Rapid methods for the calibration of solid-state detectors

D. Walker,[a] S. M. Clark,[b]* R. L. Jones[b] and L. M. D. Cranswick[b]

[a]*Lamont Doherty Earth Observatory, Columbia University, Palisades, NY 10964, USA, and* [b]*CLRC, Daresbury Laboratory, Warrington WA4 4AD, UK. E-mail: s.m.clark@dl.ac.uk*

A complementary pair of rapid methods for the energy calibration of solid-state detectors have been developed. Each method requires only a single measurement from either (i) a glass sample containing elements chosen to produce fluorescence lines over a suitable energy range when exposed to a polychromatic beam of X-rays, or (ii) a powder diffraction standard in the presence of diffraction slits. The fluorescent glass method has the advantage of allowing simultaneous energy calibration of a number of detectors without requiring diffraction slits. There is the potential for the glass material to be incorporated into virtually any sample holder to allow a continuous *in situ* calibration. Complementary observations of a powder diffraction standard allow simultaneous calibration of diffraction 2θ and monitoring of the detector for drift.

1. Introduction

Energy-sensitive solid-state detectors are in routine use both in the laboratory and at synchrotron sources for a variety of applications including energy-dispersive powder diffraction (Clark, 1996) and X-ray fluorescence measurements (Derbyshire *et al.*, 1999). These detectors produce an output voltage pulse proportional to a detected X-ray energy which is then usually amplified and fed to a multi-channel analyser where it is typically mapped onto 2^{10}–2^{12} channels. Before analysing the data it is usually necessary to convert from channels to energy [and then possibly on to *d*-spacing (Cole, 1970)]. To do this a calibration curve relating channels to energy is required. An energy calibration curve of the form

$$E = a_0 + a_1\mathbf{c} + a_2\mathbf{c}^2,$$

where E is the energy, $\mathbf{c}$ is the channel number and a_0, a_1 and a_2 are appropriate coefficients, is usually sufficient, although in most cases the quadratic term is found to be unnecessary. There are traditionally two methods used to determine these coefficients, as follows.

(i) X-rays or gamma-rays of known energy are shone into the detector (Buras *et al.*, 1989). A series of different X-ray or gamma-ray energies is used to cover the range of energies in use. The position of the resulting peaks (in channels) is determined and a list of channel numbers and related energies is produced. Least-squares estimates of the energy-calibration-curve coefficients are then determined from these values. Gamma-rays are usually produced by a suitable radioactive source while X-rays are usually produced as fluorescence from suitable elements excited by gamma-radiation.

(ii) Multiple orders of a reflection from the same set of lattice planes of an oriented single crystal are recorded (Skelton, 1977). Knowing the appropriate crystallographic data and the diffraction angle, a list of energies and channel numbers can be produced and least-squares estimates of the calibration-curve coefficients can be determined as above.

The main problem with the gamma-stimulated X-ray method is that each element usually has to be selected separately and the detector exposed to each set of fluorescence lines in series. This is generally time-consuming and it can become extremely tedious when multi-element detectors are in use because for many detector geometries each element of the detector has to be calibrated separately. For example, on station 16.4 of the SRS Daresbury, calibration of a single energy for a single detector takes 10–15 min. For six energies and three detectors a full calibration can take up to a whole day. Also, the range of X-ray energies available from commercially available sources is limited to below 60 keV. Gamma sources giving only a few lines suffer from the same problem as the above X-ray method, while sources containing multiple lines pose the problem of identifying the correct lines and accurately measuring their positions when they may well be overlapped with other lines. The Skelton method relies on having a suitably oriented single crystal and a suitable post-sample slit system to allow accurate diffraction data to be collected, and having the detector and post-sample slits at a suitable diffraction angle for making the measurement. Quite often these conditions cannot be met, either due to a lack of slits, *e.g.* when making spectroscopic measurements, or due to geometric restrictions that limit the placement of the crystal, the slits and the detector, *e.g.* when using multiple-element detectors.

