12.1–10   STANDARD REFERENCE MATERIALS FOR X-RAY POWDER DIFFRACTION, Camden R. Hubbard, National Bureau of Standards, Washington, DC 20234 USA

Standard Reference Materials (SRMs) from the National Bureau of Standards are samples or artifacts certified for one or more chemical, physical or engineering parameters. Today, nearly 1000 different SRMs are available including nine SRMs for x-ray powder diffraction quantitative analysis and instrument calibration. All of these have been certified within the last three years.

SRM 640a (Si powder) 2θ Standard is a replacement for SRM 640. SRM 640a is primarily used as an internal standard for the calibration of peak position in powder diffraction patterns. With calibration, peak positions can be measured accurately to better than 0.01° 2θ. SRM 675 (Fluorophlogopite) Low 2θ Standard is intended to complement SRM 640a by providing two low 2θ calibration lines. Use of SRM 675 at 2θ > 30° limits the accuracy to 0.01 to 0.02° due to a sample penetration-microcrystallite effects.

SRMs 485a, 486, 487, 488 Austenite in Ferrite and SRM 493 Spheroidized Iron Carbide in Ferrite are certified for percent Austenite and Iron Carbide, respectively. SRM 1878 Respirable Quartz is certified for the percent crystalline quartz content. Each of these SRMs can be used as primary calibration standards or for checks on laboratory procedures.

SRM 674 is a set of five powders (α-Al_2O_3, ZnO, TiO_2, Cr_2O_3, CeO_2) to be used as X-ray Powder Diffraction Intensity Standards. The relative intensities of the major lines and Reference Intensity Ratio (I/Ic) for each phase have been certified. They can be used for instrument performance checks and quantitative analysis by the internal standard method. They are also useful for semiquantitative analysis when published or calculated I/Ic values are used as calibration constants.

Current research is leading toward certification of a MgO crystallite size standard ($\sim$ 500, 1000 and 1500Å mean crystallite size), a respirable powder cristobalite standard and an instrument diffraction line profile standard. Input from the diffraction community on their calibration needs is encouraged.

12.1–11   SYNCHROTRON X-RAY POWDER DIFFRACTION. By W. Parrish[†], M. Hart[‡] and T. C. Huang[†], [†]IBM Research Laboratory, K41/281, San Jose CA. 95193, USA, [‡]Wheatstone Laboratory, Kings College, Strand, London WC2R 2LS, UK.

This paper describes the preliminary results obtained at the Stanford Synchrotron Radiation Laboratory. The purpose of the study was to determine the optimum instrumentation and techniques for various types of powder diffraction experiments, and to evaluate the results obtained with the parallel beam optics compared to conventional focusing geometry with X-ray tubes. A number of synchrotron powder studies using energy dispersive detectors have been reported and also a recent study at CHESS using monochromatic radiation and Si(111) analyzer which gave very narrow diffraction peaks [Cox, Hastings, Thomlinson and Prewitt, Nucl. Inst. Meth. (1983) 208, 573]; these were mainly aimed at structure refinement with the Rietveld method.

The easy wavelength selection permits several experiments that are impractical with X-ray tubes, e.g., obtaining patterns with wavelengths chosen near the absorption edges, separating a mixture pattern by introducing anomalous dispersion into one of the phases, and high precision lattice parameter determination by moving reflections to 2θs near 180°. The elimination of the Kα doublet and focusing aberrations gives smaller instrument function corrections and better results with profile analysis methods both for line broadening studies and crystal structure refinement. Preferred orientation can be determined by using the specimen in reflection and in transmission without changing the diffractometer.

The instrumentation uses the white beam from the ring, a channel (220) silicon monochromator mounted on the first diffractometer, diffraction from a thin foil as a monitor, a second diffractometer with vertical plane scanning driven by a high resolution stepper motor, vacuum chamber with rotating specimen, anti-scatter slits, and a scintillation counter. The automation is provided by an IBM personal computer programmed by G. L. Ayers for this application. We are indebted to C. Erickson who prepared the instrumentation and G. Lim for experimental aids. The support of the Stanford Synchrotron Radiation Laboratory staff is also greatly appreciated.

12.2–1   SEARCH/MATCH: PATTERN RECOGNITION WITH REDUCED STANDARD DATA. By T. C. Huang and W. Parrish, IBM Research Laboratory, K41/281, San Jose CA. 95193, and B. Post, Polytechnic Institute of New York, Brooklyn NY 11201, USA.

We have previously reported successful Search/Match results using twelve of the largest d reflections of the standards [Huang, Parrish and Post, Adv. X-Ray Anal. (1983) 26, 93]. In this paper, we show that the twelve intensities of the standards may also be eliminated and only the first twelve d's are generally required for successful Search/Match by computer. Although a smaller number of d's can identify high symmetry compounds, mixtures with low symmetry phases require more.

The advantages of using smaller size standard files in Search/Match analysis include the reduction of the computer storage space, increased Search/Match speed and elimination of problems from incorrect intensities arising from preferred orientation, different diffraction geometries and other factors. This development has considerable practical importance because of the recent rapidly expanding use of personal computers in laboratory automation. The smaller standard file reduces the I/O time. The computer read time required for the 12 d/I pairs standard file was about 60% of that for the complete standard file, and 30% for the reduced 12 d's file.
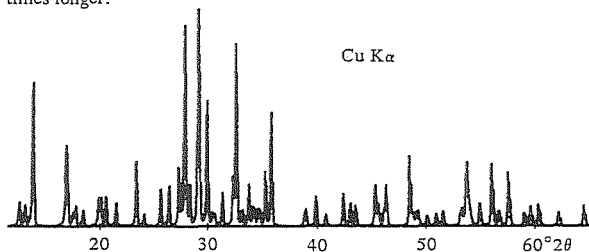
The use of smaller standard files may also reduce the experimental 2θ range and therefore the data acquisition time. The following table shows the maximum 2θ for Cu Kα of the JCPDS File. For example, half of the regular inorganics subfile ended below 69°2θ, and half the reduced 12 d's file completed before 43°.

