International Union of Crystallography

Commission on Powder Diffraction

Rietveld Refinement Round Robin. I. Analysis of Standard X-ray and Neutron Data for PbSO$_4$

BY R. J. HILL

CSIRO Division of Mineral Products, PO Box 124, Port Melbourne, Victoria 3207, Australia

Abstract

The Commission on Powder Diffraction of the International Union of Crystallography has undertaken an intercomparison of Rietveld refinements performed with two 'standard' PbSO$_4$ powder diffraction patterns: a conventional (two-wavelength) X-ray pattern collected on a Bragg–Brentano diffractometer with Cu $K\alpha$ radiation and a constant-wavelength neutron pattern collected on the D1A diffractometer at the Institut Laue–Langevin. The aims of this project were: (i) to evaluate a cross section of currently used Rietveld refinement software; (ii) to examine the range and effect of various strategies of Rietveld refinement; (iii) to assess the precision and accuracy (spread) of the parameters derived by Rietveld analysis. 23 participants provided 18 refinements with the X-ray data and 20 refinements with the neutron data, using 11 different Rietveld-analysis programs. Analysis of the submitted results shows that refinement strategies play a large part in determining the detailed outcome of a Rietveld refinement. The wide variation in the values of the agreement indices obtained in these studies of the same data sets highlights the need for standardization both of the refinement procedures and of the type of data included in the algorithms used for assessing the fit. The major factors limiting the accuracy of the derived PbSO$_4$ crystal structure parameters were: (i) use of insufficiently flexible peak shape and/or background functions; (ii) elimination of the high-angle diffraction data from the refinement; (iii) inclusion of an insufficiently wide range of diffraction angles on either side of the centroid of each peak during the step intensity calculation; and, additionally for X-rays, (iv) simultaneous release of the O-atom site-occupancy and displacement parameters. Rietveld analysis of the PbSO$_4$ X-ray powder diffraction data provided atomic coordinates and isotropic displacement parameters for the Pb and S atoms that are precise (*i.e.* have small e.s.d.s) and are in reasonable agreement with the values derived from a single-crystal study (*viz* the spread of coordinates is over the range 0.007–0.042 Å). On the other hand, the 'light' O-atom parameters show relatively poor precision and have a disconcertingly wide spread of values about the weighted mean (*viz* 0.12–0.19 Å for the coordinates). Despite the much lower intrinsic resolution of the neutron data (*i.e.* peak widths some four times those of the X-ray data), the coordinates and anisotropic displacement parameters obtained for the Pb and O atoms are very precise and have a relatively narrow distribution about the single-crystal results, namely 0.004–0.020 Å for the coordinates. The range of coordinates determined from the neutron data for the relatively 'light' S atom is correspondingly larger, namely 0.024–0.043 Å, about equivalent to that obtained from the X-ray data. In general, and as expected, the e.s.d.s from the Rietveld analyses are substantially smaller than the observed inter-refinement variation of the unit-cell dimensions, atomic coordinates and isotropic displacement parameters by factors of up to, respectively, 17, 5 and 22 for X-rays, and 25, 3 and 5 for neutrons. This investigation indicates that results of possibly high precision but low accuracy are not uncommon in Rietveld analysis. The disparity between individual refinements can be expected to increase further when, unlike here, the analyses are undertaken using data sets collected under diverse experimental conditions.

Introduction

The Rietveld method for the analysis of step-scan powder diffraction data was originally proposed to avert some of the problems associated with overlapping groups of peaks in single-wavelength neutron powder diffraction patterns (Rietveld, 1967, 1969). Dramatic expansion in the use of the method followed construction of the first wave of high-resolution single-wavelength (Hewat, 1975) and time-of-flight (Jorgensen & Rotella, 1982) neutron powder diffractometers. Extension to conventional X-ray data (Malmros & Thomas, 1977; Young, Mackie & Von Dreele, 1977; Wiles & Young, 1981) provided the catalyst for its increased usage in the wider

crystallographic community, while the most recent new application has involved the use of X-rays from synchrotron sources (Cox, Hastings, Thomlinson & Prewitt, 1983; Parrish, Hart & Huang, 1986).

As testimony to the rapid expansion of the method during the past five years, a nonexhaustive literature search undertaken at the time of writing has shown that the number of publications citing 'Rietveld' in the title and/or the reference list increased from 27 in 1986 to 452 in 1990 (with 910 in 1989). A plethora of Rietveld-analysis computer programs has arisen apace with this dramatic increase in popularity of the method, as individual research groups either modified already established and widely circulated programs, such as those of Hewat (1973) and Wiles & Young (1981) or wrote new code from scratch (for example, Pawley, 1980; Von Dreele, Jorgensen & Windsor, 1982; Baerlocher, 1982; Izumi, 1985).

Thus, both novice and experienced users of Rietveld analysis find (i) a wide range of extensively modified Rietveld computer programs at their disposal, (ii) the absence of well established and formalized *modus operandi* for execution of the method and (iii) few substantive documentations of the capabilities and limitations of the technique [Taylor (1985) is a notable exception]. Recognizing this unsatisfactory situation, the IUCr Commission on Powder Diffraction (hereafter CPD) decided, during the Perth Congress and General Assembly in August 1987, to seek the cooperation of the international powder diffraction community in undertaking a 'Rietveld Refinement Round Robin'. The goals of this project were:

(*A*) to evaluate a cross section of currently used Rietveld refinement software;

(*B*) to examine the range and effects of various strategies of Rietveld refinement;

(*C*) to assess the precision and spread of the model parameters derived by Rietveld analysis, *vis-à-vis* those obtained from single-crystal experiments;

(*D*) to compare and contrast various methods of step-scan data collection.

Aspects of powder diffraction profile analysis related to the treatment of preferred orientation, multiphase samples and the determination of crystallite size and microstrain were deliberately omitted from consideration. These features may form the subject of a future project undertaken by the CPD.

After consultation with diffractionists from a wide range of X-ray and neutron laboratories currently performing Rietveld analyses, the CPD decided that goals (*A*), (*B*) and (*C*) could be effectively examined by distributing two 'standard' medium-to-high-resolution powder diffraction data sets, one collected with conventional (sealed-tube) X-rays and the other with constant-wavelength neutrons. This decision was based on the fact that these radiations represent the most common types of X-ray and neutron diffraction data in current use. Participants in the study would then be asked to use their in-house Rietveld programs to analyse the data in the manner they 'normally' use. This constitutes Part I of the Project, the results of which are reported in the present work.

Goals (*C*) and (*D*) were to be examined by distributing two 'standard' samples of well characterized single-phase powders. The participants would be asked (i) to collect data on one or both of these samples using the method normally used in their laboratories, (ii) to use their in-house software to undertake a Rietveld analysis on these data and (iii) to submit the raw diffraction data so collected for subsequent analysis by the CPD using a 'standard' Rietveld program. No attempt would be made to dictate the conditions under which the data were either collected or analysed. This represents Part II of the Project (publication in preparation).

Selection of samples for distribution and analysis

Part I

After extensive consideration by the CPD membership and advice from representatives of the (then) US National Bureau of Standards, a sample of Ajax Chemicals $PbSO_4$ (batch no. 93240) was selected as the 'standard' material for Part I of the Project. This material is sufficiently complex, both structurally and chemically, to constitute a strong, although not severe, test of both X-ray and neutron Rietveld-analysis methodology (Table 1). It has a substantial degree of peak overlap (due to the combined effects of a moderately complex crystal structure and finite instrumental resolution), a mixture of atoms with different scattering factors/lengths (especially for X-rays) and a reasonable number of atoms in general positions.

Cu $K\alpha$ X-ray powder diffraction data were collected in the CSIRO Division of Mineral Products by Mr I. C. Madsen in August 1989 with a conventional Phillips PW1050 vertical parafocusing Bragg–Brentano goniometer fitted with incident- and diffracted-beam Soller slits (acceptance angles of about 5°), a curved-graphite diffracted-beam monochromator and a PW1710 diffractometer-controller system. The sample was back-pressed into a window of dimensions 10×20 mm and step-scan diffraction data were measured at 294 K from 10 to 160°2θ at intervals of 0.025°. A step counting time of 10 s was used and yielded a maximum step count of about 15 700. The divergence, scatter and receiving slits were set at 1°, 1° and 0.2 mm, respectively. The diffraction pattern is shown in Fig. 1(*a*); the minimum full width at half-maximum (FWHM) of the reflection profiles is about 0.09° in the lower third of the pattern.

Table 1. *Crystallographic details of materials selected for analysis in Parts I and II*

Property	PbSO$_4$	m-ZrO$_2$	ZSM-5(TPA)*
Space group	*Pbnm*	*P2$_1$/c*	*Pnma*
Unit cell: *a* (Å)	6.96	5.15	20.02
b (Å)	8.48	5.21	19.90
c (Å)	5.40	5.32	13.38
β (°)	–	99.22	--
Atoms in asymmetric unit	5	3	38 (+TPA)
Variable coordinates	11	9	>114
Unique reflections ($\lambda = 1.5$ Å)	380	340	930
(angular range)	(10–160°)	(10–160°)	(6–63°)
Sensitive parameters:†			
X-rays	O-atom positions	O-atom positions	TPA occupancy
	Atomic *B*s	Atomic *B*s	Atom positions
Neutrons	S-atom positions	Atomic β_{ij}	–
	Atomic β_{ij}		

* TPA: tetrapropylammonium.

† *B*: isotropic atomic displacement parameter; β_{ij}: anisotropic displacement coefficients.

(a)

(b)
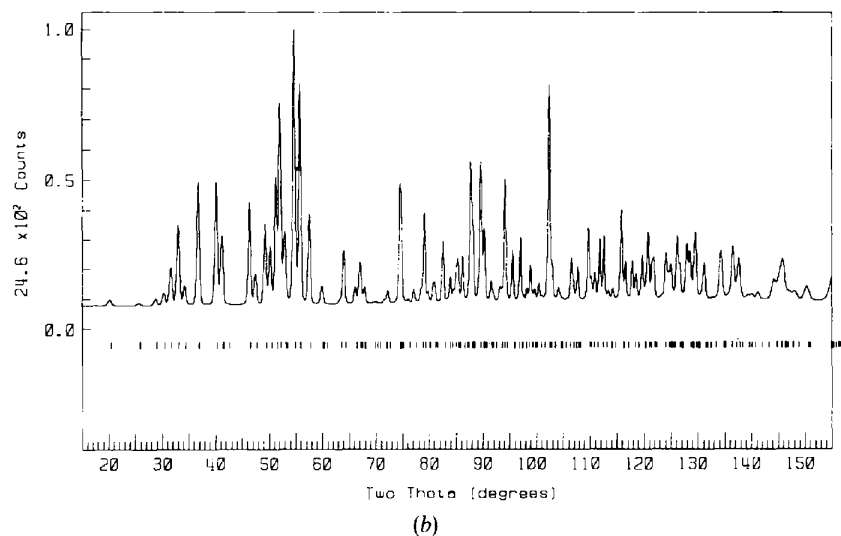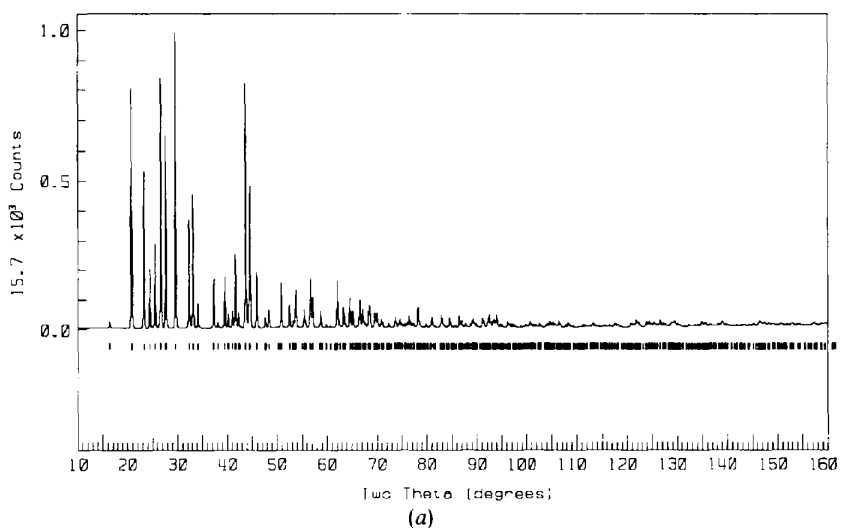
Fig. 1. Step-scan powder diffraction patterns for PbSO$_4$ using (a) Cu Kα X-rays and (b) 1.909 Å neutrons, representing the data distributed as the 'standard' data for Rietveld analysis. The positions of all possible Bragg reflections are indicated by the row of vertical tick marks below the profile of observed data.

