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Homogeneity testing of microanalytical reference materials by electron probe microanalysis (EPMA)

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ABSTRACT

Homogeneity testing of candidate reference materials requires distinguishing the effects of measurement uncertainty of the analytical method from true compositional variations within the material. Many *in situ* microanalytical techniques do not allow classical ANOVA homogeneity testing due to the infeasibility of truly replicated analyses on the same analysis volume. This also applies to the analysis of beam-sensitive and light element-bearing materials by electron probe microanalysis (EPMA). This reality has led me to reconsider the homogeneity index approach used in the testing of microanalytical reference materials by EPMA. Based on statistical considerations, I show that the homogeneity index is suitable for statistical significance testing using F and chi-squared statistics and allows estimating the contribution of compositional heterogeneity to the total uncertainty budget of the referenced values. However, there are problems of bias and masking of small compositional variations by measurement uncertainty. This contribution shows the strong impact of the total number of measurements on the resolution of a microanalytical homogeneity study and discusses how to quantify the relative contribution of heterogeneity to the total uncertainty budget. I present an example of EPMA to illustrate this approach and show some pitfalls and limitations in its application.

1. Introduction

Many fields of modern materials sciences, including research on geomaterials like minerals and glasses, rely on microanalytical techniques that operate at micrometer scale spatial resolution and provide low analytical uncertainties. Typical methods employed for chemical characterisations are electron probe microanalysis (EPMA), secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Without exception all of these techniques require the use of reference materials for the validation of measurement methods, the calibration of the instruments, the assignment of compositional values to unknown materials, and the quality control of results (e.g., Kane, 2001; ISO Guide 30:1992; ISO/IEC Guide 99:2007). A recent definition of 'Reference Material' in generic terms is given by Emons et al. (2006) as a "material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process."

Among the family of reference materials, the category of 'Certified Reference Material' (CRM) describes materials "characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability" (Emons et al., 2006). The requirements for the certification of CRMs are defined by internationally established standards (e.g., ISO Guide 35:2006) and have been discussed elsewhere in the literature (e.g., Kane and Potts, 1997, 1999).

While it is desirable to use CRMs in routine laboratory operation, very few of such materials exist that are intended and useful for *in situ* microanalysis (Marinenko, 2002). In many cases, analytical facility user will find themselves in the situation of finding a suitable reference material for their intended analyses. Choosing suitable reference materials for EPMA requires a well-considered balance between matrix matching (reducing ZAF corrections) and simple compositions with few elements at higher concentrations to detect and avoid errors due to X-ray lines being too close to be resolved. The number of reference materials desired to use is also increased by the fact that a single material can only be used for one purpose in a given measurement (Emons et al., 2006), i.e., a reference material cannot be used for calibration and for quality control at the same time, since this would obscure systematic errors.

Owing to the multitude of different materials needed, it is common practice to use non-certified reference materials that are either natural or synthetic substances and characterised 'in-house', by other research groups or scientific institutions, or supplied commercially. Examples are the 91500 zircon (e.g., Wiedenbeck et al., 1995, 2004), Durango fluorapatite (Young et al., 1969), San Carlos olivine (widely used, but no interlaboratory compilation

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of chemical and physical properties exists), and many reference materials produced by the United Stated National Museum of Natural History (USNM)/Smithsonian Institution (e.g., Jarosewich, 2002; Donovan et al., 2002, 2003). Quality of information accompanying such and other materials varies widely ranging from extensive, multi-laboratory data sets to informally circulated analytical results to simple idealised compositions. The assessment of homogeneity is therefore a common issue for operators dealing with in-house or commercial reference materials suspect of problematic compositional variations. The central problem in interpreting the apparent homogeneity of a reference material is to differentiate between intrinsic compositional variations and the variations due to the analytical device, i.e., the analytical precision.

Common methods of chemical characterisation and homogeneity studies usually employ replicate analyses to characterise the analytical precision of the measurement method, which has substantial meaning for the absolute level of heterogeneity that can be resolved (e.g., Van der Veen and Pauwels, 2000; Van der Veen et al., 2001; Linsinger et al., 2001; Pauwels et al., 1998). A major difficulty arising from the characteristics of microanalysis by EPMA, SIMS and LA-ICP-MS is that a single sample volume can be analysed only once, either because it is intentionally destroyed by sputtering or ablation (SIMS, LA-ICP-MS) or damaged by diffusive processes, structural changes, and surface contamination due to electron irradiation (EPMA; e.g., Stormer et al., 1993; Noguchi et al., 2004). To circumvent the problem of non-repeatable analyses, it is possible to determine measurement precision and uncertainty on a very similar material with known homogeneity – unfortunately such materials will not be available in the majority of cases. However, because the data acquisition of all three named microanalytical techniques employs the counting of discrete events (ions or X-ray photons reaching detectors), a basic statistical evaluation of measurement precision can be done using Poisson statistics as introduced by Boyd et al. (1967) in terms of the so called homogeneity index. In spite of being quite widely used (e.g., for the USNM microprobe reference materials, Jarosewich et al., 1979, 1980), the interpretation of homogeneity indices is not straightforward due to often missing or ill-defined statistical concepts. Here I present approaches for homogeneity testing with particular relevance to *in situ* microanalysis by EPMA and I discuss the interpretation of the resulting parameters.

