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Quantitative Phase Analysis of Mixtures of Three Components using Rietveld and Rius Standardless Methods. Comparative Results

Eight samples, supplied by the Commission on Powder Diffraction of the International Union of Crystallography, through the Round Robin on quantitative phase analysis, were analized using standardless methods. Samples were mixtures of corundum, zincite and fluorite in different ratios. The Rietveld method, using the DBW 3.2 and FULLPROF software, and the Rius method, using MENGE-PC software, were used. Results obtained agree well with the real composition supplied (*a posteriori*) by the IUCr.

Keywords: quantitative analysis, X-ray powder diffraction, standardless method

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1. Introduction

Quantitative X-ray powder diffraction (QXRPD) is known as a powerful and versatile analytical technique. The integrated intensity of reflections for a compound in a multiphase powder diffraction pattern is related to the phase abundance in the mixture. This property has been used for many years in quantitative phase analysis (KLUG & ALEXANDER, 1974) and significant advances have occurred in the last twenty years (see, for instance, Snyder & BISH, 1989; HILL, 1991; DAVIS, 1992; SNYDER, 1992; ZEVIN & KIMMEL, 1995; SCARDI, GUALTERI & BELLOTO, 1997). The method can be applied to a wide range of materials, from basic science research to technological studies and industrial quality control, but instrumental and sample-related effects (e.g. preferred-orientation, extinction, microabsorption, separation of overlapping and broad reflections, detection of trace and amorphous components,...) can influence the accuracy of the results. Improved analysis methods are continually sought, but without accomplishing a satisfactory level yet. Diffraction measurements of phase abundance can be performed in many ways, but traditional methods require the acquisition of standard reference data for each phase present in the mixture to be analyzed. An error within 4 wt% is the best accuracy found by QXRD methods.

The Rietveld method of quantitative phase analysis minimizes or eliminates many current problems present in traditional methods (WERNER *et al.*, 1979; BISH & HOWARD, 1986, 1988; HILL & HOWARD, 1987; BISH & POST, 1993; ESTEVE *et al.*, 1997a). Rietveld refinement was originally developed as a method of refining crystal structures using powder neutron diffraction data (RIETVELD, 1969), and some time later it was applied to quantitative X-ray powder phase analysis (POST and BISH, 1989). This method requires the knowledge of the approximate crystal structures of all phases of interest in the mixture. The Rietveld method of analysis provides many advantages over conventional quantitative analysis methods. As the method uses a whole pattern-fitting algorithm, all lines for each phase are explicitly considered, and even severely overlapped lines are usually not a problem. Thus it is not necessary to decompose patterns into separate Bragg peaks, as is often the case for traditional methods. The use of all reflections in a pattern rather than a few minimizes the effects of the preferred orientation, primary extinction, and non linear detection systems. Also, failure to consider a phase in the analysis will yield obvious differences between the observed and calculated diffraction pattern and reveal unsuspected minor phases. Preferred orientation is one of the most serious problems in the Rietveld method; however, numerous sample preparation techniques and analytical functions have been used to minimize the problem.

When no pure standards are available, or when it is difficult to obtain standards with the same crystallinity as the compounds in the sample, it is mandatory to use standardless methods. Below are presented two different cases of these methods, described for quantitative X-ray analysis.

(a) Standardless analysis methods based on X-ray data only (MOORE, 1965; SALYN & DRITS, 1972; ZEVIN, 1977; FIALA, 1980; STARKS *et al.*, 1984; FANG and ZEVIN, 1985; RIUS *et al*. 1987; BISH and POST, 1993; ESTEVE *et al*., 1997b; ZANGALIS, 1998). Here the number of phases is considered to be given and one or more nonoverlapping reflections correspond to each phase. RIUS *et al.* (1987) devised a standardless method that does not need any standard, only diffracted intensity data from several multiphase samples, along with calculated phase absorption coefficients. As the authors point out, the conditions necessary for this method are: firstly, that there are essential differences in quantitative phase composition of the analyzed samples; secondly, that a sufficient number of samples are measured to ensure the statistical validity of the least-squares procedure. Estimated phase absorption coefficients are calculated from the known or assumed chemical composition of the phases together with the tabulated mass absorption coefficients of the elements.

