# Use of sampling based correction for non-radioactivity

# X-ray energy calibration

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**Abstract** As the requirement of non-radioactivity measurement has increased in recent years, various energy calibration methods applied in portable X-ray fluorescence (XRF) spectrometers have been developed. In this paper, a sampling based correction energy calibration has been discussed. In this method both history information and current state of the instrument are considered and relative high precision and reliability can be obtained.

Key words X-ray fluorescence spectrometers, Energy calibration, Correction index

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## 1 Introduction

Energy-dispersive spectrometer system became available in the early 1970s.<sup>[1]</sup> It has found a wide range of application due to the ability to display information at the same time and to do quantitative analysis of all elements in the periodic table from F(atomic number 9) upwards. Newer developments allow the determination of the ultra low atomic number elements including B, C, O and N. Accuracies of a few tenths of one percent are possible for most of the atomic number range, and elements are detectable in many cases to the low parts per million (ppm) level. Excellent data treatment software is available allowing the rapid application of quantitative and semi-quantitative procedures.

Energy calibration is realized usually with a radioactive source with double or more known energies to measure their corresponding energy peak positions in Multi-Channel Analyzer (MCA), then a linear relation is established between energy and channel address. Based on this relation energies are calibrated precisely and unknown energies are recognized by their peak positions conveniently.<sup>[2]</sup>

Common energy calibration procedures used in X-ray spectrometers include:<sup>[3]</sup> (1) calibrating to sharp drops or Bragg "glitches" in the primary beam intensity, due to the excitation of secondary Bragg reflections in the monochromator; (2) measuring the transmission extended XAFS(EXAFS) of a standard sam-

ple, with known absorption edge features at tabulated energies, and (3) measuring the Bragg angle using an analyzer crystal. Common radioactive sources such as <sup>55</sup>Fe are used in energy dispersive spectrometers to make precise energy calibration. Though precision of energy calibration is a required qualification in X-ray spectrometers, the increasing demand is the use of non-radioactivity methods instead of radioactive sources in such portable instruments. At present, standard samples based energy calibration becomes more and more popular in various X-ray instruments.

This article mainly discusses a simple and reliable method of energy calibration based on sampling correction used in portable energy dispersive X-ray fluorescence analyzer. This method is factually a combination of history information of the instrument and its current state obtained from a pre-measurement as energy calibration. These two factors reflect stability and current measuring conditions of the X-ray spectrometer. Based on these factors, energy calibration could gain relatively high precision without radioactivity.

# 2 Sampling based correction energy calibration

## 2.1 Principle

To apply sample's data instead of radioactive sources in energy calibration, the first step is to collect

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and store plenty of sample's

information, which reflects the shift range of the spectrometer to be calibrated and acts as history information of final energy calibration. History information only reflects stability of the spectrometer, so it cannot act as energy calibration individually because current state information obtained before a formal measurement is much closer to the measuring conditions. According to history information, current state could be used to test whether the spectrometer is in good measuring conditions. For each measured sample, its information is added to the sample database and changes history information immediately.

As has been well known, sample data follow *t*-distribution when population standard deviation is not known. Given a prior distribution (*t*-distribution), collect data to obtain parameters of the observed distribution, and then calculate the confidence interval of the population mean at a certain confidence level. Make a trial measurement to test current measuring conditions. If it is good to work, use the current data and history information as energy calibration, otherwise adjust the instrument and make another trial measurement. This statistical procedure is called Bayesian Analysis.<sup>[4]</sup>

#### 2.2 Student's *t*-distribution<sup>[5]</sup>

Given *n* independent measurements  $\{x_1, x_2, ..., x_n\}$ , let  $t \equiv \frac{\overline{x} - \mu}{S / \sqrt{n}}$ , where  $\mu$  is the popu-

lation mean,  $\overline{x}$  is the sample mean:  $\overline{x} = \frac{1}{n} \sum_{k=1}^{n} x_k$ , and

S is the estimator for population standard deviation (i.e., the sample variance) defined by  $g_{1}^{2} = \frac{1}{2} \sum_{n=1}^{n} \left( \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{$ 

 $S^{2} \equiv \frac{1}{n-1} \sum_{i=1}^{n} (x_{i} - \overline{x})^{2}$ . Student's *t*-distribution is de-

fined as the distribution of the random variable t, which is the "best" without knowing population standard deviation  $\sigma$ . As N increases, Student's *t*-distribution approaches the normal distribution.