2. Microanalytical approaches for homogeneity testing

2.1. 'Bottle' homogeneity testing vs. microanalysis

Fundamental experimental and statistical concepts for the classical homogeneity testing are discussed by Van der Veen et al. (2001). Chemometric terminology commonly refers to 'between-bottle' and 'within-bottle' homogeneity, owing to the fact that most reference materials are shipped in bottles. The extension of these concepts to microanalysis leads to the equivalent concepts of compositional variations between individual specimens (between-samples) and within individual specimens (within-sample). The within-sample case will be the most frequently met situation in practical testing of a reference specimen, while between-sample testing will occur if a whole batch of reference specimens needs to be tested. The following sections will concentrate on the former case. Pauwels et al. (1998) and Van der Veen et al. (2001) used the following relation to express the combined uncertainty s_c due to within-sample compositional heterogeneity s_h and measurement uncertainty s_{meas} (s^2 is the corresponding variance):

$$s_c^2 = s_h^2 + s_{meas}^2 \quad (1)$$

If data are not acquired incrementally but by a single acquisition, like in case of EPMA, an estimation for s_{meas} of a single analysis spot cannot be derived reliably, because repeated analyses of the same spot leads to sample deterioration and, in consequence, to a meaningless variance. However, considering the sources of statistical variation, it is possible to partition the method's measurement variance into components relating to variations due to the Poisson process of counting detector events (s_{Pois}) and variations due to combinations of instrumental effects (s_{inst}). The variance of the applied method is thus:

$$s_{meas}^2 = s_{Pois}^2 + s_{inst}^2 \quad (2)$$

If the measurement uncertainty is strongly dominated by the count rate (that is, by a low number of counts), s_{inst} may become negligible. In case of modern EPMA, s_{inst} is very small due to the highly reproducible placing of the analyser crystals and the control and measurement of the beam current (the major contributions to s_{inst}; however, care must be taken for time dependent instrumental drift as shown in the example below).

In cases of negligible s_{inst}, s_{Pois} can be taken as only source of uncertainty and used as approximation and estimator of s_{meas} through the well-known Poisson relation to the total number of detected events C (detector counts):

$$s_{meas} \approx s_{Pois} = \sqrt{C} \quad (3)$$

In practice, the relation is more complicated than given in Eq. (3) due to the fact that not only the signal of the measured quantity is derived as counts, but also two background signals needs to be counted and subtracted. The measurement uncertainty resulting from such a procedure is expressed by Eq. (3-3) of Appendix 3. In any case, the highest possible instrument stability should be maintained during data acquisition, analyses should be obtained in temporal proximity and instrumental drift should be carefully monitored (see Section 3).

2.2. The homogeneity index

A criterion for assessing the homogeneity of microanalytical reference materials for EPMA was first introduced by Boyd et al. (1967). They suggested using a ratio of standard deviations termed sigma ratio or homogeneity index. In this ratio, the numerator is the observed standard deviation obtained from the entire pool of measured values and the denominator is the standard deviation predicted from counting statistics, i.e., derived from the square root of the total number of accumulated counts.

In the ideal case involving a perfectly homogeneous material ($s_h = 0$) and an instrumental method totally free of variation ($s_{inst} = 0$), the observable variance would be solely due to Poisson-derived uncertainties resulting from the counting process of X-ray photons; both standard deviations would be equal, leading to an ideal result of the homogeneity index being $H = 1$. Given a representative number of analyses, Boyd et al. (1967) suggested an upper value of 3 for the homogeneity index, above which they, rather arbitrarily, defined heterogeneity as being significant. Potts et al. (1983) even suggested a value of 4 when instrumental effects (in the sense of s_{inst}) contribute to measurement variance. In the past decades the homogeneity index and the $H < 3$ criterion for its interpretation became widely adopted in the geoscientific community (e.g., Jarosewich et al., 1980; Jarosewich and Boatner, 1991; Hunt and Hill, 1996; Patino-Douce et al., 1994; Camara et al., 2004; Goldstein and Luth, 2006; Bertoldi et al., 2006).

The homogeneity index is the ratio of the expected values of the total combined uncertainty $E(s_c)$ and the measurement uncertainty $E(s_{meas})$ (E is the expectation operator). Because the expected (or 'true') values cannot be known precisely from a

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