The neutron powder diffraction pattern was collected by Dr A. W. Hewat in August 1989 from a sample of the same batch (*i.e.* Ajax Chemicals bottle) of $PbSO_4$ at a wavelength of 1.909 Å with the multidetector D1A instrument at the Institut Laue–Langevin, Grenoble, France. The sample was contained in a 50 × 16 mm diameter vanadium canister and data were measured at about 295 K from 10 to 156°2θ with a step interval of 0.05° and a monitor count of 100 000. Data accumulated by (one or more of) the ten counters were averaged to yield the pattern corresponding to Fig. 1(*b*); the maximum step count of 2500 represents about 22 000 counts if collected on a single-counter machine. That part of the neutron pattern between 60 and 110°2θ was collected with the full complement of counters and thus has slightly better counting statistics than the X-ray pattern, but the remainder has much poorer statistics. The minimum FWHM in the neutron pattern is about 0.37° at 110°2θ.

Part II

The selection of two materials to be circulated for data collection and analysis by the participants in Part II of the project was not easy. These samples were required to be (i) single phase, (ii) structurally and chemically uniform and stable, (iii) well characterized chemically and crystallographically, (iv) available in sufficient quantities and (v) an appropriately difficult test for both X-ray and neutron Rietveld analysis (as for $PbSO_4$ in Part I). Monoclinic (*m*) ZrO_2 was considered to satisfy all of the above requirements for diffractionists using conventional (*i.e.* sealed-tube) X-ray sources and/or most reactor and spallation neutron sources (Table 1). After much in-house examination of material from a variety of origins, a high-purity very fine grained 1 kg sample of *m*-ZrO_2 from the Osaka Cement Company Ltd (OZC-OS, Lot No. UP6856, courtesy of Professor T. Yamanaka, Osaka University) was selected for distribution. This sample contains less than 0.03% *w/w* Al_2O_3 and SiO_2 and has a surface area of 6.6 m^2 g^{-1} and a mean crystallite size of 620 Å (all values as quoted by Osaka Cement). The free-flowing uniformly white bulk sample was hand mixed and shaken and then 5 or 13 g aliquots were placed in small pillboxes, the amount depending on whether X-ray or neutron data, respectively, were to be collected. In view of the high chemical and phase purity and fine grain size of this material, it is most unlikely that different aliquots will display measurable differences in their physical and/or crystal structure properties.

It was decided that the second sample for Part II of the project should provide a much harder test for users of synchrotron X-ray and high-resolution spallation neutron sources. The pentasil zeolite ZSM-5, with the tetrapropylammonium (TPA) template molecule resident in the channels of the structure, was eventually considered to satisfy this more stringent requirement (Table 1). Samples of ZSM-5(TPA) synthesized with various crystallite sizes were obtained from the catalysis group of Broken Hill Pty Ltd (courtesy of Ms S. Bessell). To prevent chronic preferred orientation from dominating the data collection and resultant Rietveld analysis, the material finally selected contained some degree of peak broadening, primarily due to small crystallite size. In hindsight, the latter decision was not the best, as specimen broadening of the reflection profile so limited the resolution that the extraction of full crystallographic detail was virtually impossible, even for the instruments with best resolution. The smaller density of ZSM-5(TPA) relative to *m*-ZrO_2 allowed smaller quantities of the material to be distributed, namely, 3 and 7 g for X-ray and neutron data collection, respectively.

Distribution of data and samples

After extensive prior publicity, packets of samples and documents to be used for Parts I and II of the project were distributed between November 1989 and October 1990, upon request, to 45 individuals or groups in 18 countries. Each packet contained:

(i) a detailed set of instructions and a check list;

(ii) a magnetic tape containing two files of step-scan diffraction data collected on the standard sample of $PbSO_4$ with Cu *K*α X-rays and 1.909 Å neutrons;

(iii) samples of *m*-ZrO_2 and ZSM-5(TPA) zeolite for in-house X-ray (*X*) and/or neutron (*N*) data collection;

(iv) forms for reporting the *X* and *N* data-collection procedures and instrumental parameters;

(v) questionnaires for reporting the *X* and *N* structure-refinement procedures;

(vi) forms for reporting the structure-refinement results for $PbSO_4$ (*X* and *N*), *m*-ZrO_2 and ZSM-5(TPA).

The magnetic tape was designated to be used for return of the raw diffraction data collected on *m*-ZrO_2 and/or ZSM-5(TPA).

Results and discussion

Summary of participants' responses

23 responses were received up to the time of writing (June 1991), representing slightly more than a 50% return rate. Although relatively small in absolute terms, this number of participants compares favourably with earlier round robins conducted on related subjects, namely, 16 for the IUCr Single-Crystal Intensity Measurement Project on D(+)-

Table 2. *Summary of all responses*

X = X-rays, d = diffractometer, f = film scanner, t = transmission, s = synchrotron, N = neutrons, c = constant wavelength, tof = time of flight, nr = not refined.

Participant no.	PbSO$_4$ refined? X-ray	Neutron	Data collected m-ZrO$_2$	λ(Å)	Data collected ZSM-5	λ(Å)
2	Yes	Yes	$Xf/t_{1,2}$	Cu $K\alpha_1$	–	–
3	–	Yes	Nc	1.909	–	..
6	.	.	Nc	1.500	–	–
7	–	Yes	Xs	1.19752	Xs	1.5194
8	Yes	Yes	Xs	1.50164	Xs	1.45072
9	Yes	Yes	Xd	Cu $K\alpha$	Xd	Cu $K\alpha$
11	.		Nc	1.7080	–	.
12	Yes	Yes	Xt	Mo $K\alpha_1$	–	.
13	Yes	Yes	$Xd_{1,2}$	Co $K\alpha_1$	Xd	Cu $K\alpha$ (nr)
14	Yes	..	Xd	Cu $K\alpha$	.	–
15	Yes	Yes	Xd	Cu $K\alpha$	Xd	Cu $K\alpha$
18	Yes	Yes	–		.	–
19	Yes	Yes	Xd	Co$K\alpha$	.	
20	Yes	.	Xd	Cu $K\alpha$	.	–
21	Yes	Yes	$Nc_{1,2}$	1.0907	–	.
23	.	Yes	$Nc_{1,2}$	1.113, 1.530	–	–
25	Yes	..	Xd	Cu $K\alpha$	–	–
26		Yes	–		–	.
28	Yes	Yes	Xt/Nc	Cu $K\alpha_1$, 1.470	–	.
29			Ntof			–
34	Yes	Yes	Xd	Cu $K\alpha$	–	.
37	Yes	Yes	Ntof	–	–	.
40	Yes	Yes	Xd	Cu $K\alpha$	Xd	Cu $K\alpha$

tartaric acid (Abrahams, Hamilton & Mathieson, 1970), 21 for the IUCr Intercomparison of Neutron Powder Diffraction Instruments (Andresen & Sabine, 1977), 12 for the JCPDS-ICDD Round Robin on Systematic Errors Found in Routine X-ray Diffraction Raw Data (Schreiner & Fawcett, 1984), 9 for the IUCr Project on Comparison of Structural Parameters and Electron Density Maps of Oxalic Acid Dihydrate (Coppens *et al.* 1984), 9 for the JCPDS-ICDD/NBS Round Robin on Establishing an Instrumental Peak Profile Calibration Standard for Powder Diffraction Analysis (Fawcett *et al.*, 1988) and 22 for the JCPDS-ICDD Intensity Round Robin (Jenkins & Schreiner, 1989).

Table 2 gives a numerical list of the participants and a summary of the information that they submitted. Respondents can identify their data from the numbers in the first column of Table 2; these numbers were assigned (chronologically) during distribution of the samples and documents. The raw data sheets, plots and computer printouts submitted by each participant are held by the CPD Secretary, while the details extracted therefrom have been deposited.*

Not all participants completed all of the analyses and data collections requested (Table 2). Responses related to Part I of the project include 18 and 20 refinements, respectively, of the X-ray and neutron data for PbSO$_4$. Of the 26 data sets collected on the sample of m-ZrO$_2$ in Part II of the project, 17 used conventional X-rays, 2 used synchrotron X-rays, 6 used single-wavelength neutrons and 2 used time-of-flight (TOF) neutrons. Only 6 data sets were submitted on ZSM-5(TPA) as most participants (correctly) concluded that this material contained too much crystallite-size broadening of the peaks to permit full refinement of the zeolite framework structure.

For reasons of organizational clarity, the remainder of this paper will deal only with the responses obtained for Rietveld refinements using the two PbSO$_4$ data sets. The more complicated analysis of the data submitted on m-ZrO$_2$ and ZSM-5(TPA) will be reported later.

Summary of refinement techniques/strategies

Throughout the following discussion, it is assumed that the reader is familiar with the general philosophy, technique, applications and limitations of Rietveld analysis; those who are not so experienced are referred to descriptions/reviews of the method by Cheetham & Taylor (1977), Albinati & Willis (1982), Wiles &

* A compilation of the results submitted by each respondent has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55098 (108 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Rietveld analysis software used in Parts* I *and* II

Frequency	Name	Author(s)
7	DBW3.2S (etc.)	D. B. Wiles, A. Sakthivel, R. A. Young
6	LHPM8 (etc.)	R. J. Hill, C. J. Howard (modified DBW2.9)
2	EDINP/ALLHKL	G. S. Pawley (modified by G. A. Mackensie, M. S. Lehmann)
2	GSAS	A. C. Larson, R. B. Von Dreele
2	PREP/PROF	H. M. Rietveld, A. W. Hewat (modified by P. Clarke, P. Bendall, C. R. Thomas)
1	PROFPV	PREP/PROF modified by D. E. Cox, B. H. Toby, P. Zolliker, R. B. Von Dreele
1	MPROF	P. Murray, A. Fitch, J. Cockroft (modified PREP/PROF)
1	ARIT 1/4	A. Le Bail
1	MRIA-PC	O. K. Anston
1	PC/WYRIET	J. Schneider (modified DBW3.2S)
1	PFSR	Stoe Pty Ltd

Other software mentioned as available, but not used for this study:

4	'Original' Rietveld code	H. M. Rietveld
2	XRS-82	C. Baerlocher
1	PROFILE	(Not stated)
1	TF12/15LS	(Not stated)

Young (1981), Taylor (1985), Hewat (1986), Hill & Madsen (1987), Bish & Post (1989) and Young (1992).