2. Experimental

We have developed a method of calibrating the whole energy range of a number of detectors simultaneously. It is based upon a method recently developed for calibrating area X-ray detectors (Moy *et al.*, 1996). A glass containing selected elements is held in a polychromatic beam of X-rays and the fluorescence lines from the selected elements are used for the energy calibration. The energy range of interest for our experiments was 30–120 keV so elements with suitable fluorescence were selected to cover this range (Table 1). The health and safety implications of including radioactive materials led us to produce two glasses, one containing uranium, the other not. The glasses were made by mixing appropriate quantities of the relevant oxides, carbonates or, in the case of uranium, acetate, together with a glass-making flux (Table 1). This mixture was heated to 1423 K over one hour and then held at that temperature for another hour before the liquid was quenched to glass by pouring the molten mixture into a suitable mold. This procedure was found to give a clear glass with no diffraction lines. Fig. 1 shows a spectrum collected from the uranium-containing glass on station 16.4 (Clark, 1996) of the Daresbury synchrotron radiation source. The data-acquisition time of 15 min for the complete calibration of three detectors compares very favorably with the gamma-source procedure described above. The spectra are seen to be composed entirely of the expected fluorescence lines and escape peaks with no contribution from diffraction lines caused by precipitation of crystalline compounds

during the glass-making process. Fig. 2 shows the linearity of the fit obtained between channels and energy. This gave an energy calibration curve with the following parameters: $a_0 = 6.22$ (6), $a_1 = 0.02703$ (8) and $a_2 = 5$ (2) $\times 10^{-8}$.

A powder diffraction pattern was collected shortly after this calibration from a sample of NBS 640b silicon, which serves as a detector angle calibration standard. Table 2 contains a list of the observed and calculated peak positions obtained from the refinement of this particular detector angle ($7.631°\ 2\theta$) and unit cell [$a = 5.4325$ (5)]. The excellent agreement between these values over the entire energy range observed indicates the quality of the detector energy calibration. This is in contrast to energy calibrations limited to <60 keV based on commercial fluorescence sources. These limited calibrations introduce errors up to 2 keV at 100 keV. When powder diffraction standards are routinely used to determine the detector angle, as at the SRS Daresbury, then a complementary method of detector energy calibration monitoring can be used. If one assumes the cell parameters of the diffraction standard are well enough known, in principle any collection of indexable reflections can be used to solve for the detector energy response polynomial over the energy range of observed reflections. One needs at least as many reflections as the number of parameters a_0, a_1, a_2. For example, the ten Si reflections in Table 2 were used to calculate the following values: $a_0 = 6.13$ (6), $a_1 = 0.02719$ (5) and $a_2 = 1$ (1) $\times 10^{-8}$.