# 2.3 Process of sampling based correction energy calibration

The flow chart of the samping based correction energy calibration is shown in Fig.1.



Fig.1 Flow chart of sampling based correction energy calibration.

To determine whether a spectrometer is in good conditions, use a standard sample containing three or more elements with distinct characteristic lines to test the instrument. Supposed this standard sample includes three elements: A, B, C. Their corresponding characteristic lines are  $L_A$ ,  $L_B$ ,  $L_C$ , and the characteristic energies are  $E_A$ ,  $E_B$ ,  $E_C$ .

**Step 1** When the system starts up, the sample is exposed to X-rays and the elements give out their characteristic lines, each line has a peak position:  $P_A$ ,  $P_B$  or  $P_C$  in MCA (Fig.2), the peak positions will be recognized and recorded.





Let 
$$E_{\overline{BA}} = \frac{E_{B} - E_{A}}{P_{B} - P_{A}}$$
 stand for average energy

per channel between channel  $P_A$  and  $P_B$ , and

$$E_{\overline{_{CB}}} = \frac{E_{_{C}} - E_{_{B}}}{P_{_{C}} - P_{_{B}}}$$
,  $E_{\overline{_{CA}}} = \frac{E_{_{C}} - E_{_{A}}}{P_{_{C}} - P_{_{A}}}$  have similar

meanings.

Let 
$$E_{\overline{ABC}} = E_{\overline{BA}} \times \alpha + E_{\overline{CB}} \times \beta + E_{\overline{CA}} \times \gamma$$
; where

 $\alpha$ ,  $\beta$ ,  $\gamma$  are correction indexes, and  $\alpha + \beta + \gamma = 1$ . Selection of correction indexes is according to weightiness and stability of  $E_{\overline{BA}}$ ,  $E_{\overline{CB}}$  and  $E_{\overline{CA}}$ .

**Step 2** Measure *N* sets of  $P_A$ ,  $P_B$ ,  $P_C$  and calculate  $E_{\overline{BA}}^i$ ,  $E_{\overline{CB}}^i$ ,  $E_{\overline{CA}}^i$  and  $E_{\overline{ABC}}^i$ , where *i* is an integer in the interval [1, *N*]. Next use Bayesian Analysis<sup>[6]</sup> to analyze these data.

Step 3 As has been quoted above,  $t = \frac{\overline{E_{\overline{ABC}}^{N}} - \overline{E_{\overline{ABC}}}}{S / \sqrt{N}}$  follows *t*-distribution, where  $\overline{E_{\overline{ABC}}}$ 

is population mean. Calculate sample mean  $E_{ABC}^N$  and

sample variance 
$$S^2 = \frac{1}{N-1} \sum_{i=1}^{N} \left( E_{\overline{ABC}}^i - \overline{E_{\overline{ABC}}^N} \right)^2$$
. Be-

cause N is very big,  $t = \frac{\overline{E_{ABC}^N} - \overline{E_{ABC}}}{S / \sqrt{N}}$  follows the

normal distribution. Determine confidence level p and look up a corresponding value in the normal distribution form, then compute confidence interval of  $\overline{E_{_{\overline{ABC}}}}$ ,

i.e.  $(\overline{E_{ABC}^{N}} - \lambda \times S, \overline{E_{ABC}^{N}} + \lambda \times S)$ , where  $\lambda$  is a value under a certain confidence level. Since a high confidence level will reject data not bad, and lower level will decrease accuracy of energy calibration, an appropriate confidence level is needed, for example p=95%.

**Step 4** Measure the standard sample and record  $P_A$ ,  $P_B$  and  $P_C$  as No.K set of data. Compute  $E_{\overline{ABC}}^K$ , then determine whether  $E_{\overline{ABC}}^K$  is in the interval

 $(\overline{E_{ABC}^{N}} - \lambda \times S, \overline{E_{ABC}^{N}} + \lambda \times S)$ : if it is true, accept this measurement and recalibrate energy; if not, reject this measurement and adjust the analyzer.

**Step 5** Next use  $E^* = \overline{E_{ABC}^N} \times \phi + E_{ABC}^K \times \phi$  as

energy calibration, where,  $\phi, \phi$  are correction indexes and  $\phi + \phi = 1$ .

