Quantitative Analysis (QXRD)

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Recommended Text:

"Quantitative X-Ray Diffractometry"

Lev S.Zevin, Giora Kimmel
ed Inez Mureinik
Springer-Verlag, New York, 1995
Cost: approx. $99 A

OUTLINE

- Nomenclature
- Introduction/Background
- Basic Concepts
- Techniques
  - Absorption-Diffraction
  - Internal Standard Analysis (RIR)
  - Doping or Spiking method
  - Dilution method
  - Complete n-phase analysis (external standard method)
  - Whole pattern profile matching
- Notes of interest
  - Rapid method using PSD (Cressey)
  - Matrix method (Knudsen)

NOMENCLATURE (consistent with Klug and Alexander)

i,j,k, … (lowercase subscript) lines in diffraction pattern

I,J,K, … (uppercase subscript) components of a mixture

S subscript referring to component used as reference standard

ρ_J Density of component J

f_J Volume fraction of component J in a mixture

x_J Weight fraction of component J in a mixture

μ_J Linear absorption coefficient of component J for x-ray wavelength λ

$\mu_J^* = \mu_J / \rho_J$ Mass absorption coefficient of component J for x-ray wavelength λ

μ	Linear absorption coefficient of sample with a number, N of components
μ^*	Mass absorption coefficient of sample with a number, N of components

$$\mu^* = \sum_{J=1}^{N} x_J \, \mu_J^*$$

I_{iJ}	Intensity of i^{th} line of component J in mixture
$(I_{iJ})_0$	Intensity of i^{th} line of pure component J
I / I_{cor}	Ratio of intensity of strongest peak of each component to a common standard, synthetic corundum, in a 1:1 mixture of sample and standard
$RIR_{J,S}$	Reference Intensity Ratio of phase J with respect to phase S

INTRODUCTION AND BACKGROUND

Powder XRD ideal for crystalline mixture analysis:

- Each component produces characteristic pattern superimposed on those of the other components – unscrambling these superimposed patterns leads to identification of the components

- Intensity of lines in each components pattern is proportional to the concentration of that component, disregarding the effects of absorption.

Quantitative analyses first undertaken in the 1920’s and 30’s (eg Clarke and Reynolds developed scheme for mine dust analysis using an internal standard procedure).

The first Geiger-counter diffractometers were used in 1945 and these allowed data of sufficient precision to be recorded for QA.

Absorption: When a mixture contains both a weak and a strong absorber, lines of the weak absorbing compound appear weaker (and those of the strong absorbing compound stronger) than calculated from a linear relationship between pattern intensity and composition.

In 1948 Alexander and Klug gave the theoretical mathematical background for the effects of absorption on diffracted intensities from a flat powdered cake. Many developed methods have used their basic equations.

Issues

Note: From IUCr CPD Round Robin on Quantitative Phase Analysis

(http://www.dl.ac.uk/SRS/XRD/IUCR/QARR/intro.htm)

"The round robin will address the following analytical issues:"

Type of analysis

- diffraction (X-ray /Neutron) vs non- diffraction
- internal std vs external std vs spiking etc
- standardless methods

Sample features

- representivity & homogeneity
- particle & crystallite size
- statistics & microabsorption
- crystallinity & surface roughness
- preferred orientation, microabsorption & extinction

Data collection

- type of instrument / geometry (eg Bragg-Brentano, Seemin-Bohlin, Guinier, reflection or transmission, Debye Scherrer)
- sample preparation
- data range and wavelength

Data analysis

- integrated intensities vs full-profile
- Rietveld vs data-base of observed patterns
- use of constraints and corrections
- software systems & methods
- complexity of the pattern - peak overlap

BASIC CONCEPTS

- Integrated intensity proportional to analyte phase concentration
- Intensity functionally dependent on absorbing power of mixture for X-rays
- Dependence is generally non-linear and unknown
- Absorption

$$I_{iJ} = K'_{iJ}\ f_J \,/\, \mu \quad = \quad K'_{iJ}\ x_J \,/\, \rho_J\, \mu^*$$