(b) Standardless methods based on chemical and X-ray data simultaneously (ZANGALIS, 1991, 1998; STARKS *et al*., 1984; WANG & PU, 1991). These methods treat the crystal chemistry of the phases in the mixture as an unknown and determine it. It is a standardless method for samples, containing amorphous phases or phases without X-ray data. The analysis is made simultaneously for more than one, but fewer samples than those of case (a). This method has yielded encouraging results. The computation of the unknown quantities is complicated and often not satisfactorily conditioned. The combined method distinguishes between two kinds of phase characteristics (concentration, X-ray calibration coefficients, chemical composition, mass-absorption coefficients): the known (stable) and the unknown (changeable) ones. The method utilizes the former to determine or to avoid the latter. The ratio of known and unknown variables for the different phases may run through all possible combinations.

Each one of the cases (a) and (b) of the above standardless methods have their advantages under some circumstances and conditions. From a practical point of view, the mathematical expressions all of these methods are rather complicated.

In this work eight mixtures of corundum (Al_2O_3), zincite (ZnO) and fluorite (CaF_2) called CPD-1A to CPD-1H corresponding to sample #1, covering a wide range of compositions of each phase. Mixtures were prepared by the Commission on Powder Diffraction of the International Union of Crystallography, and have been analysed by X-ray diffraction with the aim to study the quantification of these three phases in different mixtures and estimate variations in the results found by different laboratories. In this work, X-ray diffraction patterns were registered at Castellón and Valencia (Spain) by the authors participating in the Round Robin on quantitative phase analysis and at Victoria (Australia) by the XRD Laboratory at CSIRO Minerals.

Obtained results are compared with the real composition of mixed samples and the analysis by X-ray fluorescence (XRF).

2. Methods

2.1 X-ray powder analysis

XRD data were obtained on dried material. Samples were manually pressed into standard sample holders in Valencia and Castellón, respectively. XRD powder patterns were taken at room temperature (22 ±2ºC) using a Siemens D500 (Valencia data, Spain), Siemens D5000 (Castellón data, Spain) and Philips 3020 (Victoria data, Australia) X-ray powder diffractometers with Bragg-Brentano geometry. Experimental conditions are summarized in Table I.

	Valencia, Spain	*Castellón, Spain*	*Victoria, Australia*
Diffractometer	Siemens D-500	Siemens D-5000	Philips 3020
Radiation type,Source		X-ray, sealed tube, Cu Kα	
Instrument power	40 kV, 30 mA	40 kV, 30 mA	40 kV, 40 mA
λ discrimination		secondary graphite monochromator	
Detector	scintillation	scintillation	Proportional
Divergence slit	0.15º	0.2 mm	0.15º
Receiving slit	1º	2 mm	1º
Scatter slit	0.15º	0.6 mm	0.15º
Specimen form		horizontally packed powder in an airtight diffractometer holder	
Particle size		sample grounded in micronising mill to pass 60 µm	
Range of 2θ	from 5º to 120º	from 20º to 120º	from 5º to 150º
Step	0.02º	0.02º	0.02º
Time per step	10 s	20 s	3 s
Specimen motion		None	
Intensity measuring procedure		numerical registration of peak heights	

Table I: Data collection by X-ray powder diffraction

2.2 Rietveld method

The phase abundance of these eight mixtures were derived from XRD powder patterns using two different PC Rietveld programs [(DBW 3.2) and (FULLPROF, v. 3.2c)], originally devised by WILES & YOUNG (1981), modified by BISH & HOWARD (1988) and RODRÍGUEZ-CARVAJAL, FERNÁNDEZ-DÍAZ & MARTÍNEZ (1991). The Rietveld refined parameters are summarized in Table II.

