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Some difficult problems still existing in the preparation and certification of CRMs

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Abstract Differences between particle size measurements of CRMs by various methods are discussed and the importance of the reliability of such data for proper estimation of the homogeneity of the material is emphasized. On the basis of a very simple model, the dependence of the Ingamells' sampling constant on the average mass of a single particle of the material is derived, and theoretical predictions are compared with the experimental results. Various approaches to the certification of the candidate RMs are briefly reviewed. The merits of the approach being used in this laboratory to evaluate data obtained in the interlaboratory comparison, and to assign certified and information values, is discussed. The conclusions are supported by results obtained for selected trace elements by use of "definitive" (primary) and "very accurate" methods. Some observations on the unusual resistance of some biological materials to wet ashing and the resulting possibility of making analytical errors are mentioned.

Introduction

Rapid development and globalization of trade, the need for harmonization of efforts in environmental protection, etc., require constant care about the quality of results supplied by analytical laboratories throughout the world. Certified reference materials (CRMs) are an indispensable element of quality assurance in analytical chemistry. Because a good CRM should, where possible, closely match the samples being analyzed, in respect of matrix type and analyte concentration, there is an increasing need for new CRMs. Although the general principles of production and certification of the CRMs are fairly well established and described in scientific papers and books, and in guides issued by international organizations [1–6], there are still some prob-

lems which deserve further attention. Some relating to the preparation and certification of CRMs for inorganic trace analysis will be discussed.

Homogeneity and particle size

Preparation and certification of certified reference materials (CRMs) is a difficult and complex task consisting of many stages. Failure at any stage of this process might render all previous effort worthless [2]. An important feature of the CRMs is homogeneity, defined as the extent to which a property or substance is randomly distributed throughout a material [7]. In the language of analytical chemistry this means that subsamples of a material have the same average composition within appropriately chosen confidence limits. It should be added that the notion of homogeneity is not absolute, and should be considered taking into account such factors as type of a material, sample size, particle size, types of analyte, requirements of the user with respect to accuracy and precision of the determination, etc. [8].

For natural matrix CRMs which contain particles of different composition and are intrinsically inhomogeneous on a microscopic scale, the apparent homogeneity is achieved by comminution to a fine mesh size and thorough mixing. Homogeneity is directly related to particle size.

In a model in which the sample consists of two types of otherwise similar particles, first the fraction which amounts to p , containing P_1 percent of component A, and the second containing P_2 percent of component A, the sampling error R_s (percent relative standard deviation as a result of material inhomogeneity) is related to the number of particles, n , by the Benedetti–Pichler formula [9]:

$$n = p(1-p) \left(\frac{d_1 d_2}{d^2} \right)^2 \left(\frac{(P_1 - P_2)100}{P_{av} R_s} \right)^2 \quad (1)$$

where in addition to earlier defined symbols P_{av} is the percentage of A in the overall sample, and d_1 , d_2 , and d are

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densities of the two types of particle and the overall sample, respectively.

So, according to this model, sampling error is inversely proportional to the square root of the number of particles in the sample. Therefore measurement of CRM particle sizes can give some information about the homogeneity of a material, provided they are sufficiently accurate.

One of the ways of numerical expressing homogeneity is Ingamells' sampling constant, K_s , [10, 11] defined as:

$$K_s = R_s^2 \cdot m \quad (2)$$

where: R_s^2 is sampling variance and m is sample mass.

K_s is expressed in the units of mass and is numerically equal to the sample mass necessary to limit the error arising from sample inhomogeneity (sampling uncertainty) to 1% (with 68% confidence).