Density is constant for given phase so can be included in *K*, so simplified to:

$$I_{iJ} = K_{iJ}\ x_J \,/\, \mu^* \ = \ K_{iJ}\ x_J \,/ \sum_{K=1}^{n} x_K \mu_K^* \qquad \textbf{... (1)}$$

$$I_{iJ} = K_{iJ}\ x_J / \mu^* \qquad \ldots (1)$$

Object is to determine x_J … achieve this by:

- Measuring intensity of I_{iJ}
- Determining mass absorption coefficient of sample μ^*
- Determining calibration constant K_{iJ}

TECHNIQUES

1. Absolute techniques where the intensity of the peak in the pure analyte $(I_{iJ})_0$ is involved in the equations to solve for x_J Note these techniques depend on experimental conditions (instrument type, settings etc) so it is difficult to compare results from different laboratories.

2. Relative or **Ratio** techniques where ratios, not absolute intensities, are used. (eg internal and external standard techniques). Independent of experimental conditions.

TECHNIQUES

6 Basic Techniques to be described

- **Absorption-Diffraction** … known mass absorption coefficient for mixture
- **Internal Standard** … sample doped with reference
- **Doping (Spiking)** … sample spiked with the analyte phase
- **Dilution** … sample diluted with inert diluent
- **Complete n-phase Analysis**
- **Whole Pattern Profile Matching**

TECHNIQUE #1 Absorption-Diffraction

Known Mass Absorption Coefficient …
(absolute class)

μ^* previously determined by:

- calculation from known composition, summation of atomic absorption coefficients
- direct absorption measurement
- measurement of Compton scattering
- case with constant μ^* (includes phase transitions where chemical composition remains unchanged during the transition)

General case:
multiple phases, variable absorption coefficient

- requires measurement of $(I_{iJ})_0$ for the pure phases in the mixture
- applying … **(1)** to the pure phase (ie $x_J = 1$) $(I_{iJ})_0$ is defined:

$$(I_{iJ})_0 = K_{iJ} / \mu^*{}_J$$

- By combining this with … **(1)** Leroux et al (1953) obtained expression for phase abundance:

$$x_J = I_{iJ} / (I_{iJ})_0 \bullet \mu^* / \mu^*{}_J \qquad \textbf{...(2)}$$

- Suggested measurement of μ^* by direct transmission through the specimen … hence called *diffraction-absorption* technique
- Leroux's equation can be re-written:

$$\log x_J - \log [I_{iJ} / (I_{iJ})_0] = \log [\mu^* / \mu^*{}_J]$$

- Plot of log x_J -log $[I_{iJ} / (I_{iJ})_0]$ vs log $[\mu^* / \mu^*_J]$ at constant x should be straight line of slope -1
- In practice large deviations because of microabsorption# so … **(2)** becomes:

$$x_J = I_{iJ} / (I_{iJ})_0 \bullet [\mu^* / \mu^*_J]^{\alpha}$$

where α is the slope of the regression line of log $[\mu^* / \mu^*_J]$ vs log x_J -log $[I_{iJ} / (I_{iJ})_0]$

NB Microabsorption occurs when two substances of different mass absorption coefficients are mixed.

- α is not constant but depends on grain size of analyte and the nature of the matrix of other phases.
- Note that microabsorption effects can be severe in this method due to the possibility of the pure phase *J* and the multiphase sample having different absorption properties and crystallite size distributions.

Precision: Approximately 5% relative error

Detection Limit: Measured in tenths of percent

(NB precision and LOD as quoted by Zevin are probably optimistic)

TECHNIQUE #2 Internal Standard Analysis

(relative class)

Sample doped with known amount of reference material (internal standard)

- The weight fraction of the unknown phase *J* in the doped sample x'_J is given by:

$$x'_J = x_J(1-x_S)$$

where x_J is weight fraction of phase *J* in the undoped sample, x_S is the weight fraction of the internal standard.