Parameters	DBW 3.2	FULLPROF 3.1c
Scale factor	Refined	
Background	Refined	
Zero parameter	Refined	
Preferred orientation	Not refined	Not refined

Profile shape	Pearson	Pseudo-Voigt
U, V, W (CAGLIOTTI et al., 1958)	Refined	
Structural parameters	Fixed	
Unit cell parameters	Fixed	Refined
Brindley corrections	None applied	
Agreement indices (WILES & YOUNG, 1981)	$R_p = \frac{\sum \lvert y_{io} - y_{ic} \rvert}{\sum y_{io}}$ $R_{wp} = \left[\frac{\sum_i w_i (y_{io} - y_{ic})^2}{\sum_i w_i y_{io}^2} \right]^{\frac{1}{2}}$	$R_{exp} = \left[\frac{N - P}{\sum_i w_i y_{io}^2} \right]^{\frac{1}{2}}$
Number of refined cycles	5	5-12

Table II: Parameters optimised for Rietveld refinement for each XRD pattern after the initial refined starting model was defined

2.3 Rius method

The standardless method used, based on XRD data only, was proposed by RIUS *et al*. (1987). This method determines calibration constants using only diffracted intensities and calculated phase absorption coefficients through a least-squares procedure, was applied to eight mixtures studied using the computer program MENGE-PC from Rius, modified by Esteve and Ochando (ESTEVE, 1995) for PC running.

The peaks used for this phase quantitative analysis were: corundum 113, zincite 101 and fluorite 220. Net integrated intensities were used. In all calculations, the mass absorption coefficients of the crystalline phases were derived from the mass absorption coefficients of the elements tabulated in *International Tables for X-ray Crystallography, Vol. III*. These are for corundum = 31.1, zincite = 50.7 and fluorite = 91.1 $cm^2\ g^{-1}$.

3. Results

	DBW 3.2	Rp Rwp Rexp	FULL PROF 3.1c	Rp Rwp Rexp	MENGE	Mixed Compos.	XRF
CPD-1A							
Corundum	0.00	40.93	0.00	16.6	0.00	1.15	1.22
Zincite	3.31	48.76	3.87	24.4	3.57(1)	4.04	4.12
Fluorite	96.69	11.06	96.13	7.12	96.4(1)	94.81	94.11
CPD-1B							
Corundum	91.77	48.26	94.61	15.9	94.9(2)	94.31	94.73
Zincite	1.56	57.11	1.22	21.5	1.24(1)	1.36	1.38
Fluorite	6.67	7.10	4.17	6.83	3.87(1)	4.33	4.32
CPD-1C							
Corundum	5.70	38.48	2.79	18.7	6.70(1)	5.04	5.12
Zincite	92.66	49.48	95.59	27.1	92.6(2)	93.59	93.15
Fluorite	1.64	5.09	1.62	4.88	0.73(1)	1.36	1.33

CPD-1D							
Corundum	13.26	36.64	13.91	15.5	19.62(3)	13.53	13.80
Zincite	27.69	44.35	32.57	22.3	29.08(4)	32.89	32.98
Fluorite	59.05	7.15	53.53	6.88	51.31(7)	53.58	52.99
CPD-1E							
Corundum	50.60	48.08	56.61	14.1	59.1(1)	55.12	55.79
Zincite	14.12	55.46	14.62	19.8	13.02(2)	15.25	15.34
Fluorite	35.28	7.10	28.77	6.88	27.85(4)	29.62	29.39
CPD-1F							
Corundum	26.27	41.82	27.26	15.5	33.36(6)	27.06	27.32
Zincite	50.82	49.40	54.85	22.4	49.59(8)	55.22	54.88
Fluorite	22.91	5.96	17.90	5.75	17.05(2)	17.72	17.44
CPD-1G							
Corundum	34.09	35.94	36.46	14.2	40.58(7)	31.37	31.70
Zincite	28.09	43.42	30.69	20.7	28.66(4)	34.21	34.01
Fluorite	37.82	7.77	32.85	7.77	30.76(4)	34.42	33.86
CPD-1H							
Corundum	32.89	58.82	37.71	15.4	41.76(7)	35.12	35.35
Zincite	26.78	66.29	28.95	21.7	26.03(4)	30.19	30.03
Fluorite	40.33	7.80	33.34	7.50	32.21(4)	34.69	34.26

Table III: Results obtained with patterns recorded at Valencia (Spain), compared with mixed composition and XRF (wt %).