(a) Rietveld-analysis software

A summary of the software used for crystal structure and diffraction-profile refinements using the $PbSO_4$ (and m-ZrO_2) data sets is given in Table 3. Only a handful of the 15 Rietveld programs cited in this table can claim to be totally original since most contain large slabs of software written by H. M. Rietveld himself in the late 1960s or, later, by A. W. Hewat, R. B. Von Dreele, R. A. Young, D. B. Wiles and others. Nevertheless, each program is unique in the sense that local and often very extensive modifications have been made over a long period, so that there is now considerable divergence from the original 'grandfather' code. In other cases, such as GSAS, XRS-82 and EDINP, the program is capable of undertaking considerably more than a traditional Rietveld analysis (see below).

Of the 11 programs used in the current study, the program DBW et seq. (Wiles & Young, 1981) has made by far the greatest numerical impact on the execution of Rietveld analysis; 7 of the 23 participants cited DBW3.2S directly, while another 6 used LHPM et seq. (Hill & Howard, 1986), a not-too-distant relative. This usage pattern is unlikely to change dramatically in the near future since DBW is now being widely distributed in a form suitable for a personal computer.

The program GSAS (Larson & Von Dreele, 1986) was used by only two respondents in this survey, even though it provides the greatest range of Rietveld-analysis options. This program allows the simultaneous refinement of multiple data sets collected from a variety of different instruments and/or radiations, hard/soft constraints, links to a host of accessory programs for geometric and visual representation of the structure, together with the refinement of parameters relating to sample transparency, sample displacement, crystallite size/microstrain, preferred orientation, X-ray beam polarization and extinction.

It is appropriate to mention here that an error was discovered in the DBW3.2S code during in-house analysis of the m-ZrO_2 data submitted during the course of Part II of the project. This error involved an incorrect assignment of the multiplicity of reflections of the type $0kl$ in point group $2/m$. Although not producing a catastrophic refinement result, the profile agreement indices were larger than normal and the derived crystal structure parameters showed a wider than expected deviation from the accepted values. All participants who used this software were informed of a cure to the problem and asked to submit a reanalysis of their m-ZrO_2 data. This is a clear example of the important role that intercomparison projects can have in highlighting problems with refinement software.

(b) Refinement strategies and statistics

Details of the refinement strategies and statistics used for the $PbSO_4$ X-ray and neutron Rietveld refinements are provided in Table 4. It is clear from this table that there is a wide variety of opinion among individual practitioners about the best method of treating the raw diffraction data and the *modus operandi* for Rietveld analysis.

In regard to the raw data, 4 of the 16 X-ray and 5 of the 17 neutron respondents chose to truncate the data set submitted to them, either at the top or bottom of the pattern (Table 4). Removing the low-angle X-ray data up to $18°2\theta$ (but no higher) can be understood since, for 1° divergence slits and a sample of length 20 mm, the specimen does not intercept all of the incident beam below 18°. In the case of the neutron data, there are only a few very low-intensity

Table 4. *Summary of refinement strategies and statistics for* PbSO$_4$

	X-rays	Neutrons
Number of refinements	18	20
Range of data used; low/high limit (°)	10/24 → 125/160*	10/30 → 132/156
Cu $K\alpha_2/\alpha_1$ intensity ratio	0.50 → 0.54	–
Monochromator correction factor	0.7998 → 0.937	–
Number of parameters refined	22 → 50	22 → 49
Convergence criterion (parameter shift as % of last e.s.d.)	1 → 30	1 → 30
Calculation range ($\pm$ FWHM)†	2 → 20	1.5 → 6
Frequency of background style:		
Refined‡	10 (3 → 9 parameters)	6 (3 → 6 parameters)
Interpolated	6 (8 → 61 points)	10 (7 → 41 points)
Peak asymmetry refined (yes)	12	11
Preferred orientation released (yes)	3	2
Occupancy of atom sites released (yes)	2	3
Anisotropic atomic displacement (yes)	4§	6

* Three X-ray respondents deleted every second data point to give a step size of 0.05°2θ.
† One respondent used a range of $\pm 2.4°2\theta$ from the peak centroid, another two used ± 0.1 or $\pm 0.5\%$ of the peak height.
‡ One refined background model was a cosine Fourier series.
§ Two X-ray respondents released only the Pb and/or S atoms anisotropically; another two refinements provided non-positive-definite ellipsoids for the S and/or O atoms.

Table 5. *Summary of Rietveld analysis agreement indices for* PbSO$_4$

	X-rays	Neutrons
Background included, full pattern*		
R_p (%)	7.3 → 16.6	2.2 → 11.1
R_{wp} (%)	8.2 → 20.0	2.4 → 12.3
R_{exp} (%)	1.5 → 7.0	1.7 → 10.1
GofF	1.3 → 7.4	1.0 → 3.1
R_B (%)	2.8 → 10.3	0.7 → 8.8

In-house tests on data from respondent number 9:

	R_p	R_{wp}	R_p	R_{wp}
Background included, full pattern* (%)	7.44	10.21	2.17	2.61
Upper 2θ limit of 130° (%)	7.14	10.08	2.01	2.53
Background subtracted, peaks only† (%)	10.50	12.59	5.03	4.88

* Young, Prince & Sparks (1982).
† Hill & Fischer (1990).

peaks below 30° (Fig. 1b), so several participants decided not to bother with this region of the pattern. No substantive case was made for deleting the data in the high-angle region in either the X-ray or neutron patterns though it is likely that for some respondents a limitation may have been imposed by the dimensions of the program arrays.

Three respondents chose to delete every second data point from the X-ray pattern to give a step size of 0.05 rather than 0.025°2θ, perhaps again for reasons of program size. In combination with the cutoffs described above, this has meant that the total number of steps included in the refinements varies from 2900 to 6000 among different respondents. Furthermore, values assumed (or calculated) for the Cu $K\alpha_2/\alpha_1$ integrated intensity ratio and the diffracted-beam graphite-monochromator polarization correction factor varied substantially from the 'ideal' values of 0.5 and 0.7998, respectively (Table 4). On the other hand, the neutron scattering lengths varied little and all but one respondent used neutral atomic scattering factors for the X-ray refinements.

In respect of the refinement process, all X-ray respondents used a weighting scheme based on the reciprocal of the observed intensity (*i.e.* $1/Y_{obs}$). One participant provided two additional refinement results, one based on a unit weighting scheme and the other based on $1/(Y_{obs})^{1/2}$. The Rietveld agreement statistics listed in Table 5 refer only to refinements undertaken with the conventional $1/Y_{obs}$ weighting scheme; discussion of the impact of the other exotic schemes is treated separately.

Since the neutron data were collected with a multicounter instrument, the correct counting-statistics weight applied to each step is N/Y_{obs}, where N is the number of counters used to provide the average

count at the step. Although only three respondents specifically indicated that they used this weighting scheme, it can be assumed to have been applied by all but one of the other participants since (i) the software they used is known to have the ability to deal with multicounter data or (ii) they work routinely with multidetector instruments. In any event, it is clearly evident if a respondent has used $1/Y_{obs}$ rather than N/Y_{obs} since the value of the Rietveld-refinement goodness-of-fit parameter (Young, Prince & Sparks, 1982) then has a value substantially less than unity (*viz* about 0.6).

The number and type of parameters released in the refinements were essentially the same for the X-ray and neutron data; in both cases the number varied from 22 to around 50, the difference corresponding roughly to the use of isotropic *versus* anisotropic atomic displacement parameters in combination with a fixed *versus* refined background, respectively. In fact, with a total of 19 parameters required to refine the unit cell, atomic coordinates and individual isotropic displacements, the lower limit of 22 leaves only 3 parameters available to define the characteristics of the background and reflection profiles! The definition of convergence was also flexible, refinements being terminated when parameter shifts decreased to values ranging from 1 to 30% of the corresponding e.s.d.; the upper limit must be considered rather too large to guarantee full convergence (see below).

There was also substantial variation in the selection of the angular region over which a peak was considered to make a contribution to the surrounding step intensities (Table 4). This was especially true for the X-ray refinements, where the number of FWHMs used for the intensity calculation on either side of the peak centroid varied between 2 and 20. For neutrons the variation was only 1.5 to 6.0 times the FWHM; the implications of this choice are discussed later. In only three cases was a parameter other than the FWHM used to define the range of calculation; one respondent used a fixed range of $\pm 2.4°2\theta$ and two used ± 0.1 and $\pm 0.5\%$ of the peak height. The use of a cutoff dictated by a fixed proportion of the peak height has the distinct advantage that it is independent of the peak-shape model used and is, therefore, recommended as the preferred means of peak truncation for all Rietveld analyses.

Treatment of the background varied markedly, both among respondents and between the X-ray and neutron cases. Refinement of the coefficients of a polynomial in 2θ was the most common means of defining the background for the X-ray data, whereas, for neutrons, linear interpolation was the most popular choice (Table 4). For refinement, two types of polynomial were used (in equal numbers), one a simple function of the form $B_m(2\theta)^m$ and the other having the form $B_m(2\theta/Q - 1)^m$, where Q is a value of 2θ near the middle of the pattern. The latter type of background model is expected to be more stable during refinement since the 'origin' of the polynomial can be chosen well away from the lower extreme of the pattern. In both cases, the number of background parameters refined, or points used for interpolation, varied substantially (Table 4). Two respondents used a model based on a cosine Fourier series.

Most respondents assigned individual displacement parameters to each of the five atoms in the structure, but three X-ray participants chose to release a single isotropic parameter for the three O atoms and one assigned a global B value to all atom types. All X-ray and neutron respondents showed a general reluctance to refine an anisotropic atomic displacement model. This is understandable in the case of X-rays, for which the relative intensity of the peaks falls away at high scattering angles much more severely than for neutrons. Nevertheless, four X-ray respondents used at least a partial anisotropic model; two released the coefficients of the 'heavy' Pb and/or S atoms and achieved satisfactory results, but the two who refined all atoms anisotropically obtained non-positive-definite displacement ellipsoids for at least one atom. The six anisotropic neutron refinements were all successful and it is surprising that more respondents did not take this course.

All but three of the X-ray respondents allowed the peak shape to vary with diffraction angle, but more than half of the neutron refinements were executed with a fixed shape across the pattern (see below). Most participants released a peak asymmetry parameter, but very few attempted refinement of preferred orientation or atomic site occupancy (Table 4). It is possible in the latter two cases that most of the respondents established early on in their refinements that the patterns did not display preferred orientation and that the sample of $PbSO_4$ was stoichiometric, and so fixed these parameters in the later stages.

(c) Agreement indices

Considering that all of the participants were provided with the same diffraction data, it was surprising to encounter such a large variation in the values of the Rietveld agreement indices (Table 5, Fig. 2). Definitions of the conventional agreement indices R_p (profile), R_{wp} (weighted profile), R_{exp} (expected), GofF (goodness of fit) and R_B ('Bragg') are provided by Young, Prince & Sparks (1982). All respondents stated that they used the conventional algorithms (but see the discussion below). Thus, the spread of R_{wp} values is particularly alarming, ranging as it does from 8.2 to 20.0% for the X-ray data and from 2.4 to 12.3% for the neutron data. The R_B value is also spread widely, from 2.8 to 10.3% for X-rays and from 0.7 to 8.8% for neutrons.

Most of this variation arises from differences not in the agreement-index algorithms themselves but rather in the definition of the individual step-intensity terms used in the calculation, that is, whether or not the sums include (i) the background in the step intensity and (ii) those regions of the pattern containing no intensity contribution from a peak. Most 'first-generation' Rietveld-analysis software involves a preliminary background-subtraction and peak-range assignment step, so that the indices obtained from these programs generally include neither the background nor those parts of the pattern with no peaks; two respondents used code with this feature. Furthermore, whether the program is old or new, if the background is interpolated rather than refined (*viz* 16 out of a total of 38 cases considered here), then it is usually assumed to contain no error and the background intensity is once again routinely deleted from the agreement-index sums.