- Phase J and the internal standard must have at least one resolved diffraction peak then:

$$I_{iJ} = K_{iJ}\ x_J\ (1-\ x_S\ )\ /\ \mu_d^{\ *} \qquad \text{(for phase } J\text{)}$$

$$I_{hS}\ = K_S\ x_S /\ \mu_d^{\ *} \qquad \text{(for internal standard)}$$

Note: $\mu_d^{\ *}$ is mass absorption coefficient of doped sample

- Therefore, the ratio of intensities is independent of absorption:

$$I_{iJ}\ /\ I_{hS}\ =\ K_{iJ}\, x_J(1\text{-}x_S)\ /\ K_{hS}\ x_S \qquad \textbf{...(3)}$$

- From (3) weight fraction x_J is a linear function of intensity ratio:

$$x_J = [x_S / (K_{iJ} / K_{hS}) (1-x_S)] \bullet [I_{iJ} / I_{hS}]$$

$$= \text{constant} \bullet [I_{iJ} / I_{hS}]$$

- Internal standard method can be used to analyze any phase in a mixture without analyzing remaining phases. If all phases determined, then mass balance will hold.

Precision: Approximately 1% relative error

Detection Limit: Measured in tenths of percent

Reference Intensity Ratio

Easiest way to bring diffraction peak intensities to common scale is to scale them to a particular peak in a common reference phase.

- deWolff and Visser (1964) suggested the (113) peak in corundum (100% line).
- Hence, **Reference Intensity Ratio (RIR)** is ratio of strongest peak of phase *J* to that of the corundum (113) in a 1:1 (w/w) mixture.

$$RIR_{J,c} = I_{i,J} \,/\, I_{h,c}$$

- Extension to general case RIR of phase α wrt phase β

$$RIR_{\alpha,\beta} = I_{i,\alpha} \,/\, I_{h,\beta}$$

Reference Intensity Ratio

- Usually quoted as ratio of direct peak heights but integrated intensities also used
- Any number of constituents may be quantified
- Mixture may contain amorphous components
- Mass absorption coefficient of mixture need not be known in advance

TECHNIQUE #3 Doping or Spiking Method

(absolute class)

Sample to be analysed is spiked with known amount of the analyte phase *J*

- **Weight fraction of phase *J* in spiked sample**

  M = mass sample
  M_{JD} = mass dopant phase *J*
  $x_J M$ = mass of phase *J* in undoped sample
  x_{JD} = weight fraction of dopant = $M_{JD} / (M + M_{JD})$

$$(x_J)_D = (x_J M + M_{JD}) / (M + M_{JD}) = x_J (1 - x_{JD}) + x_{JD}$$

- **Mass absorption coefficient of doped sample**

Mass absorption coefficient of doped sample, μ_D^* , is the sum of the ratios of the doped fraction x_{JD} , with absorption coefficient μ_J^*, and the remaining fraction $(1- x_{JD})$ with absorption coefficient μ^*

$$\mu_D^* = \mu^* (1 - x_{JD}) + \mu_J^* x_{JD}$$

Now substitute these values for $(x_J)_D$ and μ_D^* into **...(1)**

$$(I_{iJ})_D = K_{iJ} [x_J (1-x_{JD}) + x_{JD}] \;/\; [\mu^* (1- x_{JD}) + \mu_J x_{JD}]$$

$$= K_{iJ} [x_J (1-x_{JD}) + x_{JD}] \;/\; [\mu^* \{1+ x_{JD}(\mu_J^* - \mu^*) / \mu^* \}]$$

...(4)

- In some cases the dopant will not change the overall μ^* significantly. i.e. $\mu^* \approx \mu_D{}^*$