	DBW 3.2	Rp Rwp Rexp	FULL PROF 3.1c	RP Rwp Rexp	MENGE	Mixed Compos.	XRF
CPD-1A							
Corundum	1.37	41.79	1.65	19.3	0.00	1.15	1.22
Zincite	3.09	51.05	3.96	24.4	4.07(1)	4.04	4.12
Fluorite	95.54	11.08	94.38	10.6	95.94(7)	94.81	94.11
CPD-1B							
Corundum	93.02	37.54	94.70	25.5	94.38(9)	94.31	94.73
Zincite	1.40	43.71	1.22	32.4	1.27(1)	1.36	1.38
Fluorite	5.58	8.76	4.09	8.32	4.35(1)	4.33	4.32
CPD-1C							
Corundum	6.75	43.22	5.52	11.7	5.32(1)	5.04	5.12
Zincite	91.33	56.24	93.15	15.8	94.60(8)	93.59	93.15
Fluorite	1.93	6.74	1.33	6.36	0.09(1)	1.36	1.33
CPD-1D							
Corundum	16.07	41.61	14.91	16.8	14.66(1)	13.53	13.80
Zincite	27.19	49.75	32.29	20.9	35.55(2)	32.89	32.98
Fluorite	56.74	9.02	52.79	8.57	49.78(2)	53.58	52.99

CPD-1E							
Corundum	55.22	35.75	57.00	19.8	57.04(5)	55.12	55.79
Zincite	12.36	43.14	14.47	25.7	15.54(1)	15.25	15.34
Fluorite	32.42	9.20	28.52	8.59	27.42(2)	29.62	29.39
CPD-1F							
Corundum	32.40	40.68	28.39	15.1	28.37(2)	27.06	27.32
Zincite	45.65	50.21	54.10	19.6	57.10(4)	55.22	54.88
Fluorite	21.95	7.42	17.51	7.02	14.53(1)	17.72	17.44
CPD-1G							
Corundum	34.39	37.57	33.21	15.8	33.40(3)	31.37	31.70
Zincite	26.95	46.23	33.16	20.4	34.97(3)	34.21	34.01
Fluorite	38.66	8.78	33.63	6.02	31.63(2)	34.42	33.86
CPD-1H							
Corundum	37.86	40.93	36.23	15.8	36.38(3)	35.12	35.35
Zincite	24.63	48.41	29.71	20.4	31.92(2)	30.19	30.03
Fluorite	37.51	8.48	34.05	8.33	31.69(2)	34.69	34.26

Table IV: Results obtained with patterns recorded at Castellón (Spain), compared with mixed composition and XRF (wt %).

	DBW 3.2	Rp Rwp Re	FULL PROF 3.1c	Rp Rwp Re	MENGE	Mixed compos.	XRF
CPD-1A							
Corundum	1.32	40.82	1.55	12.1	0.00	1.15	1.22
Zincite	3.38	48.61	3.86	17.4	3.60(1)	4.04	4.12
Fluorite	95.31	11.06	94.62	11.5	96.40(4)	94.81	94.11
CPD-1B							
Corundum	92.53	44.72	94.43	31.0	94.55(4)	94.31	94.73
Zincite	1.53	52.32	1.26	38.6	1.24(1)	1.36	1.38
Fluorite	5.94	8.56	4.31	8.58	4.21(1)	4.33	4.32
CPD-1C							
Corundum	6.09	38.92	5.78	9.95	5.52(1)	5.04	5.12
Zincite	92.03	50.44	92.9	13.3	93.68(4)	93.59	93.15
Fluorite	1.88	6.17	1.32	6.38	0.80(1)	1.36	1.33
CPD-1D							
Corundum	14.34	37.64	14.97	11.5	14.64(1)	13.53	13.80
Zincite	27.42	45.56	31.90	15.7	31.73(1)	32.89	32.98
Fluorite	58.25	8.87	53.13	9.17	53.63(2)	53.58	52.99
CPD-1E							
Corundum	53.42	35.45	56.55	17.7	56.48(2)	55.12	55.79
Zincite	13.12	42.49	14.42	24.3	14.11(1)	15.25	15.34
Fluorite	33.46	8.85	29.03	9.10	29.41(1)	29.62	29.39