In general, the indices calculated with the background included in the sums (whether or not the background has been refined) tend to be smaller than those obtained with the background excluded (Eriksson, Louër & Werner, 1989; Hill & Fischer, 1990); the greater the relative level of the background (*i.e.* the lower the signal-to-noise ratio), the larger will be the effect. Table 5 shows, for in-house analysis of the X-ray and neutron $PbSO_4$ data, the effect on the agreement indices of background subtraction and the inclusion only of the regions involving peaks. When the background is eliminated from the sums, the values of R_p and R_{wp} increase by 40 and 25%, respectively, for the X-ray data, and by 130 and 90%, respectively, when the neutron data are used. The effect is greater in the neutron case since the peak-to-background ratio is lower than for the X-ray data.
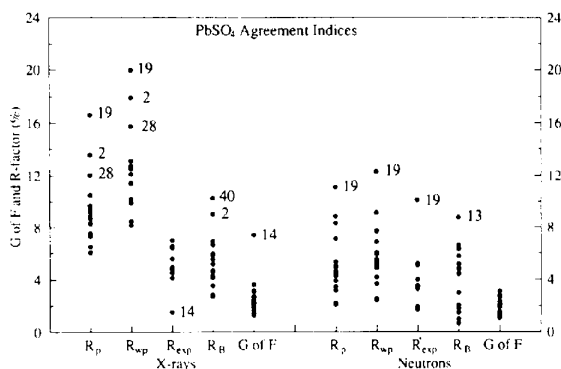
Thus it is clear that the continued existence of these two 'kinds' of agreement-index sum can, and often does, cloud comparisons between refinements undertaken on different samples with different instruments and/or wavelengths. This is not to say that the background-included versions of the indices should not be calculated; in fact, the full intensity version of the R_{wp} index remains the most appropriate measure of the overall fit between the calculated and observed diffraction patterns. Nevertheless, it is strongly recommended that the background-subtracted forms of all of the indices be calculated to facilitate comparisons *between* different refinements.

A further variation in the agreement indices can be attributed to the fact that several respondents truncated the data set. The three respondents who terminated the pattern at 145° or lower obtained, as expected, among the lowest values for both R_p and R_{wp}. This was tested by in-house refinements of the X-ray and neutron data with the upper limit set at 130° (Table 5); there is a small reduction in the R_p and R_{wp} values in both cases due to the elimination of the poorer-quality high-angle data from the agreement-index sums. Note, however, that changing the step interval has no effect on the profile indices (Hill & Madsen, 1986), so that the three participants who deleted every second data point from the original pattern did not (directly) influence the indices by this action.

Even allowing for the different data cutoffs and classes of data included in the indices, Table 5 and Fig. 2 show that there is considerable additional variation due to the particular characteristics of the individual refinement strategies, that is, to the peak-shape model used, the calculation range, the number of parameters in the model *etc.* This is discussed in detail below. Of particular concern in Fig. 2 is the fact that a few refinements, especially in the X-ray case, have provided very poor agreement between the calculated and observed profiles, namely, maximum values of R_p and R_{wp} of between 16 and 20% and a largest R_B of around 10%.

For the neutron refinements, the spread of the agreement indices is about the same as for X-rays, but the 'best' refinements have substantially lower values of R_p, R_{wp} and R_B. This appears to confirm the generally held belief that constant-wavelength neutron powder diffraction patterns are more effectively modelled by existing peak shape and width algorithms than are those of X-rays, no doubt partly due to the usually lower resolution of the pattern in the neutron case (*viz* minimum FWHM of 0.09 *vs* 0.37°2θ for the X-ray and neutron data, respectively). Nevertheless, there is reason for concern with several of the neutron refinements too; the maximum values of R_p and R_{wp} are larger than 11% and the biggest R_B is around 9%.

Fig. 2. Plots of the Rietveld agreement indices (see text for details) obtained by each respondent for analyses of the $PbSO_4$ diffraction patterns collected with X-rays and neutrons. Participant numbers have been placed alongside selected outlier reults.

One intriguing aspect of the data in Table 5 and in Fig. 2 (though not entirely obvious here because of multiple overlaps of points) is that there are three quite distinct clusters of R_{exp} values; for X-rays, the R_{exp} values group around 1.5, 4.9 or 6.5%, while, for neutrons, the values mostly occur near 1.9, 3.5 or 5.1%. In-house calculations show that the X-ray values near 4.9 and 6.5, and the neutron values near 1.9 and 3.5, are characterized by the inclusion or absence of the background (and non-peak regions), respectively, in the agreement-index sums. However, since the calculation of R_{exp} should otherwise be determined only by the numerical values of the raw diffraction step intensities (with a minor effect due to different numbers of refined parameters), it is difficult to understand how different calculated values can be produced from the same raw data. This is particularly worrisome in the cases of the low value of 1.54% for X-rays and the high value of 10.3% for neutrons; these respondents (numbers 14 and 19, respectively) should examine their code for possible errors in these calculations.

Finally, it is noteworthy that there are two distinct and equally popular definitions of the goodness-of-fit parameter provided by respondents. The form used here is that given by Schwarzenbach et al. (1989), namely, $GofF = R_{wp}/R_{exp}$; the other form used is the square of this quantity. Even after standardizing all of the contributed values to the unsquared form, the values in Table 5 show a large variation. Furthermore, the values GofF are generally much larger than their expected value of unity (especially for the X-ray refinements; Fig. 2), indicating that (i) the refinements have not been carried through to convergence and/or (ii) there are systematic errors in the refinement models used, the effects of which have not been incorporated into the weighting schemes for least-squares analysis (Rollett, 1982; Hill & Madsen, 1986). As stated by Schwarzenbach et al. (1989), deviation of the square of the GofF parameter from unity is a measure of the validity of the least-squares model and of the estimate of the variance–covariance matrix and hence of the parameter variances themselves.

With respect to refinement convergence, it is relevant to note the wide range of convergence criteria used (Table 4). Termination when parameter shifts are still 30% of the corresponding e.s.d. (as used by four respondents) leaves considerable scope for further improvement in the model parameters and thus in the GofF and all of the other agreement indices. However, in the case where convergence has indeed been achieved, the GofF parameter may remain large due to the presence of any or all of the following residual systematic errors: inappropriate reflection-profile shape and width functions (including neglect of asymmetry); neglect of reflection-profile variation with diffraction angle; insufficient range of profile calculation on either side of the reflection centroid; inappropriate background function; incorrect monochromator polarization.

(d) Profile-width functions

The vast majority of the X-ray and neutron respondents modelled the variation in the reflection-profile width reasonably successfully as a function of 2θ using the conventional Caglioti, Paoletti & Ricci (1958) quadratic in tan θ, some with adjustments to allow separate treatment of the Gaussian and Lorentzian components. There is, however, a substantial variation in the detailed form of the resultant 'resolution function' obtained for the X-ray diffractometer used to collect the data, especially at the top and bottom of the pattern (Fig. 3, and discussion below). All of the neutron and all but two of the X-ray refinements used three parameters to define the peak-width variation.

There is some inconsistency in the determination of X-ray peak widths above $100°2\theta$ (Fig. 3a) by some respondents. Indeed, the difference between the largest
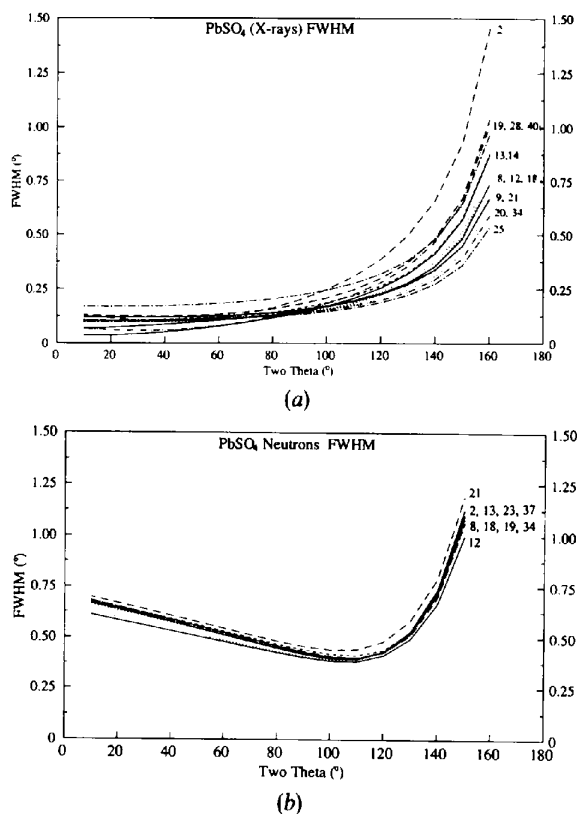

(a)

(b)

Fig. 3. Plots of the peak full width at half-maximum (FWHM) as a function of diffraction angle calculated from the values of the parameters U, V and W in the Caglioti et al. (1958) relationship as provided in refinements using (a) X-ray and (b) neutron data. The participant numbers have been placed adjacent to the appropriate curves.

Table 6. *Frequency of usage of peak-profile shape functions*

	X-rays	Neutrons
Shape type		
Gaussian	–	7
Intermediate Lorentzian (fixed)	3	1
Pseudo-Voigt	8	4
Pearson VII	3	1
Voigt		1
'Learned' (analytical Fourier series)	1	1
Shape variation with 2θ		
Fixed	3	8
Number of parameters: 1	2	1
2	4	1
≥ 3	7	5
Peak asymmetry		
None	4	5
Nonzero, but fixed	1	1
Variable	10	9

and the smallest peak widths in the X-ray pattern at the 'node', or crossover point, near $80°2\theta$ in Fig. 3(*a*) is a factor of two (*i.e.* 0.18 *vs* 0.09°). The spread of width values probably reflects a varying quality of discrimination between the peak wings and the background and is particularly evident in the high peak-overlap regions at large diffraction angles. This poor discrimination is most probably a result of inappropriate selection of the background or peak-shape function (see below) and/or the use of an insufficient number of FWHMs for the peak-intensity calculation. The variation does not augur well for the reliability of estimates of crystallite size and microstrain information extracted from X-ray patterns using a full-pattern (rather than single-peak) approach.

On the other hand, the neutron data provide no such difficulties with peak-width definition (Fig 3*b*). The more stable refinement of reflection widths and shapes for neutrons is not related to differences in the absolute intensities (*i.e.* counting statistics) and/or signal-to-noise ratios of the X-ray and neutron peaks at high angles since there is approximate correspondence between the step intensities of the two data sets in this region (Fig. 1). Rather, it appears that the X-ray fits are less stable and more inconsistent due to the generally poorer modelling of the basic peak shapes and widths and especially their angle dependency.

(*e*) *Profile-shape functions*

Table 6 gives the frequency of usage of the six peak-shape models invoked in the refinements of the $PbSO_4$ structure. For the X-ray data, the pseudo-Voigt function was by far the most popular, with equal second place assumed by various 'intermediate' (fixed-shape) Lorentzians and by the Pearson VII

function [for a detailed description of these peak-shape models, see Young & Wiles (1982)]. The pseudo-Voigt is commonly used to model profile shape since it is conveniently expressed (and visualized) as a percentage of Lorentzian character between 0% (pure Gaussian shape) and 100% (pure Lorentzian). For neutrons, the most commonly used shape was the Gaussian, followed by the pseudo-Voigt. It should be noted that the average character of the peak shape across the neutron pattern, when described in terms of a simple mixture of Gaussian and Lorentzian end members, is about 30% Lorentzian (*cf.* 80% for the X-rays). Thus, the use of a pure Gaussian neutron peak shape (with a small number of FWHMs used in the calculation of the step-intensity profile on either side of the peak; Table 4), as invoked by seven respondents, is clearly inappropriate for this pattern.