The a_2 parameter almost vanishes in the powder-diffraction-based calibration as it did in the fluorescent-glass-based calibration. Both calibrations of the same
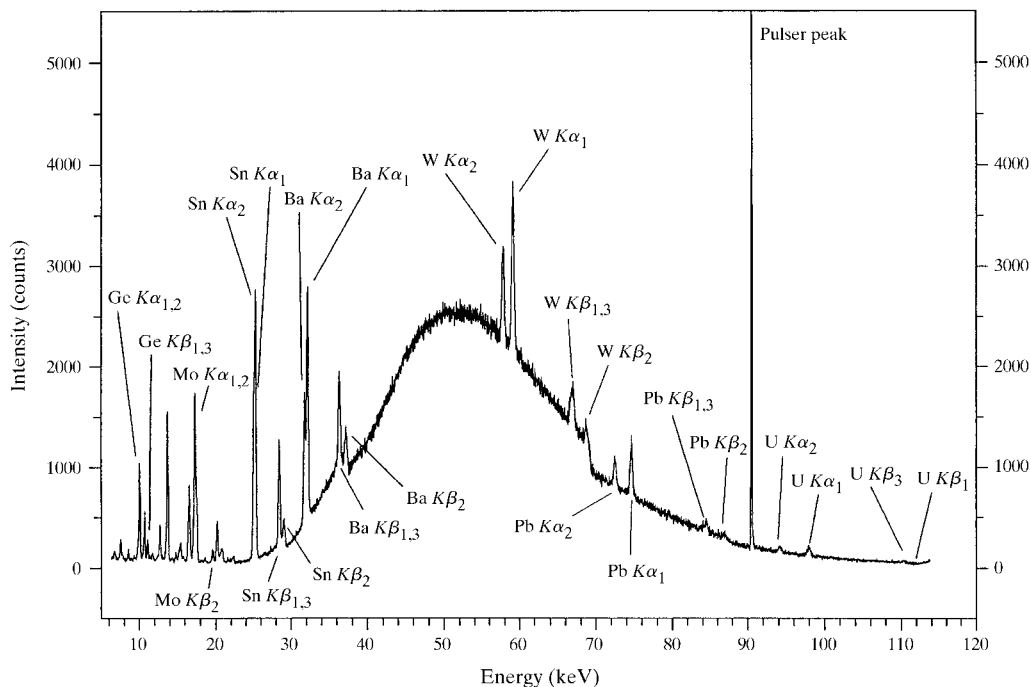
Figure 1
Energy-dispersive pattern collected from the uranium-containing glass using a polychromatic beam of X-rays to stimulate the fluorescence. The Pulser peak was added electronically as an aid to checking the stability of the detector electronics. The unassigned peaks at low energy are due to escape events (Stuan Olsen, 1974).
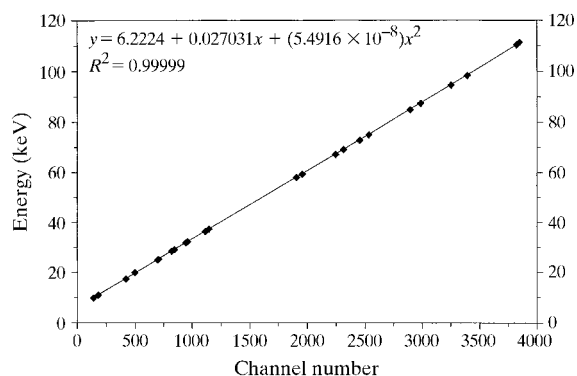
Table 1

A list of the characteristic fluorescence lines, their positions and the proportions of materials used to produce both the uranium-containing and non-uranium-containing glasses.

Fluorescence line	Peak position (channel)	(keV)	Added as	Glass with U (wt%)	Glass with no U (wt%)
Ge $K\alpha_{1,2}$	139.2	9.877	GeO_2	13.6	13.6
Ge $K\beta_{1,3}$	179.9	10.981			
Mo $K\alpha_{1,2}$	418.4	17.444	MoO_2	3.6	4.9
Mo $K\beta_2$	495.5	19.960			
Sn $K\alpha_2$	696.1	25.044	SnO_2	3.1	3.9
Sn $K\alpha_1$	704.6	25.272			
Sn $K\beta_{1,3}$	822.3	28.474			
Sn $K\beta_2$	844.8	29.122			
Ba $K\alpha_2$	945.2	31.817	$BaCO_3$	3.0	3.9
Ba $K\alpha_1$	959.0	32.194			
Ba $K\beta_{1,3}$	1112.0	36.353			
Ba $K\beta_2$	1143.1	37.270			
W $K\alpha_2$	1906.6	57.982	WO_3	4.6	5.8
W $K\alpha_1$	1955.6	59.312			
W $K\beta_{1,3}$	2243.8	67.146			
W $K\beta_2$	2311.2	69.100			
Pb $K\alpha_2$	2451.0	72.804	PbO_2	4.4	5.8
Pb $K\alpha_1$	2530.6	74.969			
Pb $K\beta_{1,3}$	2894.9	84.774			
Pb $K\beta_2$	2986.6	87.367			
U $K\alpha_2$	3252.6	94.659	$UO_2(CH_3.COO)_2$	19.9	
U $K\alpha_1$	3392.5	98.440			
U $K\beta_3$	3825.1	110.424			
U $K\beta_1$	3849.3	111.303			
			Li_2CO_3	17.8	23.3
			B_2O_3	30.0	38.8