CPD-1F							
Corundum	28.50	36.95	27.91	12.3	28.52(1)	27.06	27.32
Zincite	48.58	46.01	54.09	17.1	54.45(2)	55.22	54.88
Fluorite	22.92	7.26	18.00	7.54	17.03(1)	17.72	17.44
CPD-1G							
Corundum	31.34	35.92	32.71	12.8	32.94(1)	31.37	31.70
Zincite	28.89	44.07	33.21	17.9	33.03(1)	34.21	34.01
Fluorite	39.77	8.33	34.08	8.63	34.03(1)	34.42	33.86
CPD-1H							
Corundum	34.19	39.92	35.94	13.9	36.46(1)	35.12	35.35
Zincite	26.00	47.03	29.37	19.3	29.22(1)	30.19	30.03
Fluorite	39.81	8.44	34.69	4.87	34.32(1)	34.69	34.26

Table V: Results obtained with patterns recorded at Victoria (Australia), compared with mixed composition and XRF (wt %).

4. Conclusions

	DBW 3.2	FULL PROF 3.1c	MENGE	Between methods
CPD-1A				
Corundum	0.9(8)	1.1(9)	0.00(1)	0.6(7)
Zincite	3.3(2)	3.9(6)	3.7(3)	3.6(3)
Fluorite	95.8(7)	95.0(9)	96.3(3)	95.7(8)
CPD-1B				
Corundum	92.4(6)	94.6(1)	94.6(3)	93(1)
Zincite	1.50(9)	1.23(2)	1.25(2)	1.3(1)
Fluorite	6.1(6)	4.2(1)	4.1(2)	5(1)
CPD-1C				
Corundum	6.2(5)	5(2)	5.8(7)	6(1)
Zincite	92.0(7)	94(1)	94(1)	93(1)
Fluorite	1.8(2)	1.4(2)	0.5(4)	1.36(6)
CPD-1D				
Corundum	15(1)	14.6(6)	16(3)	15(2)
Zincite	27.4(3)	32.2(3)	32(3)	31(3)
Fluorite	58(1)	53.1(4)	52(2)	54(3)
CPD-1E				
Corundum	53(2)	56.7(2)	58(1)	56(2)
Zincite	13.2(9)	14.5(1)	14(1)	14(1)
Fluorite	34(1)	28.8(3)	28(1)	30(3)
CPD-1F				
Corundum	29(3)	27.8(6)	30(3)	29(2)
Zincite	48(3)	54.45(4)	54(4)	52(4)
Fluorite	22.6(6)	17.8(3)	16(1)	19(3)

CPD-1G				
Corundum	33(2)	34(2)	36(4)	34(3)
Zincite	28(1)	32(1)	32(3)	31(3)
Fluorite	39(1)	33.5(6)	32(2)	35(3)
CPD-1H				
Corundum	35(3)	37(1)	38(3)	37(2)
Zincite	26(1)	29.3(4)	29(3)	28(2)
Fluorite	39(2)	34.0(7)	33(1)	35(3)

Table VI: Results and deviations between results and methods.