For the X-ray data, all but three respondents allowed the peak profile shape to vary with diffraction angle and 11 provided two or more parameters for this purpose (Table 6). Fig. 4 shows the variation in X-ray peak shape for the six respondents who incorporated a simple constant or linear angle-dependent pseudo-Voigt function (*i.e.* one or two variable parameters). As often observed in X-ray patterns (Hill, 1984), the Lorentzian character of the peaks increases with diffraction angle for most of the functions plotted in Fig. 4. In fact, at the top end of the $PbSO_4$ pattern, the Lorentzian character fitted to the reflection profiles rises above 100% (in a purely mathematical sense) to produce the so-called 'super Lorentzian' shape (Wertheim, Butler, West & Buchanan, 1974); this effect has been attributed to the presence of different particle-size distributions in the sample (Young & Sakthivel, 1988). One respondent (no. 14; Fig. 4) refined a quadratic function in 2θ
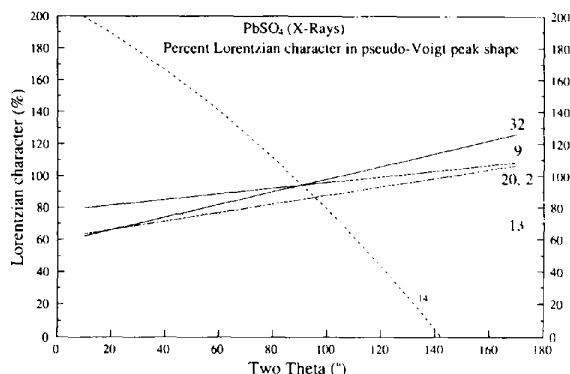

Fig. 4. Plots of the variation in percent Lorentzian character with diffraction angle for a selection of those X-ray pattern refinements using a fixed or variable pseudo-Voigt peak-shape function. The participant numbers have been placed adjacent to the appropriate curve.

for pseudo-Voigt peak shape that produced the reverse trend, namely a decrease from more than 200% Lorentzian character at $10°2\theta$ to a negative value beyond 140°; in this case, the data are clearly unable to support the prescribed three-parameter function, perhaps in part because every second data point in the pattern had been deleted to provide a step width of 0.05°.

For the neutron data there was some reluctance to allow the shape to vary with 2θ (or from pure Gaussian at all, for that matter), but in those seven cases where the shape was released, an attempt was generally made to model correctly the effects of microstrain and/or crystallite-size broadening, rather than merely to fit a nonphysical polynomial in 2θ. This was accomplished by separate consideration of the Gaussian and Lorentzian components of both the peak width and shape, as described by David & Matthewman (1985), Larson & Von Dreele (1986) and Thompson, Cox & Hastings (1987).

Most respondents provided for peak asymmetry by the introduction of a (nonzero) fixed or variable parameter (Table 6). The most commonly used model was the empirical function introduced by Rietveld (1969), but four neutron respondents used a Simpson's-rule sum to model the asymmetry arising from the finite vertical height of the detector (Howard, 1982). It is important to note that these two functions have quite different effects on the calculated profile; Rietveld's function shifts the base of the peak to one side, leaving the maximum in the theoretical position, while the Simpson's-rule function tends to shift the top of the peak, leaving the base essentially fixed. In addition to these corrections, one respondent introduced asymmetry through an analytical Fourier series used to provide the 'learned' profile and one X-ray respondent used a split Pearson VII function (Toraya, 1986) to generate different peak widths on the low- and high-angle sides of the peak centroid.

The Simpson's-rule asymmetry correction models the peak profile from a sound physical basis and, perhaps for this reason, provides a substantially better fit for the neutron low-angle reflections than the simple empirical Rietveld function. For X-rays, Simpson's rule has less to recommend it since the correction is not designed specifically for Bragg–Brentano geometry where other factors, such as sample transparency and flat-specimen effects, contribute to the asymmetry (Klug & Alexander, 1974). In fact, a suitable asymmetry correction for X-ray peaks awaits implementation; for this sample of $PbSO_4$, neither the analytical series nor the split Pearson function provided an identifiable improvement to the fit relative to that obtained with the conventional Rietveld asymmetry correction.

For X-rays, factors additional to the exact choice of peak-shape model (most of which were quite

flexible) controlled the quality of the refinement. For neutrons, on the other hand, those seven respondents who restricted the peak shape to pure Gaussian and/or imposed a severe limitation on the number of FWHM included in the calculation, generally obtained poorer results, as measured by the agreement indices. These effects are discussed in greater detail in the next section.

Crystal structure parameters

Plots of the unit-cell dimensions, atomic coordinates and displacement parameters obtained for $PbSO_4$ by all respondents are provided in Figs. 5–8. The ranges observed for the parameters, their weighted means and values of the 'external' and 'internal' estimated standard deviations and variance ratios (see below) are given in Tables 7–9. In Tables 7 and 9, the weighted mean parameter values are compared with those determined from single-crystal X-ray diffraction data by Miyake, Minato, Morikawa & Iwai (1978). It is accepted that single-crystal unit-cell dimensions are usually determined with an accuracy sufficient only to reproduce successfully the positions of the reflections for the diffractometer intensity measurements and that the atomic coordinates and displacement parameters can be adversely influenced by the effects of inadequate absorption and extinction corrections.
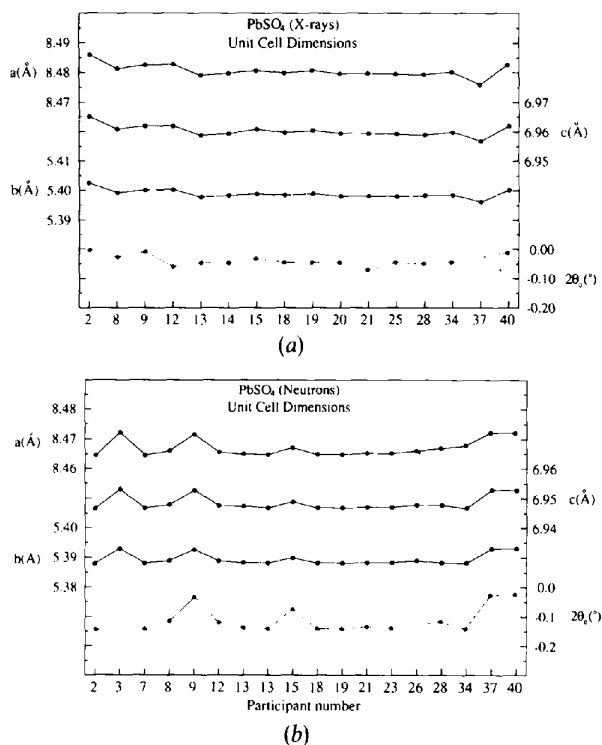

Fig. 5. Variation of the unit-cell dimensions determined by refinements using (a) the X-ray and (b) the neutron data.

Table 7. *Ranges and weighted means of* $PbSO_4$ *crystal structural parameters*

	X-rays Range	X-rays Mean*	Single crystal†	Neutrons Mean*	Neutrons Range
a (Å)	8.4764–8.4859	8.4804 (4)	8.482 (2)	8.4667 (6)	8.4646–8.4723
b (Å)	5.3962–5.4024	5.3989 (3)	5.398 (2)	5.3889 (2)	5.3879–5.3930
c (Å)	6.9568–6.9650	6.9605 (4)	6.959 (2)	6.9477 (2)	6.9466 6.9530
Pb x	0.1875–0.1883	0.18783 (4)	0.1879 (1)	0.18773 (5)	0.1874–0.1881
z	0.1669–0.1683	0.16752 (9)	0.1667 (1)	0.16731 (5)	0.1670–0.1677
S x	0.0621 0.0673	0.0642 (2)	0.0633 (6)	0.06490 (17)	0.0638–0.0666
z	0.6799–0.6860	0.6838 (4)	0.6842 (7)	0.68443 (28)	0.6804–0.6866
O1 x	0.902–0.924	0.9083 (13)	0.908 (2)	0.90857 (14)	0.9069–0.9093
z	0.585–0.601	0.5945 (7)	0.596 (3)	0.59535 (7)	0.5946–0.5958
O2 x	0.177–0.200	0.1850 (11)	0.194 (2)	0.19366 (12)	0.1930–0.1947
z	0.523 0.548	0.5398 (13)	0.543 (2)	0.54329 (8)	0.5425 0.5438
O3 x	0.071–0.080	0.0778 (5)	0.082 (1)	0.08084 (4)	0.0806–0.0812
y	0.018–0.041	0.0262 (13)	0.026 (2)	0.02701 (5)	0.0264 0.0272
z	0.806–0.819	0.8139 (7)	0.809 (2)	0.80852 (8)	0.8080 0.8092
B Pb (Å²)	0.90–2.39	1.42 (11)	1.48	1.59 (3)	1.18–1.78
S (Å²)	0.29–1.37	0.98 (8)	0.74	0.67 (4)	0.36–0.97
O1 (Å²)	0.50–4.2	1.24 (10)	1.87	2.11 (3)	1.80 2.33
O2 (Å²)	0.1–5.8	1.31 (13)	1.76	1.67 (3)	1.30–2.05
O3 (Å²)	0.8–4.6	1.27 (11)	1.34	1.55 (3)	1.31–1.70

* Weighted mean of the 16 X-ray and 17 neutron parameter values, with an e.s.d., σ_{ext}, calculated from the agreement among the experiments using equation (2).

† X-ray data of Miyake, Minato, Morikawa & Iwai (1978); B values are equivalent isotropic parameters calculated according to Hamilton (1959). These parameter values are taken to be the 'true' estimates for assessing the accuracy of the various Rietveld-refinement results (see text).

Table 8. *E.s.d.s σ and variance ratio $\Re$ of the weighted mean parameter values in* $PbSO_4$

The values of σ_{ext}, σ_{int} and $\Re$ are defined in (2)–(4) in the text.

	X-rays σ_{ext}	X-rays σ_{int}	X-rays $\Re$	Neutrons σ_{ext}	Neutrons σ_{int}	Neutrons $\Re$
a (Å) ($\sigma \times 10^6$)	364	26	201	639	26	609
b (Å)	288	19	220	160	9	302
c (Å)	412	24	292	214	9	522
Pb x ($\sigma \times 10^6$)	44	23	3.6	52	24	4.6
z	86	33	6.7	47	39	1.5
S x ($\sigma \times 10^5$)	24	14	2.9	17	8	4.9
z	40	19	4.4	28	10	7.8
O1 x	132	32	16.7	14	5	9.9
z	72	38	3.6	7	5	2.4
O2 x	115	36	10.4	12	5	6.6
z	127	48	7.0	8	6	1.6
O3 x	48	21	5.4	4	3	1.6
y	130	29	20.6	5	4	1.6
z	73	30	5.7	8	4	4.7
B Pb ($\sigma \times 10^3$)	115	5	487	29	6	21.2
S	81	22	14	37	15	6.2
O1	100	32	9.7	26	12	5.2
O2	132	32	16.6	33	10	10.1
O3	105	29	12.9	25	6	16.3

Nevertheless, for the purpose of this analysis, and in the absence of other measurements (not from Rietveld analysis), the single-crystal values are taken to be the 'true' values of the structural parameters for $PbSO_4$.