Substance	File	½	¾
Inorganics	All d's	69°	88°
	12 d's	43	57
Organics	All d's	46	53
	12 d's	26	31

Since the maximum 2θs of the 12 d's standard patterns are about 40% smaller, the experimental range required for recording the pattern of the unknown can generally be reduced.

The method was tested with a large variety of organics, inorganics and minerals, in two to six compound mixtures using published examples and specimens run with our Series/1 automation system. Both peak search data reduction [Huang and Parrish, Adv X-Ray Anal. (1984) 27] and Search/Match were done on the host IBM 3083 computer. The figure of merit (FOM) was calculated from the weighted match of the d's, and the fractions of the standard and the unknown reflections matched in the experimental 2θ range. Chemical prescreening further reduced the search time. The correct compounds had the highest FOMs and were easily identified.

An example of the method is the analysis of the unknown pattern with 69 reflections shown below which was synthesized from published data [sample U-3.6 in Frevel, Anal. Chem. (1965) 37, 471]. Search/Match parameters were: error windows = 0.075°2θ, elements present = Y, As, Ag, Pb, Se and K; undetermined = H to F; and absent = remaining elements. Six candidates were found by Search/Match the frequently encountered phases (FEP) section of the 12 d's inorganics subfile: As_2O_3 (FOM=86), Ag_3AsO_4 (76), Y_2O_3 (75), $PbSeO_4$ (71), KH_2AsO_4 (69) and BeB_6 (41). The last phase (BeB_6) had a much lower FOM and was deleted. By comparing the matched table and plots, the true components in this mixture were easily identified to be the top five phases. Search/Match was done in 0.3 second CPU time. The CPU time for Search/Match of the FEP section of the regular inorganics subfile (standard patterns with all d's and I's) was more than three times longer.

Cu Kα

pharmaceutical uses; therefore, its purity is also subject to pharmacopeial standards and appropriate reference standard quality material is readily available.

When compared to the current IR absorption method, the use of ZnO to determine the RIR is found to be sufficiently sensitive to quantitate amounts of the undesired A polymorph in the 0-20 percent range. Preferred orientation effects, while significant for both polymorphs, are much less for the large peaks of the B polymorph. As a result, the precision of the quantitation is enhanced by an amount which exceeds the loss of precision due to preferred orientation. A procedure for quantitation of the polymorphic content of CMP, based on the above considerations, has been developed. Its validation for drug standardization purposes is described.

Aguiar, A. J., Krc, J. Jr, Kinkel, A. W. and Samyn, J. C. (1967). J. Pharm. Sci. 56, 847-853.

Szulzewsky, K., Kulpe, S., Schulz, B. and Fichtner-Schmittler, H. (1982). Acta Pharm. Suec. 19, 457-470.

USP XX. (1980). United States Pharmacopeial Convention, 12601 Twinbrook Parkway, Rockville, Md. 20852.

12.2-2　QUANTITATIVE ANALYSIS OF THE POLYMORPHIC CONTENT OF CHLORAMPHENICOL PALMITATE BY X-RAY POWDER DIFFRACTION.

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Chloramphenicol palmitate (CMP) is known to exist in three polymorphic forms, designated as A, B and C (Aguiar, Krc, Kinkel and Samyn, 1967), or as β, α and γ, respectively (Szulzewsky, Kulpe, Schulz and Fichtner-Schmittler, 1982). The most stable form (A or β) is also the most resistant to enzymatic hydrolysis to chloramphenicol, and thus the least bioavailable. Although the polymorphic content of CMP is not controlled in the bulk drug substance, a compendial specification for CMP Oral Suspension requires that the content of polymorph A crystals be not more than 10 percent. The monograph in United States Pharmacopeia XX (1980) considers only "A" and "non-A" polymorphs, and quantitates the more desirable "non-A" polymorph by measurement of ratios of peaks in the IR spectra. The B and C polymorphs cannot be distinguished by their IR spectra.

Both the A and B polymorphs may be characterized by powder diffraction patterns which have the most intense peak at a very low angle (below 4° 2θ for CuKα X-rays). ZnO (rather than corundum) is used as an internal standard in the determination of a reference intensity ratio (RIR). This choice is based on reasons of convenience rather than technical reasons. ZnO has certain

12.3-1　X-RAY POWDER DIFFRACTION STUDY OF RUBIES.

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Ruby is the red gemstone in the corundum species. As with all gems, the value of corundum gems depends on color, clarity, and the quality of cutting. In general corundum crystallizes in the hexagonal system, the chemical compound is aluminum oxide (Al_2O_3), and pure corundum is colorless. But gems in this specie have different colors caused by the impurity. Ruby has different colors such as red, purple-red and medium to dark red that depend on the quantity of chromic oxide (Cr_2O_3) in the aluminum oxide compound. Variety of colors of natural ruby and synthetic ruby are compared by powder photographs taken with a Guinier-Hagg focusing camera. The powder diffraction data are obtained in the form of tables. The unit cell dimensions of different rubies are refined by the least-squares method. The ratio of impurity in Al_2O_3 to different color of ruby is identified by the powder diffraction method.