	DBW 3.2	Deviation respect Real comp. Absolute (%)	FULL PROF 3.1c	Deviation Respect real comp. Absolute (%)	MENGE	Deviation respect real comp. Absolute (%)
CPD-1A						
Corundum	0.9(8)	- 0.25 (21.7)	1.1(9)	- 0.05 (4.3)	0.00(1)	- 1.15 (---)
Zincite	3.3(2)	- 0.74 (18.3)	3.9(6)	- 0.14 (3.5)	3.7(3)	- 0.34 (8.4)
Fluorite	95.8(7)	+ 0.99 (1.1)	95.0(9)	+ 0.19 (0.2)	96.3(3)	+ 1.49 (1.6)
CPD-1B						
Corundum	92.4(6)	- 1.91 (2.0)	94.6(1)	+ 0.29 (0.3)	94.6(3)	+ 0.29 (0.3)
Zincite	1.50(9)	+ 0.14 (10.3)	1.23(2)	- 0.13 (9.6)	1.25(2)	- 0.11 (8.1)
Fluorite	6.1(6)	+ 1.77 (40.9)	4.2(1)	- 0.13 (3.0)	4.1(2)	- 0.23 (5.3)
CPD-1C						
Corundum	6.2(5)	+ 1.16 (23.0)	5(2)	- 0.04 (0.8)	5.8(7)	+ 0.76 (15.1)
Zincite	92.0(7)	- 1.59 (1.7)	94(1)	+ 0.41 (0.4)	94(1)	+ 0.41 (0.4)
Fluorite	1.8(2)	+ 0.44 (32.4)	1.4(2)	+ 0.04 (2.9)	0.5(4)	- 0.86 (63.2)
CPD-1D						
Corundum	15(1)	+ 1.47 (10.9)	14.6(6)	+ 1.07 (7.9)	16(3)	+ 2.47 (18.3)
Zincite	27.4(3)	- 5.49 (16.7)	32.2(3)	- 0.69 (2.1)	32(3)	- 0.89 (2.7)
Fluorite	58(1)	+ 4.42 (8.3)	53.1(4)	- 0.48 (0.9)	52(2)	- 1.58 (2.9)
CPD-1E						
Corundum	53(2)	- 2.12 (3.8)	56.7(2)	+ 1.58 (2.9)	58(1)	+ 2.88 (5.2)
Zincite	13.2(9)	- 2.05 (13.4)	14.5(1)	- 0.75 (4.9)	14(1)	- 1.25 (8.2)
Fluorite	34(1)	+ 4.38 (14.8)	28.8(3)	- 0.82 (2.8)	28(1)	- 1.62 (5.5)
CPD-1F						
Corundum	29(3)	+ 1.94 (7.2)	27.8(6)	+ 0.74 (2.7)	30(3)	+ 2.94 (10.9)
Zincite	48(3)	- 7.22 (13.1)	54.45(4)	- 0.77 (1.4)	54(4)	- 1.22 (2.2)
Fluorite	22.6(6)	+ 4.88 (27.5)	17.8(3)	+ 0.08 (0.5)	16(1)	- 1.72 (9.7)
CPD-1G						
Corundum	33(2)	+ 1.63 (5.2)	34(2)	+ 2.63 (8.4)	36(4)	+ 4.63 (14.8)
Zincite	28(1)	- 6.21 (18.2)	32(1)	- 2.21 (6.5)	32(3)	- 2.21 (6.5)
Fluorite	39(1)	+ 4.58 (13.3)	33.5(6)	- 0.92 (2.7)	32(2)	- 2.42 (7.0)

CPD-1H						
Corundum	35(3)	- 0.12 (0.3)	37(1)	+ 1.88 (5.4)	38(3)	+ 2.88 (8.2)
Zincite	26(1)	- 4.19 (13.9)	29.3(4)	- 0.89 (2.9)	29(3)	- 1.19 (3.9)
Fluorite	39(2)	+ 4.31 (12.4)	34.0(7)	- 0.69 (2.0)	33(1)	- 1.69 (4.9)
Deviation Average (24 values range)		- 7.22 to + 4.88 (13.8)		- 2.21 to + 2.63 (3.3)		- 2.42 to + 4.63 (8.9)

Table VII: Results and deviations between methods and real composition.