The *weighted mean parameter values* μ were obtained from

$$\mu = \sum_i (P_i/\sigma_i^2) \bigg/ \sum_i (1/\sigma_i^2), \tag{1}$$

where P_i is the parameter value and σ_i is its e.s.d. obtained in the usual way from the Rietveld refinement procedure.

At this point it should be noted that the e.s.d. σ_i is the *minimum* possible probable error in the Rietveld-parameter value, based on random errors alone. This e.s.d. is a direct measure of the precision of the determination, but is not a good measure of accuracy (Schwarzenbach *et al.*, 1989) and should not be used for the latter purpose.‡ In the present case, the accuracy of a particular determination (and of the weighted mean) is assessed relative to the 'true' value determined in the single-crystal analysis.

To make a quantitative determination of the spread of the experimentally derived parameter values about their weighted mean (*i.e.* a measure of their probable error) and to assess the presence or absence of systematic errors in the refinement models, two values for the e.s.d. of the weighted mean value were

‡ *Accuracy* is taken here to mean the closeness of agreement between the measured value of an estimate, derived from a physical measurement, and the true value of the quantity estimated (Schwarzenbach *et al.*, 1989). The reference to the 'true' value implies that accuracy cannot be exactly evaluated. *Precision*, on the other hand, is taken to be the closeness of agreement between the values of a measurement or of an estimate obtained by applying a strictly identical experimental procedure several times (Schwarzenbach *et al.*, 1989). It is expressed numerically by a standard deviation or variance. Note that precise estimates are not necessarily accurate.
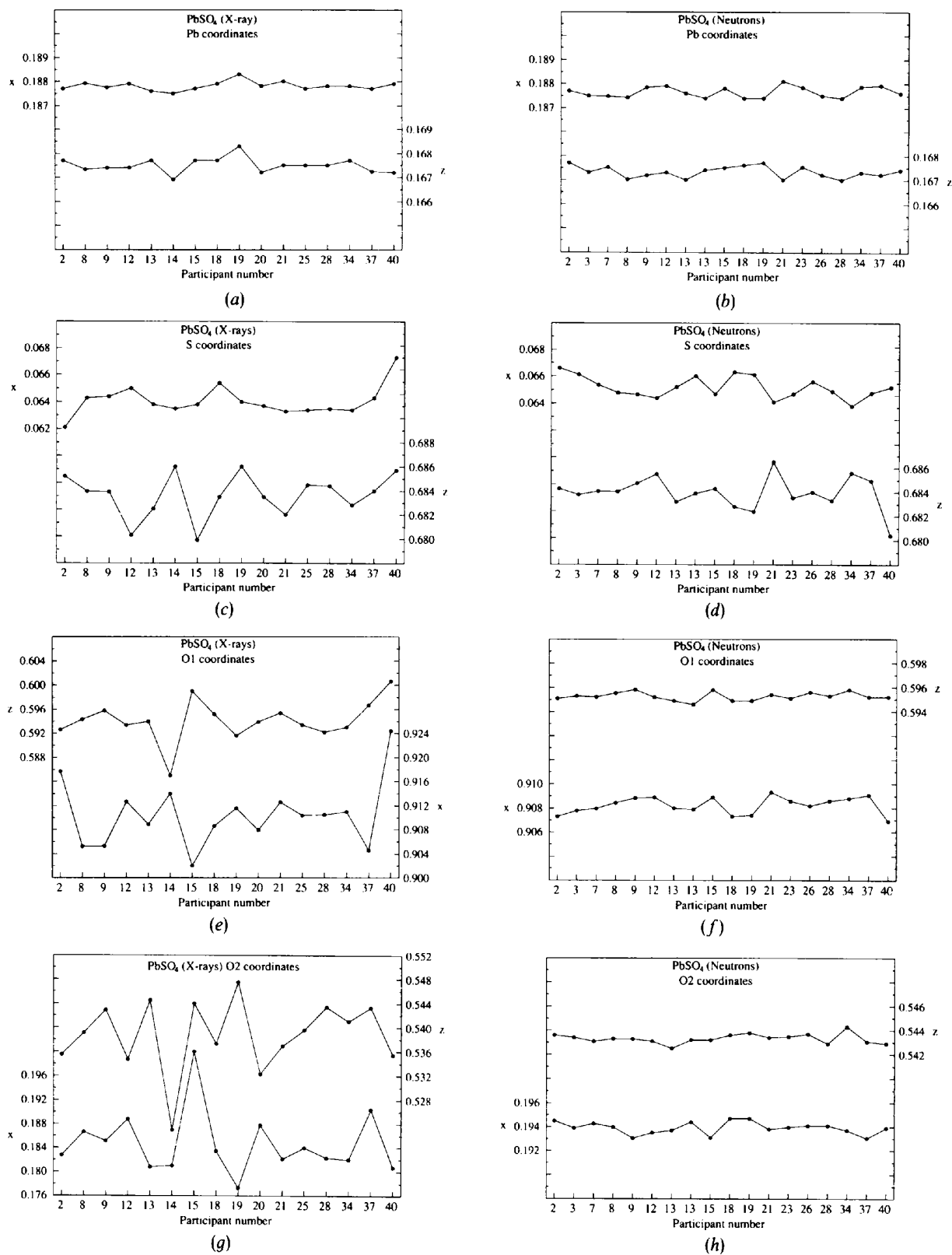
Fig. 6. Variation of the atomic coordinates of the Pb, S and O atoms determined by refinements using the X-ray data (parts a, c, e, g, i) and the neutron data (parts b, d, f, h, j).

calculated, using the formalism of Hamilton & Abrahams (1970):

(i) σ_{ext}, the e.s.d. of the weighted mean, based on the agreement among the individual determinations

$$\sigma_{ext} = \left\{ \sum_i [(P_i - \mu)^2/\sigma_i^2] \Big/ \left[(n - 1) \sum_i (1/\sigma_i^2) \right] \right\}^{1/2},$$

(2)

where n is the number of determinations;

(ii) σ_{int}, the e.s.d. of the weighted mean, based on the individual e.s.d.s from each Rietveld determination

$$\sigma_{int} = \left[\sum_i (1/\sigma_i^2) \right]^{-1/2}.$$

(3)

A so-called 'variance ratio', $\mathfrak{R}$, can then be calculated as

$$\mathfrak{R} = (\sigma_{ext}/\sigma_{int})^2.$$

(4)

In the work of Hamilton & Abrahams (1970), a fixed analytical procedure was applied to different data sets and any departure of $\mathfrak{R}$ from a value of unity was taken as an indication of the presence of systematic errors in the data and/or structural model. In the present study, different procedures and programs for

(i)

(j)

Fig. 6 (cont.)

Rietveld analysis have been applied to the same data and any departure of $\mathfrak{R}$ from unity gives a measure of how sensitive is a particular parameter to the Rietveld-refinement program/model used for its determination. Stated another way, in the absence of an accepted 'standard' Rietveld-refinement program/model, the spread among the n determinations of any parameter (i.e. σ_{ext}) can be taken as a measure of its probable error (or accuracy) and any difference between this quantity and the internal e.s.d.s from the Rietveld-analysis (i.e. σ_{int}) is then an indication of the presence of inadequacies (systematic errors) in the Rietveld-refinement model(s) for this parameter. Furthermore, for what it is worth, the numerical relationship between the probable error/accuracy and precision of the parameter can be approximated by $\mathfrak{R}^{1/2}$.*

Unit-cell dimensions

The values of the unit-cell dimensions derived from the X-ray and neutron data are displayed in Figs. 5(a) and (b), respectively. Lattice parameters derived from neutron data are normally not directly comparable with those from X-ray data obtained with characteristic radiation because the neutron wavelength is not nearly as well known. In the present study, the participants were given a neutron wavelength to use (1.909 Å), so comparisons among the neutron results are in order, though not neutron to X-ray. Since there is little doubt about the absolute value of the Cu $K\alpha$ wavelength, it is not surprising that the weighted means of the X-ray cell dimensions are much closer

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* It is tempting to state (as has been done many times in the past) that the Rietveld e.s.d.s are, therefore, under- or over-estimated by the factor $\mathfrak{R}^{1/2}$. However, this wrongly presupposes that the e.s.d.s are something other than simply estimates of the minimum possible probable error based on random errors alone (i.e. the precision).
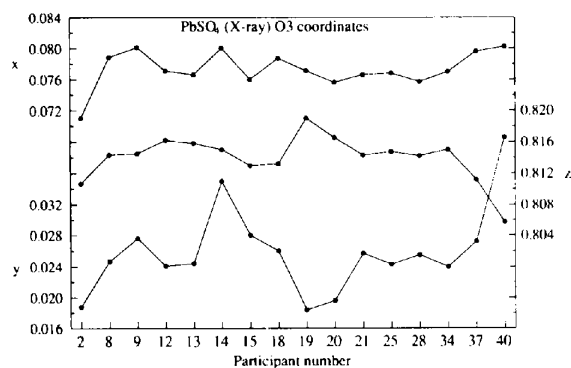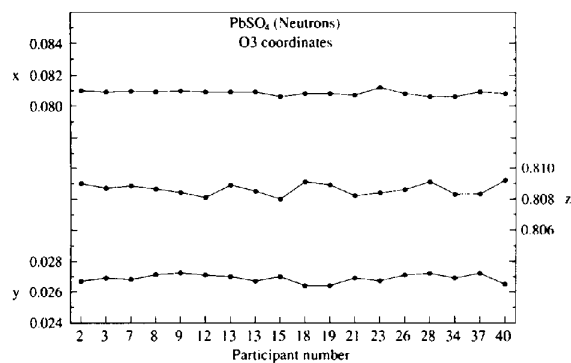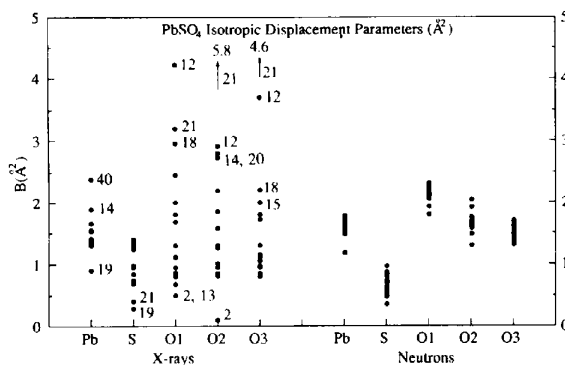
Fig. 7. Variation of the isotropic displacement parameters, B, determined by refinements using the neutron and X-ray data. Participant numbers have been placed alongside selected outlier results.

