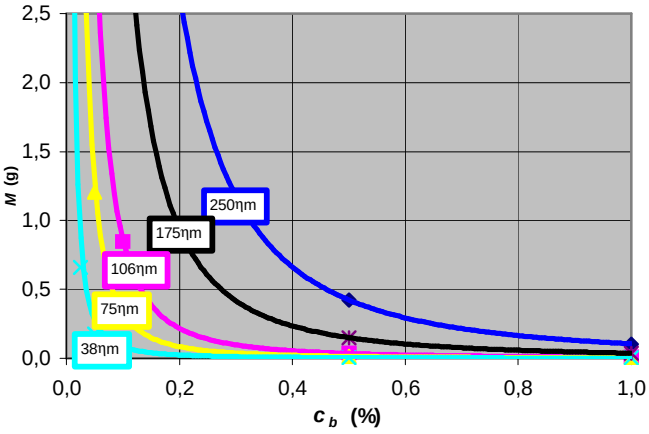

Figure 1. Smallest masses calculated for mixed quartz and hematite.

5. DISCUSSION

The method proposed is quite easy to use, by means of an electronic worksheet. It generates an approximated smallest sample masss to be taken in order to guarantee results with reduced variability. The better the information about the particles, the better the estimates for the smallest sample mass.

Figure 1 shows how the concentration and the particle sizes influence the smallest sample mass. We can see that as the concentrations decrease, we should use finer particles, in order to have the same sample mass. Once, practically, we can not continuously reduce particle sizes, sometimes we need to enlarge our sample mass in order to maintain the precision required.

Experimental tests are required to confirm the results of this method, and despite this, using the method the analyst can prepare simpler and faster experimental designs.

6. CONCLUSIONS

In this work a simplified method of calculation was presented, capable to give an estimate of the smallest sample mass that must be taken from the bulk, so that the results of chemical analysis can come with controlled accuracy.

The method is recommended to esteem the best option of particle size and sample masses, that produce a pre-defined accuracy. Starting from the estimated sample mass, produced by this method, some experiments should be done for the necessary validation.

REFERENCES

[1] American Society for Testing and Materials, 1999, ASTM E 122 – 99 - Standard Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process, (USA).

[2] Funk, W.; Danmann, V. and Donnevert, G., 1995, Quality Assurance in Analytical Chemistry, VCH Verlagsgesellschaft, Weinheim (Federal Republic of Germany).

[3] Gy, P., 1967, Sampling of Materials in Bulk, Vol. 1, Societé de l´Industrie Minérale, St. Étienne, (France).

[4] Ingamells, C. O. and Switzer, P., 1973, A proposed Sampling Constant for Use in Geochemical Analysis, Talanta, Vol 20, pp 547 to 568, Pergamon Press.

[5] ISO Guide 31, 1981, Contents of Certificates of Reference Materials, International Organization for Standardization.

[6] Rossbach, M., and Grobecker, 1999, Homogeneity studies of reference materials by solid sampling – AAS and INAA, Accred. Qual. Assur, 4: 498-503, Springer-Verlag.

[7] Taylor, J. K., 1987, Quality Assurance of Chemical Measurements, Lewis Publishers, Inc. (USA).

[8] Visman, J., 1972, General Theory of Sampling – Discussion 3, J. Mater. 7 (3), 345-350.

[9] Zucchini, R.R., 2000, Estudo da Repetitividade da Determinação do Teor de Enxofre em Blend de Carvão Mineral, Anais do 55º Congresso Anual da Associação Brasileira de Metais; Rio de Janeiro, (Brasil).

[10] Zucchini R.R.; Alves da Silva, M.A.; 2000; Método Simplificado de Avaliação do Erro de Amostragem em Análise Química de Sólidos, Anais do Congresso Internacional de Metrologia - Metrologia 2000, 567-576, São Paulo, (Brasil).