#### 2.4 Selections of correction indexes

Determination of correction indexes is an empirical task and it is difficult to give strict expressions of these indexes. Selection of  $\alpha$ ,  $\beta$ ,  $\gamma$  mainly depends on linearity (i.e. weightiness and stability of  $E_{\rm BA}$ ,  $E_{\rm CB}$  and  $E_{\rm CA}$ ) of MCA. Let  $\alpha = \beta = \gamma$  and then adjust  $\alpha$ ,  $\beta$ ,  $\gamma$ . If the MCA has a good linearity in lower energy range,  $\alpha$  is set to 0.5 and  $\beta$ ,  $\gamma$  are set to about 0.25. But selection of  $\phi$ ,  $\phi$  involves the difference between  $\overline{E_{\rm ABC}^N}$  and  $E_{\rm ABC}^{\kappa}$ . As has explained above,  $\overline{E_{\rm ABC}^N}$  reflects stability (history information) of the system to be calibrated, while system current state will

we use 
$$\varphi = \frac{\left|\overline{E_{ABC}^{N}} - E_{ABC}^{K}\right|}{\lambda \times S}$$
 and  $\phi + \varphi = 1$  as the

be much closer to the successive measurements. Here

selection rule. Another selection rule is based on the

instrument stability, i.e. 
$$\phi = \frac{\left|\overline{E_{ABC}^N} - E_{ABC}^K\right|}{\lambda \times S}$$
 and  $\phi + \phi = 1$ .

#### **3** Experiments and results

#### 3.1 Example A

1) Suppose the spectrometer to be calibrated has about 5% linear shift of peak positions. Get 100 sets of prior data;

2) Compute 
$$\overline{E_{ABC}^{100}}$$
,  $S^2 = \frac{1}{99} \sum_{i=1}^{100} \left( E_{ABC}^{(i)} - \overline{E_{ABC}^{100}} \right)^2$ ,

 $\alpha$ ,  $\beta$  and  $\gamma$  are set to 0.5, 0.2, 0.3 respectively.

## 3) Confidence level is

set	to	95%,	confidence	interv	val	is
$(\overline{E_{AB}^{100}})$	$\frac{1}{c}$ - 1.96	$5 \times S, \overline{E_{\overline{ABC}}^{100}}$	$+1.96 \times S$ ).			
	4) Get	No.101 n	neasurement,	calculate	and	test

 $\overline{E_{ABC}^{101}}$ 

5) If 
$$\overline{E_{ABC}^{101}}$$
 falls in the confidence interval,

compute  $E^* = \overline{E_{ABC}^{100}} \times \phi + E_{ABC}^{101} \times \phi$  as energy calibration, where  $\phi, \phi$  are set to 0.35, 0.65 respective-

ly.

6) Compare  $E^*$  with  $E_{abs}$ ,  $E_{fix}$  (Fig.3), where  $E_{abs}$  is the absolute energy calibration that means the calibration of instrument with radioactive sources before every measurement, and  $E_{fix}$  is the fix energy calibration, which means that once the instrument has been calibrated, the energy calibration is fixed for any measurement.



**Fig.3** Relative error of  $E^*$  and  $E_{\text{fix}}$  to  $E_{\text{abs}}$  for example A.

#### 3.2 Example B

Suppose the analyzer has about 2% linearity shift, repeat above process, and  $\alpha$ ,  $\beta$ ,  $\gamma$  are set to 0.5, 0.2, 0.3 respectively; confidence level is set to 95%;  $\phi$ ,  $\phi$  are set to 0.65, 0.35 respectively. Compare  $E^*$  with  $E_{abs}$ ,  $E_{fix}$  (Fig.4).

### 4 Discussion

The sampling based correction energy calibration method is simple and effective, but will cause a slight decrease of system precision. This method is applicable in portable energy dispersive X-ray fluorescence analyzers.



**Fig.4** Relative error of  $E^*$  and  $E_{\text{fix}}$  to  $E_{\text{abs}}$  for example B.

Compared with fixed energy calibration, this method used in our portable X-ray analyzer has a comparatively low absolute error. When the system to be calibrated has good linearity, this method averagely reduces about one-third absolute error, and it reduces about one-fifth absolute error if the system shifts in a bigger range. Compared with the radioactive source calibration method, this method uses a standard sample to correct energy calibration only at a cost of very small loss of precision in such portable analyzers. It is important to diminish the public's fear of radioactivity when similar nuclear instruments are used.

Correction indexes should be carefully chosen according to the system's conditions. More measurements are needed to give more accurate values of these correction indexes. On the other hand, a spectrometer could still get best precision if it is recalibrated periodically by the radioactive sources method.

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