Table 9. *Ranges, weighted means and other statistics for the anisotropic displacement coefficients* (Å^2) *in* $PbSO_4$

The values of σ_{ext}, σ_{int} and $\Re$ are defined in (2)–(4) in the text; all values of σ are $\times 10^5$.
The single-crystal X-ray determination results are those of Miyake *et al.* (1978).
N = neutron data; X = X-ray data.

|		Range	σ_{ext}	σ_{int}	$\Re$	Weighted mean	Single crystal
Pb β_{11}	N	0.0038–0.0043	9	5	3.2	0.0041	0.0039
	X	0.0027–0.0044					
β_{22}	N	0.0179–0.0200	30	15	3.8	0.0187	0.0166
	X	0.0124–0.0140					
β_{33}	N	0.0067–0.0080	24	9	6.3	0.0072	0.0072
	X	0.0075–0.0090					
β_{13}	N	0.0003–0.0015	16	5	9.5	0.0006	0.0004
	X	−0.0004–+0.0004					
S β_{11}	N	0.0012–0.0032	29	15	3.6	0.0025	0.0025
	X	−0.0014–+0.0036					
β_{22}	N	0.0071–0.0098	46	34	1.8	0.0083	0.0070
	X	0.0010–0.0030					
β_{33}	N	0.0018–0.0058	61	23	7.0	0.0044	0.0035
	X	0.0060–0.0140					
β_{13}	N	−0.0008–+0.0014	28	20	1.9	0.0003	−0.0003
	X	0.0005–0.0020					
O1 β_{11}		0.0038–0.0052	23	10	5.8	0.0044	0.0040
β_{22}		0.0260–0.0291	46	24	3.5	0.0269	0.0250
β_{33}		0.0101–0.0119	26	14	3.7	0.0112	0.0080
β_{13}		−0.0041–+0.0046	143	9	277	−0.0014	0.0030
O2 β_{11}		0.0053–0.0067	23	10	5.9	0.0059	0.0040
β_{22}		0.0165–0.0217	88	24	13.2	0.0182	0.0270
β_{33}		0.0073–0.0088	21	12	3.0	0.0079	0.0050
β_{13}		−0.0033–+0.0035	136	10	199	0.0010	−0.0020
O3 β_{11}		0.0050–0.0065	18	5	11.8	0.0056	0.0060
β_{22}		0.0093–0.0130	52	14	14.4	0.0109	0.0080
β_{33}		0.0076–0.0094	23	9	6.6	0.0083	0.0070
β_{12}		0.0002–0.0011	15	5	8.1	0.0008	−0.0010
β_{13}		−0.0007–+0.0009	28	5	30.2	0.0003	−0.0010
β_{23}		−0.0033–+0.0031	130	9	231	0.0006	−0.0010

(a)　　　　　　　　　　(b)　　　　　　　　　　(c)
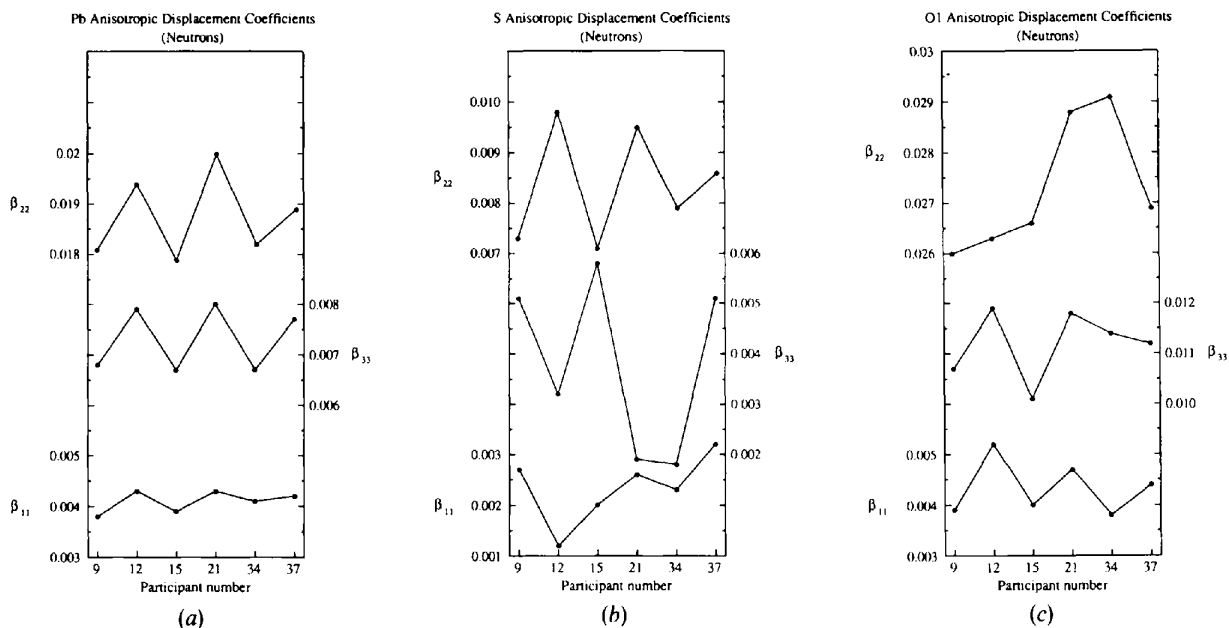
Fig. 8. Variation of the anisotropic displacement coefficients β_{ij} of (a) the Pb, (b) the S and (c) the O1 atoms, determined by refinements using the neutron data.

to the single-crystal values than are those derived from the neutron data (Table 7). By back calculation it is likely that the neutron wavelength is actually closer to 1.912 Å.

Only three X-ray determinations of the cell dimensions (respondents 2, 37 and 40) show a small departure from the mean (and single-crystal) values and none of these display a substantial correlation with the 2θ-zero parameter. The reason for the departure of the results of respondent 2 is not clear from the information submitted, although the refinement was of low overall quality (Fig. 2). On the other hand, the deviant X-ray unit-cell dimensions obtained by respondents 37 and 40 may perhaps be explained by their use of the Simpson's-rule asymmetry correction; however, it is unclear why this should have produced an opposite affect on the deviation of the unit-cell dimensions of these two studies from the mean. As indicated above, the Simpson's-rule asymmetry correction is not an entirely appropriate procedure for application to Bragg–Brentano X-ray data since the correction was specifically devised for the neutron case and Debye–Scherrer geometry. Thus, in the absence of an alternative function, the Rietveld correction seems adequate for the analysis of X-ray data from this highly absorbing sample.

For the neutron determinations, four respondents (3, 9, 37 and 40) provided unit-cell dimensions much larger than the weighted means and closer to (though still substantially smaller than) the X-ray powder and single-crystal values (Table 7). In these four cases, the improvement can be clearly attributed to the use of the Simpson's-rule sum for the asymmetry correction, prompting the recommendation that the Rietveld asymmetry correction be replaced by the Simpson's-rule algorithm in all studies using constant-wavelength neutron data. A fifth respondent (15) also obtained a slightly more accurate (i.e. closer to the single-crystal values) set of unit-cell dimensions, perhaps because the peak asymmetry was defined as part of a 'learned' profile. The residual difference between the neutron and X-ray values can be ascribed to a miscalibration of the neutron wavelength as documented earlier.

It has been observed previously (Hill & Madsen, 1986) that the e.s.d.s calculated for the unit-cell dimensions in a Rietveld analysis have values much smaller than the probable error of these parameters determined by replication of the experiment. Calculations of $\Re$ using (2)–(4) indicate that variations in refinement strategy/programs also produce large probable errors relative to the derived values of precision; $\Re$ has values in the range 201–292 for the X-ray data and 302–609 for the neutron data (Table 8). In other words, the experimentally determined probable errors of the unit-cell dimensions are between 14 and 25 times (i.e. $\Re^{1/2}$) larger than the individual Rietveld e.s.d.s.

For the individual Rietveld refinements, the generally large values of the GofF parameter (Fig. 2) are further confirmation of the presence of substantial uncorrected systematic errors in the Rietveld-calculated models, including those applied to the unit-cell parameters (Hill & Madsen, 1986; Schwarzenbach et al., 1989).

Atomic coordinates

As might be expected for X-ray data, the weighted mean coordinates obtained for the more strongly scattering Pb and S atoms are in acceptable agreement with those obtained from single-crystal data (Table 7). Nevertheless, the individual x- and z-coordinate values are spread over a range of 0.007 and 0.010 Å, respectively, for Pb, and over 0.010 and 0.042 Å, respectively, for S. Similar observations apply to the neutron-derived Pb and S coordinates, even though S is a relatively light scatterer in this case: the spread of x- and z-coordinate values is 0.004 and 0.005 Å for Pb and 0.024 and 0.043 Å for S.

For both the X-ray and the neutron results, the values of $\Re$ (Table 8) are relatively small, indicating that (i) the Pb and S X-ray coordinates are relatively insensitive to the refinement strategy used, (ii) there are no serious systematic errors in the model (or, alternatively, all models have the same or very similar systematic errors) and (iii) the average probable error in the coordinates is only a factor of two or so larger than the precision (e.s.d.s) indicated by the individual refinements.

On the other hand, the scattering of X-rays by O atoms is quite weak relative to Pb and, to a lesser extent, S. Thus, the precision of the X-ray estimates of the O-atom coordinates (both powder and single-crystal) is substantially poorer in comparison with the corresponding neutron powder determinations. In fact, it could be argued that the weighted mean neutron powder results are more accurate measurements of the coordinates of the O atoms than are the single-crystal X-ray results, although it is comforting to note that the two sets of values are actually very similar (Table 7).

In any event, the O-atom coordinates determined from the X-ray powder data show a much larger range of values than do those obtained from the neutron pattern, with the result that the values of σ_{ext} are much larger for the X-ray quantities than they are for the neutron determination (Tables 7 and 8). In fact, the x, y and z X-ray coordinates for the O atoms are spread over ranges of 0.195, 0.124 and 0.174 Å, respectively, while the corresponding spreads of neutron values are much smaller, namely, 0.020, 0.004 and 0.009 Å, respectively. These values may be

compared to the results of the IUCr single-crystal intercomparison projects on $D(+)$-tartaric acid (Hamilton & Abrahams, 1970; X-rays only) and oxalic acid (Coppens *et al.*, 1984; X-rays and neutrons), in which the positional parameters were found to be reproducible to better than 0.01 and 0.001 Å, respectively.*

The largest difference between the weighted mean X-ray and neutron parameter values occurs for O2, which is 0.08 Å (or $8\sigma_{\text{ext}}$) away from the neutron measurement along the x axis. However, unlike the unit-cell dimensions, the σ_{int} values of the X-ray O-atom coordinates are correspondingly large, so that $\Re$ is relatively small; the mean X-ray $\Re$ value is 9.9, indicating that the experimentally determined probable errors for the individual parameters are larger than the e.s.d.s by a factor of 3.1. The corresponding mean neutron $\Re$ value for the O-atom coordinates is 4.1, leading to a difference between the e.s.d. and probable error of only a factor of two. These values are typical of the differences generally encountered in Rietveld-analysis results (Young, 1980; Scott, 1983; Hill & Madsen, 1986) and also of those observed in systematic single-crystal studies (Hamilton & Abrahams, 1970; Coppens *et al.*, 1984).

The trends are revealed in greater detail when the individual measurements of the coordinates from each respondent are examined together (Fig. 6; note the decreased plot scale for the X-ray O-atom determinations). As indicated above, the Pb-atom position is well determined from both the X-ray and neutron data [Figs. 6(*a*) and (*b*)], but the y coordinate obtained with X-rays shows a greater spread of values than does x, even after allowing for the slightly smaller value of the c unit-cell dimension (*viz* 6.96 *vs* 8.48 Å).

The variability of the S-atom coordinates [Figs. 6(*c*) and (*d*)] is greater than that displayed by Pb, due to the lower scattering cross section of S for both X-rays and neutrons. In fact, S is virtually a 'light' atom for neutrons, since its scattering length of 2.85 fm is somewhat swamped by the values of 9.40 and 5.80 fm for Pb and O atoms, respectively; thus, S is the most poorly located atom in the neutron results. As observed for the Pb atom, the X-ray z coordinate of the S atom shows a much greater spread of values than the x coordinate (Fig. 6*c*). The reason for this is unclear, but it is interesting to note that the two lowest values of z were obtained by respondents 12 and 15, who truncated the X-ray data at 125 and 132°2θ, respectively; without these two measurements, the spread of values is substantially reduced.