Accuracy obtained with the three methods is good and no standards were necessary. The Rietveld method implemented in FULLPROF software yields the best results, accuracy is between 0.2 and 9.6 per cent, and it is only necessary to know the structures of phases present. This data is easily obtained from ICSD Inorganic database from FIZ, Karlsruhe or other bibliographic sources. The Rius method is also good, but it yields larger errors in phases present in low concentrations. Its major advantage is the short time needed for pattern recording and there is no need to know the structural data, but only the chemical formulas of present phases.

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References

BISH D.L. & HOWARD S.A. (1986): “Quantitative analysis via the Rietveld method. Workshop on Quantitative X-ray Diffraction Analysis”. (National Bureau of Standards, June) pp. 23-24
BISH D.L. & HOWARD S.A. (1988). J.Appl. Crystallogr. 21, 86-91.
BISH D.L. & POST J.E. (1993). Am. Mineral. 78, 932-940.
DAVIS (1992): “Accuracy in Powder Diffraction II” in NIST Spec. Publ. No. 846, edited by Prince & Stalick (US Dept. of Commerce, Gaithersburg MA) pp. 7-16.
ESTEVE V. (1995): Methodology and analytical techniques for mineral particulate deter-mination Castellón atmosphere. Thesis University of Valencia, Valencia (in Spanish).
ESTEVE V., CARDA J., REVENTÓS M.M. & AMIGÓ J.M. (1997a). Powder Diffr. 12(3), 151-154.
ESTEVE V., RIUS J., OCHANDO L.E. & AMIGÓ J.M. (1997b). Atmospheric Environment 31, 3963-3967.
FANG J.H. & ZEVIN L.S. (1985). J. Sediment. Petrol. 55, 611-613.
FIALA G. (1980). Anal. Chem. 52, 1300-1304.
HILL R.J. (1991). Powder Diffr. 6, 74-77.
HILL R.J. & HOWARD S.A. (1987). J. Appl. Crystallogr. 20, 467-474.
KLUGG & ALEXANDER (1974): X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. (Wiley, New York)
MOORE C.A. (1968). Clays Clay Miner. 16, 325-336.
RIETVELD H.M. (1969). J. Appl. Crystallogr. 2, 65-71.
RIUS J., PLANA F. & PALANQUES A. (1987). J. Appl. Crystallogr. 20, 457-460.
RODRÍGUEZ-CARVAJAL J., FERNÁNDEZ-DÍAZ M.T. & MARTÍNEZ J.L. (1991). Condensed Matter. 3, 3215-3234.

SALYN A.L. & DRITZ V.A. (1972): "On the method of X-ray quantitative phase analysis of clays". (Proceedings 1972 International Clay Conference, Madrid) pp. 797-806.
SCARDI P., GUALTERI A. & BELLOTO M. (1997). Newsletter CPD-IUCr 19, 1-10.
SNYDEr (1992): "Accuracy in Powder Diffraction II" in NIST Spec. Publ. No. 846, edited by Prince & Stalick (US Dept. of Commerce, Gaithersburg MA) pp. 25-33.
SNYDER & BISH (1989): "Rietveld refinement of crystal structures using powder X-ray diffraction data" in Modern Powder Diffractometry, edited by D.L. Bish & J.E. Post (Min. Soc. Am., Washington), Reviews in Mineralogy 20, 101-144.
STARKS T.H., FANG J.H., & ZEVIN C.S. (1984). Mathematical Geology 16, 351-367.
WANG S. & PU X. (1991). Powder Diffr. 6, 62-65.
WERNER, SALOMÉ, MALMROS & THOMAS (1979). J. Appl. Cryst. 12, 107-109.
ZANGALIS K.P. (1991). J. Appl. Crystallogr. 10, 147-150.
ZANGALIS K.P. (1998). Powder Diffr. 13(2), 74-84.
ZEVIN L.S. (1977). J. Appl. Crystallogr. 10, 147-150.
ZEVIN L.S. & KIMMEL G. (1995): "Quantitative X-ray diffractometry". (Springer-Verlag, New York).

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