detector appear close to linear with agreement between the coefficient values within twice the standard error. The above energy calibration based on the Si reflections used the fluorescent glass calibration to establish trial Si peak energies from which the detector angle, 2θ, was calculated. Alternately, if the number of reflections exceeds the number of detector energy response parameters, it is possible to also solve for 2θ. Naturally the recovered value of 2θ would be based upon less information in a refinement of four parameters from ten observations than in the case of Table 2 when all ten silicon reflections are used to refine only 2θ. Likewise the fluorescent glass provides 24 lines over the energy range of interest. Refining these lines for

$$y = 6.2224 + 0.027031x + (5.4916 \times 10^{-8})x^2$$
$$R^2 = 0.99999$$

Figure 2
Result of the calculation of polynomial coefficients that best describe the fit between channel number and energy for the fluorescence lines present in Fig. 1.

detector response gives values based on more information than found in ten Si lines and is independent of any detector 2θ considerations. Thus the powder diffraction method to find both 2θ and detector response serves best as a backup procedure to the combined use of the fluorescent glass for energy response calibration and the diffraction standard for 2θ calibration.

Even though Si diffraction produces only ten observable lines in this energy range, refining them can provide both 2θ and a quick calibration of the detector energy response. The 2θ values recovered by this method are less stable than if all lines are used to refine only 2θ, and therefore the use of the silicon or other diffraction standard as the only calibrant for both energy and 2θ is recommended only for situations where no other method is available. However, if 2θ is known from an energy calibration over a limited range then the energy parameters recovered over an extended range from a diffraction standard are very stable. We have found the powder-diffraction-based method to be particularly suited to recovering extended energy calibrations (beyond the 60 keV provided by our radioactive dial source) for data sets collected before the advent of the fluorescent glass method. In practice the radioactive dial source calibration at <60 keV allows calibration of 2θ from reflections observed at <60 keV. Using this 2θ, one may then refine all the lines to retrieve an energy calibration of the detector over the whole range for which silicon reflections are observed. Another potential reason for use of the lower-precision powder diffraction standard method is that detector 2θ often needs adjustment during an

Table 2
Values of the calculated and observed peak positions for a sample
of NBS 640b silicon used to determine the diffraction angle.

The refined value of the diffraction angle was 7.634° 2θ.

H	K	L	Observed peak positions (keV)	Calculated peak positions (keV)	Difference
1	1	1	29.71	29.70	0.0087
2	2	0	48.49	48.50	−0.014
3	1	1	56.89	56.88	0.0113
4	0	0	68.60	68.59	0.008
3	3	1	74.76	74.75	0.0132
4	2	2	84.02	84.01	0.0045
5	1	1	89.11	89.11	0.0055
4	4	0	97.02	97.01	0.0151
5	3	1	101.48	101.45	0.0292
6	2	0	108.39	108.46	−0.0649

experiment. Each time a precise new 2θ is determined in
the normal way from all the reflections, a quick check that
the detector energy response remains unchanged can also
be provided. This check can be performed either by sepa-
rate refinement for 2θ with the detector parameters or else
by examining the residuals on the refinement of 2θ alone as
a function of energy. Changes in the detector parameters
generally cause anomalous systematic patterns in the resi-
duals as a function of energy. Any suggestion of detector
drift can be investigated further with recourse to the
fluorescent glass method. Spreadsheets for performing
both sorts of calibrations may be retrieved from the CCP14
web site (http://www.ccp14.ac.uk/projects/glass-calib/).

3. Conclusions

We have presented a fluorescent glass method of cali-
brating multiple energy-sensitive detectors simultaneously.
It allows the calibration lines to be selected to match the
energy range of the experiment and eliminates the
problems and expense associated with the use of radio-
active sources. As a cross check on this method, the range
of reflections observed from powder diffraction standards
in excess of those needed for 2θ refinement can be routi-
nely used as a complementary energy calibration monitor.

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