If the model leading to Eq. (1) is further simplified, i.e. the sample contains two types of spherical particle of the same density, one containing 100% of a component A and the other none of it, then the sampling error is given by [12]:

$$R_s = 100 \sqrt{\frac{1-p}{np}} \quad (3)$$

and hence:

$$K_s = 10^4 \left(\frac{1}{np} - \frac{1}{n} \right) \cdot m \quad (4)$$

If component A is present at trace levels, i.e. $np \ll n$, then p is, in fact, the concentration (mass fraction) of the component A, (C_A) [g g^{-1}] so it can be written:

$$\begin{aligned} K_s &= 10^4 \left(\frac{4\pi r^3 d}{3C_A} - \frac{4\pi r^3 d}{3} \right) \\ &= 10^4 m_{\text{particle}} \left(\frac{1}{C_A} - 1 \right) \cong 10^4 \frac{m_{\text{particle}}}{C_A} \end{aligned} \quad (5)$$

where m_{particle} is the mass of a single particle of the material.

This simplified model predicts that the sampling constant should increase with the mass of a single particle of a material and decrease with increasing concentration of the trace component. One can also note that K_s should increase with the third power of particle radius, stressing again the importance of accurate particle-size determination.

A popular method of measuring particle-size distribution employs laser diffraction instruments. The use of this method for Virginia tobacco leaves (CTA-VTL-2) CRM gave rather surprising results. When the samples were suspended in a water-detergent solution (using a powder-suspension unit), the median particle diameter obtained varied between 98 μm and 125 μm and the modal value between 164 μm and 178 μm with the less distinct maximum at $\sim 50 \mu\text{m}$.¹

Because these results seemed doubtful, taking into account that the material during preparation passed through an 80- μm sieve, the measurements were repeated with the same instrument using this time a manual dry-powder feeder. The results differed markedly from the previous ones, i.e. median particle diameter was in the range 46–50 μm and the modal value in the range 79–85 μm .²

In addition, some of the distributions were distinctly bimodal with the smaller peak on the distribution histogram corresponding to approximately 20–30 μm , and the second (distinctly larger) corresponding to ca. 83 μm . One possible interpretation is that the first can be attributed to the single particles and the second to the agglomerates. This conclusion was supported by scanning electron microscopy (SEM). Results from measurement of Martin's diameter by optical microscopy were indicative of almost unimodal distribution with a maximum at 25 μm .

The results of particle-size measurements for CTA-VTL-2 and three other CRMs are summarized in Table 1. It seems that the laser diffraction method tends to overestimate the range of particle sizes and can sometimes give misleading results. Potential sources of error when using laser diffraction have recently been discussed by several authors [13–15].

There seems no doubt that in our study microscopy gave more reliable data about the particle size of the studied CRMs than laser diffraction, especially for biological materials, the particles of which can aggregate. It should be remembered, however, that when microscopy is used some larger particles present in small amounts might sometimes be overlooked, because of the limited number of particles measured.

In Fig. 1 K_s values for several elements in fine fly ash (CTA-FFA-1) CRM [8], experimentally determined by INAA, are shown together with theoretical values calculated from Eq. (5) for:

1. particles with $2r = 4 \mu\text{m}$ (corresponding to maximum on histogram from measurements by optical microscopy);
2. particles with $2r = 25 \mu\text{m}$ (small maximum close to the end of histogram according to microscopic measurements and at the same time one of two main maxima from laser diffraction measurements; and
3. particles with $2r = 140 \mu\text{m}$ (one of prominent maxima from the distribution density curve obtained by laser diffraction measurements).

If all particles had a diameter of 4 μm the number in a 10-mg sample of CTA-FFA-1 would be ca. 1×10^8 . In the second case ($2r = 25$) the number of particles would be ca. 5×10^5 and in the third case ($2r = 140 \mu\text{m}$) this number would be only 2.8×10^3 .