As discussed above in relation to Table 7, the coordinates of the O atoms determined from X-ray data show a disconcertingly wide range of values [Figs. 6(*e*), (*g*) and (*i*)], with four cases (x and z for O2 and O3) having weighted mean values significantly different from the mean neutron values (Table 7). The results from participants 14, 15, 19 and 40 show the widest disparity. The only unusual features of these deviant analyses (as presented in the documents submitted) are that:

(i)   respondent 14 refined a three-parameter peak-shape function and obtained a physically unreasonable variation in the Lorentzian character (see Fig. 4);

(ii)   respondent 15 used a truncated data set (24–132°2θ) and an analytical Fourier series ('learned') for the peak-shape function;

(iii)   respondent 19 used a fixed peak shape and had the minimum number of variable parameters (22 in total);

(iv)   respondent 40 used a cosine Fourier series to define the background and perhaps too many parameters (namely six) to define the peak profile shape and width.

In respect to (iv), it is noted (here and below) that the simultaneous release of more parameters than is necessary to define the model may lead to large correlations and a loss of refinement stability and hence to the production of physically unreasonable values for some of the individual parameters.

On the other hand, as indicated above, there is nothing remarkable about any of the neutron data results (from any of the respondents) for the refined O-atom coordinates [Figs. 6(*f*), (*h*) and (*j*)]; all refinements produced acceptable results that conform to the weighted mean.

Atomic displacement parameters*

The ranges, weighted means and σ_{ext} statistics of the isotropic atomic displacement parameters B are listed in Table 7 and the individual determinations are given in Fig. 7. These data include the equivalent isotropic value, B_{eq}, calculated according to the method of Hamilton (1959) from the displacement coefficients β_{ij} in the four X-ray and six neutron cases for which anisotropic models were refined.

In general, there is reasonable correspondence between the weighted mean B values determined from the X-ray and neutron data and the B_{eq} values calculated from the data of Miyake *et al.* (1978). The generally smaller mean values obtained in the X-ray Rietveld refinements might be a function of surface

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* Note that the present Rietveld-analysis statistics apply only to different analyses of the *same powder diffraction data set*; the variation is expected to be much larger for analyses of different data sets collected on the same or differently prepared material (as used in the single-crystal projects). This latter aspect will be considered in Part II of the current project.

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* As recommended by Brock (1984), the term 'displacement parameter' is used here, rather than the more commonly used expression 'temperature parameter', to discriminate between the end result of all forms of displacement of the atoms from their most probable positions and that due to true thermal motion.

roughness but the effect is small, if present at all. The relative B values for the different atoms (most clearly displayed by the neutron results in Fig. 7) are consistent with the crystal structure of $PbSO_4$ in that S may be expected to have the smallest value since it is the only atom in close tetrahedral coordination by O atoms. For the same reasons (relative scattering power) discussed above in reference to the atomic coordinates, the X-ray B values obtained for Pb and S are better determined than those for the O atoms.

Although the range of B values presented by the X-ray refinements is very large (Fig. 7), the weighted mean values for the O atoms are, in fact, in reasonable agreement with the neutron determinations (Table 7). This is because the few very large X-ray B values for O atoms have large Rietveld e.s.d.s and so contribute little to the weighted mean [see (1)]. The same cannot be said for the Pb atom, which is determined very precisely (i.e. it has a small σ_{int}, see Table 8), but displays a much greater σ_{ext}. In this sense the X-ray results for the Pb-atom B values are similar to those for the unit-cell dimensions; systematic differences/errors in the refinement strategies used by the individual participants conspire to make the probable error substantially larger than the Rietveld e.s.d. (viz by a factor of 22).

In fact, consistently large X-ray B values were obtained by respondents 12, 14, 15, 18, 20, 21 and 40, while unusually small values were produced by respondents 2 and 19 (Fig. 7). In each case, the reason can be attributed to one or more of the following properties or deficiencies (systematic errors) of the refinement:

(i) fixed peak shape (i.e. 'intermediate' or 'modified' Lorentzian) across the entire pattern, causing difficulties in the correct assignment of the background level at high diffraction angles where interaction with the displacement parameters is greatest;

(ii) more peak profile width and/or shape parameters than are required to define adequately the calculated model, leading to a nonphysical variation in peak shape with 2θ [Figs. 3(a) and 4];

(iii) truncation of the peak profile too close to the peak centroid (e.g. at less than 4 FWHMs on either side), leading to underestimation of the peak intensity and overestimation of the background level;

(iv) too few or too many background parameters (i.e. ≤ 3 or ≥ 6), both leading to an inappropriate assignment of background level;

(v) removal of the high-angle data (i.e. imposing an upper limit of 125° or 132°), leading to an insufficient range in $(\sin \theta)/\lambda$ for correct discrimination between scale, displacement and background parameters;

(vi) simultaneous release of the atomic-displacement and site-occupancy parameters in the case of the

'light' S and O atoms, giving rise to a strong inverse correlation between and resultant loss of control of both classes of parameter; this is less likely to be a problem in cases for which there is not such a large spread of X-ray scattering strengths among the constituent atoms as is represented here.

The neutron determinations of the B values for the O atoms are all well behaved (i.e. close to the single-crystal values), although the $\Re$ values suggest that the precision of the results, as presented by the individual least-squares e.s.d.s, is smaller than the experimentally determined probable errors by factors of up to 5 (Table 8). This leads to the not unexpected conclusion that the neutron determinations are also sensitive to the refinement strategy and/or program used, albeit at a substantially lower level than in the X-ray data.

The ranges and weighted means of the anisotropic displacement coefficients β_{ij} provided by the six neutron and four X-ray respondents (Pb and S atoms only) who refined full or partial anisotropic models are given in Table 9. Examples of the individual β_{ij} values for the Pb, S and O1 atoms obtained from the neutron data are given in Fig. 8. The reasonable agreement among the individual determinations themselves (indicated by the relatively small values of σ_{ext}) and with the single-crystal values is very encouraging, given the very model-sensitive nature of β_{ij} coefficients; this should help to assuage the generally held scepticism about the physical significance of these parameters when derived from powder diffraction data. In fact, the maximum departure of the β_{ii} coefficients from the single-crystal values occurs for β_{22} of the O2 atoms (viz 0.0182 vs 0.0270; Table 9).

The small values of $\Re$ suggest that the β_{ii} coefficients are relatively insensitive to the refinement strategy; the neutron Rietveld e.s.d.s are, on average, a factor of only 2.5 smaller than their corresponding probable errors (σ_{ext}). Furthermore, the fact that the mean $\Re$ value obtained for the corresponding B parameters (viz 3.4; Table 8) is larger than that obtained in the anisotropic refinements appears to vindicate the expansion of the displacement model to include anisotropic terms. There is occasional sign reversal for the β_{ij} values with $i \neq j$, but these coefficients are very susceptible to systematic error, as shown by their generally larger $\Re$ values (Table 9).

For the X-ray data, the two determinations of the Pb-atom β_{ij} values are in acceptable agreement with the single-crystal results. On the other hand, one of the anisotropic refinements of the S atom and all of the refinements of the O atoms produced at least one non-positive-definite ellipsoid (Table 9).

Novel weighting schemes

Respondent 19 was the only one to provide results for refinements undertaken with weighting schemes

other than the simple reciprocal of the observed step intensity Y_{obs} (or its multidetector equivalent for neutrons); these exotic schemes included weights of unity and $1/(Y_{obs})^{1/2}$. For the neutron data, as the weights change in the sequence $1 \rightarrow 1/(Y_{obs})^{1/2} \rightarrow 1/Y_{obs}$, the values of R_{wp} and R_{exp} progressively increase from 8.8 to 12.3% and from 0.3 to 10.1%, respectively, while the GofF decreases from 26.8 to 1.2. For X-rays, the trends are the same, but more exaggerated. The values of R_p and R_B were largely unaffected by the weights, as expected.

The neutron structural parameters were also relatively insensitive to the weighting scheme, but the X-ray results displayed some subtle changes. In particular, the a and c unit-cell dimensions increased by some 8 e.s.d.s in the weighting-change sequence stated above and the x coordinate of all atoms increased by up to 6 e.s.d.s. It is doubtful if these effects are of general significance.

Concluding remarks and recommendations

General

Rietveld analyses currently being undertaken use a very wide range of software, most of which diverges significantly from the original 'grandfather' code. Upon receiving a circulated program or on undertaking modifications, users are well advised to undertake exhaustive tests of the code, both on any data distributed with it and on any 'standard' in-house data. Even then, the very 'forgiving' nature of Rietveld analysis means that errors can remain undetected for extended periods, as this survey has clearly demonstrated in the case of an incorrect calculation of reflection multiplicities for the point group $2/m$.

It is also important that users familiarize themselves with the impact of a particular refinement strategy on the results of the analysis, that is, of the influence of the various parameterizations of peak width and shape, background and choices of calculation range (peak truncation) *etc.* The refinement of more parameters than the data can support (*i.e.* an over-determined and possibly unstable model) clearly leads to as many problems as does a refinement with too few parameters. Furthermore, some users terminate their refinements well before convergence has been achieved.

There is a need for standardization of the agreement indices used in profile analysis. One of the 'standard' forms that should be quoted at the conclusion of all analyses is one that eliminates the effect of (i) different signal-to-noise ratios (*viz* by subtraction of the background during formation of the sums) and (ii) different proportions of background-only regions of the pattern (*viz* by using in the sums only those regions

that contribute to the peaks). Only when users quote an agreement index that is independent of the signal-to-noise ratio and peak density in their particular set of data can valid comparisons be made between Rietveld refinements from different samples using different instruments and wavelengths.

Specific

In Rietveld analyses of X-ray diffraction data, the determination of the atomic displacement parameters and the coordinates of 'light' atoms (as represented by the O atoms in $PbSO_4$) may be compromised by the chosen refinement strategy to the point at which little reliance can be placed on the accuracy of their values. In other words, repetitions of the refinement with different software and/or parameterization of the calculated model can produce a large spread of the parameter values about the mean. Furthermore, the presence of residual systematic errors in the refinement model (as judged, in part, by large values of the GofF index) generally causes the individual Rietveld e.s.d.s to be substantially smaller than estimates of the probable errors derived by repetition of the refinement in other circumstances. This conclusion also applies to the unit-cell dimensions determined from neutron data. In contrast, when neutron diffraction data are used for refinement of the structural parameters of $PbSO_4$, the accuracy of the coordinates and displacement coefficients is reasonable for all atoms and the spread of parameter values about their weighted mean value is much smaller, that is, they are less sensitive to the refinement strategy.

Poor fits of the calculated to the observed diffraction profile for $PbSO_4$ were generally due to (i) the use of fixed peak-shape functions, such as pure Gaussian or various forms of 'intermediate' Lorentzian, (ii) lack of variation of the peak shape as a function of diffraction angle, or the variation of more shape/width parameters than can be supported by the data, (iii) too few (≤ 3) or too many (≥ 6) background parameters and (iv) truncation of the peak profile too close to the peak centroid (*e.g.* at less than 4 FWHMs on either side, in this case).

Poor determination of the atomic displacement parameters of 'light' atoms (*i.e.* the O atoms in $PbSO_4$) can result from any or all of the deficiencies in peak profile or background fit described above, as well as from (i) the simultaneous release of atomic site occupancy and displacement parameters and/or (ii) the truncation of the upper limit of the diffraction data at a $(\sin \theta)/\lambda$ value of about 0.6 Å^{-1} (equivalent to $135°2\theta$ in a Cu $K\alpha$ pattern). In general, the X-ray data did not support the release of anisotropic atomic displacement coefficients, except for the 'heavy' Pb and S atoms. On the other hand, the neutron data collected to high diffraction angles produced aniso-

tropic displacement ellipsoids in good agreement with single-crystal values.

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