It can be inferred from Fig. 1. that this model, despite its far-reaching simplifications, is able to indicate the order of magnitude of sampling constants for the trace elements ($C_A \leq 1000 \text{ mg kg}^{-1}$). Because, however, each material has its own distribution of particle sizes, the predic-

¹ A. Fajgelj, IAEA, Vienna, personal communication August 1995

² A. Fajgelj, IAEA, Vienna, personal communication March 1996

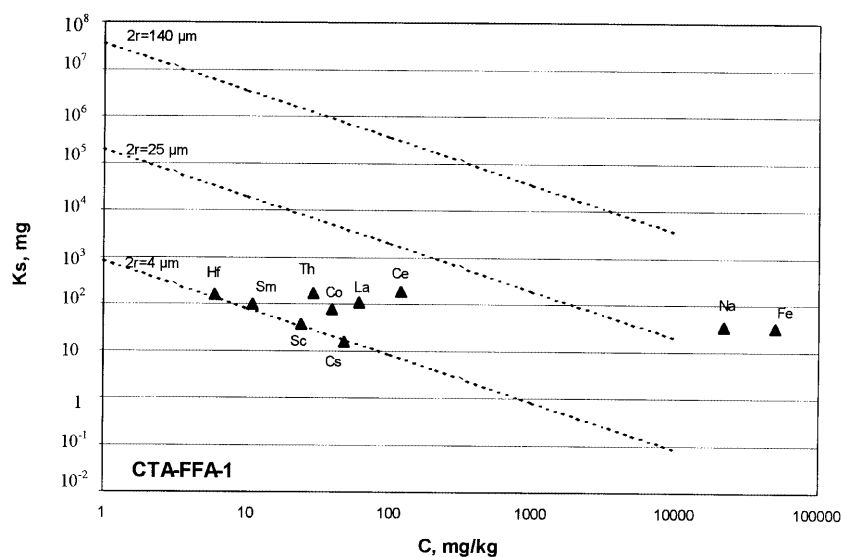
Table 1 Comparison of results of particle size measurements by various methods

| Material passing through sieve (μm) | Optical microscopy (Martin's diameter) | | Mastersizer X laser scattering instrument | | | | Scanning electron microscope (Martin's diameter) Range [μm] |
|---|--|-------------------------|--|-------------------------|--|-------------------------|--|
| | Distribution type and maximum ^a , [μm] | Range [μm] | Dry powder | | Suspension in water – detergent | | |
| | | | Distribution type and maximum ^a , [μm] | Range [μm] | Distribution type and maximum ^a , [μm] | Range [μm] | |
| Virginia Tobacco Leaves CTA-VTL-2 $\Phi < 80 \mu\text{m}$ | unimodal 25 | 2–78 | multimodal 25, 82 | 1–400 | multimodal 50, 170 | 1–400 | 1–67 |
| Oriental Tobacco Leaves CTA-OTL-1 $\Phi < 80 \mu\text{m}$ | unimodal 35 | 10–80 | multimodal 35, 110 | 1–300 | multimodal 50, 200 | 1–450 | 15–60 |
| Fine Fly Ash CTA-FFA-1 $\Phi < 60 \mu\text{m}$, (93%) | multimodal 4, 23, 38 | 1–40 | multimodal 2.5, 7, 25, 140, 310 | 1–450 | | | 1–25 |
| Apatite Concentrate CTA-AC-1 $\Phi < 125 \mu\text{m}$ | multimodal 10, 90 | 1–150 | multimodal 2, 7, 30, 65, 90 | 1–200 | | | 1–75 |

^aMaximum particle size observed in SEM pictures

For multimodal distributions most prominent maxima are shown in bold type

Fig. 1 Sampling constants as a function of mass fraction of the analyte. Predictions based on a simple model and assuming various particle sizes (straight broken lines) vs. experimental values (\blacktriangle)



tions refer rather to a range of values, which can serve as estimates of the upper limits of sampling constants.

The other conclusion is that the degree of homogeneity is not the same for all the elements but usually deteriorates with decreasing mass fraction of an element in a material.

In Fig. 2 analytical results obtained by INAA for 10-mg samples of CTA-FFA-1 are compared with the certified values for this material. It is apparent that despite the uncertainties associated with the values involved, the agreement is very good. This observation is important for all analysts employing microchemical techniques such as energy-dispersive X-ray fluorescence (EDXRF), particle-induced X-ray emission (PIXE), solid sampling atomic absorption spectrometry (SS-AAS), etc., that use in fact much smaller sample masses than those for which homogeneity is usually guaranteed by the producers (typically 100–250 mg). Similarly, we have recently demonstrated very good agreement between analytical results obtained for 10-mg and 1-mg samples of Virginia tobacco leaves (CTA-VTL-2) and the certified values [8]. One milligram of

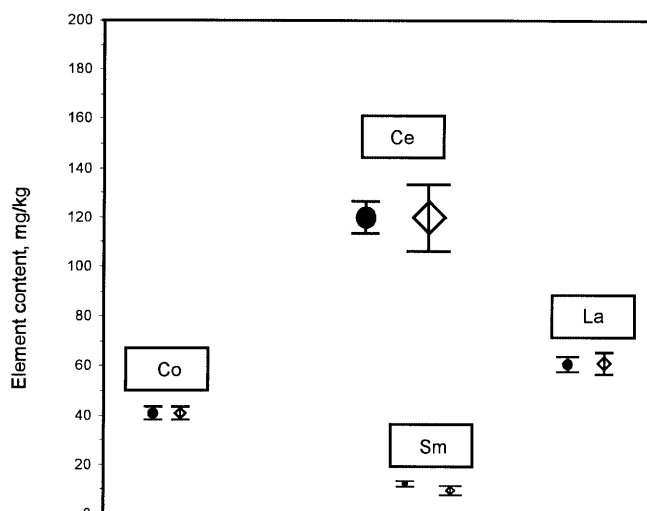


Fig. 2 Comparison of experimental results obtained by NAA for 10-mg samples of fine fly ash (CTA-FFA-1), diamonds; with the certified values, filled circles

CTA-VTL-2 contains approximately 2×10^5 particles. So, it can be assumed that the homogeneity of most of natural matrix CRMs is usually preserved if the number of individual particles in the analyzed sample is not much lower than 10^4 – 10^5 .

Assignment and validity of the certified values

Different approaches to certification have been employed by different CRM producers. Most powerful institutions like NIST favored “in house” measurements by means of a definitive (primary) method or at least two reference methods [16], although recently the contribution from external collaborating laboratories was officially approved [17]. BCR uses a select laboratory approach, i.e. interlaboratory study involving “highly specialized” laboratories [4]. Many other CRM producers employ either open interlaboratory studies or select laboratory or mixed approaches, using, except of arithmetic mean, also other ways of expressing the “central value” – median [18, 19], Gastwirth median [20], geometric mean [21], dominant cluster mode [22], various trimmed means [23], etc. In the domain of geochemical CRMs it is an historical but unfortunate tradition that “central values” were often quoted without defining the accompanying confidence limits [24–28].

The method of evaluation of results of an interlaboratory comparison and assigning certified values used in the Institute of Nuclear Chemistry and Technology is based on the work of one of us (R.D.) [29] (the approach originally used in the practice of the Analytical Quality Control Service of the International Atomic Energy Agency), together with its later modifications [1, 30]. A population of laboratory means is tested for outliers by concurrent use of four criteria (those of Dixon and Grubbs, and the coefficient of skewness and the coefficient of kurtosis). The performance of this procedure is illustrated in Fig. 3,

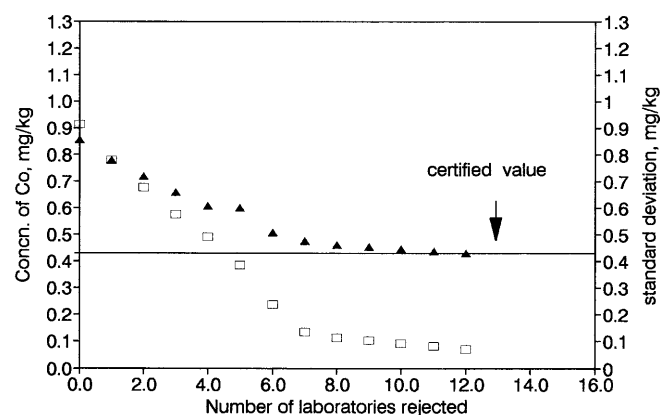


Fig. 3 Graphical representation of the consequences of outlier rejection by the “Dybczyński method” (concurrent use of four criteria, i.e. Dixon, Grubbs, coefficient of skewness, and coefficient of kurtosis at a significance level $\alpha = 0.05$) on the overall mean (▲) and standard deviation of results (□) from an interlaboratory comparison [35]. Cobalt in Virginia tobacco leaves (CTA-VTL-2). Total number of laboratories: $N = 42$

with cobalt in Virginia tobacco leaves (CTA-VTL-2) as example. As was shown earlier [29] such a procedure is relatively free from “masking effects” and gives final values which are close to the “true value”.

This method, sometimes in the literature called the “Dybczyński method” [19, 23, 31] or the “Dybczyński–Rousseau method” [32], has been adopted by several other CRM producers.

Contrary to some voices of criticism, however, this is not a purely statistical approach, because the inseparable part of the method is a set of qualifying criteria based on long-term experience.

Several “very accurate” methods for the determination of selected trace elements in biological materials were elaborated in this laboratory over the past decade [33, 34]. These methods are based on radiochemical NAA involving carefully elaborated, selective and truly quantitative post-irradiation separation of the analyte by column chromatography, followed by interference-free γ -spectrometric measurement and comparison with the standard. Because the method is based on truly quantitative isolation of the analyte in the practically radiochemically pure form (documented in several previous experiments using radioactive tracers added to a variety of biological materials), after which follows comparison with the standard by NAA, i.e. by the technique which is insensitive to the chemical form of the element, the method can be considered directly traceable to mass, and hence to mole.

Comparison of the values obtained by “very accurate methods” with the values certified in the Virginia tobacco leaves (CTA-VTL-2) [35] is shown in Fig. 4. It is readily apparent that agreement is very good for both values for

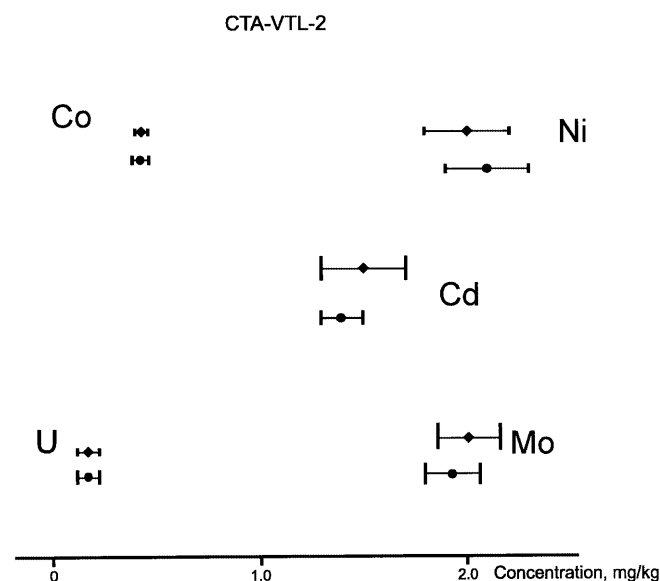


Fig. 4 Comparison of the certified values assigned on the basis of an interlaboratory comparison for Virginia Tobacco Leaves (CTA-VTL-2) with the results obtained by “very accurate methods” [37, 38] (for Co), [39] (for Mo and U), [38] (for Ni) and [40] (for Cd), respectively: *diamonds*, certified value with confidence limits; *circles*, result by “very accurate method” with confidence limits

all the elements studied. This, in turn, provides additional evidence of the reliability of our procedure used for assigning “certified values” on the basis of results from an interlaboratory comparison.

It is worth mentioning that in the course of our work on “very accurate methods” it was found that some biological materials irradiated for a long time at high neutron flux can be unexpectedly highly resistant to wet ashing, and microwave-assisted decomposition is, therefore, recommended [36] to ensure the metallic elements are always quantitatively transformed into the ionic form.

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