Then

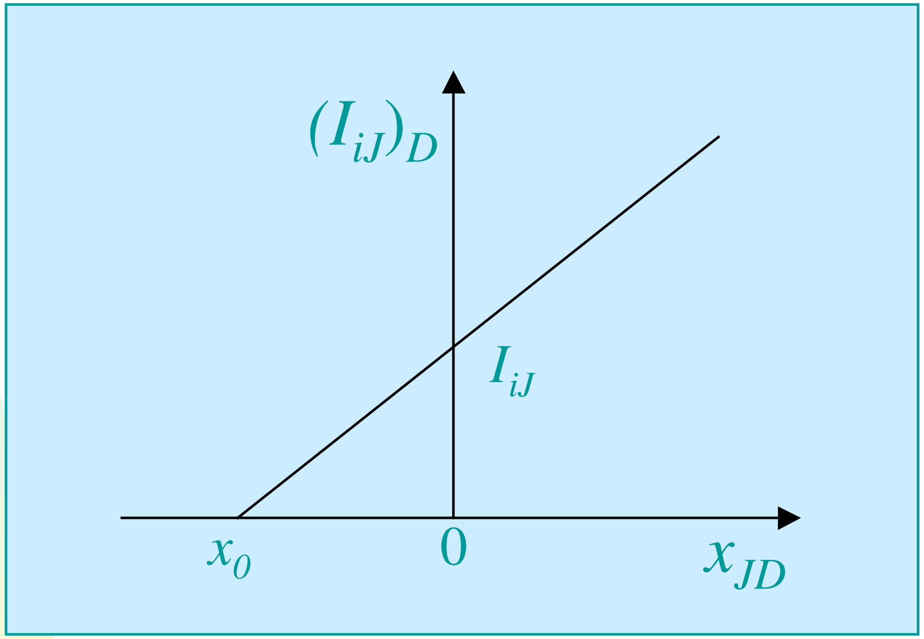
$$(I_{iJ})_D = K_{iJ}\,[x_J\,(1\text{-}x_{JD}) + x_{JD}] \,/\, [\mu^*\,\{1+ x_{JD}(\mu_J{}^* - \mu^*)\,/\,\mu^*\,\}]$$

can be simplified to

$$(I_{iJ})_D = K_{iJ}\,[x_J\,(1\text{-}x_{JD}) + x_{JD}] \,/\, \mu^*$$

$$= (K_{iJ}\,/\,\mu^*)\,x_J + (K_{iJ}\,/\,\mu^*)\,(1 - x_J)\,x_{JD}$$

Then for a series of dopant concentrations, a plot of $(I_{iJ})_D$ vs dopant concentration, x_{JD}, is linear



At x_0, $(I_{iJ})_D = 0$ and $x_J = x_0\,(1 - x_0)$

- However in most cases μ^* is not constant

In this case, can use **...(1)** for the undoped sample and **...(4)** for the doped sample

ie two equations with three unknowns, viz.

x_J , K_{iJ} and μ^*

We can introduce a third equation from the pure dopant phase viz.

$$(I_{iJ})_0 = K_{iJ} / \mu_J^*$$

and so have three equations in three unknowns.

TECHNIQUE #4 Dilution Method

(absolute class)

Sample diluted with unreactive material of known μ^*

- Diluent may be either crystalline or amorphous but should not contain phases to be analysed
- Instead of measuring sample absorption, measurements of diluted and undiluted samples are made
- Diffraction from diluent must not interfere with analytical diffraction peak
- Diluent should not fluoresce, should be chemically inert, exist as fine powder and have mass absorption coefficient close to that of the sample

Weight fraction diluent *(D)*

$x_D = \text{Mass}_D / (\text{M} + \text{Mass}_D)$ where M = Mass original sample

Weight fraction phase *J* in diluted sample

$x_J \text{M} / (\text{M} + \text{Mass}_D) = x_J (1 - x_D)$ see Zevin, p130 for derivation

Mass absorption coefficient of diluted sample

$(\mu)_D^* = \mu_D^* x_D + (1 - x_D)\mu^*$ rule of additivity

We can now use **...(1)** to make three equations in three unknowns (μ^*, $K_{i,J}$ and x_J):

(i) $I_{i,J} = K_{i,J} x_J / \mu^*$

(ii) $(I_{i,J})_0 = K_{i,J} / \mu_J^*$ ie when $x_J = 1$, ie pure phase J

(iii) $(I_{i,J})_D = K_{i,J} x_J (1 - x_D) / [\mu_D^* x_D + (1 - x_D)\mu^*]$

Solving for x_J gives:

$$x_J = [\, x_D\, \mu_D^* \;/\; (1\text{-}x_D)\, \mu_J^* \,] \bullet [\, (\, (I_{i,J})_D \,/\, (I_{i,J})_0 \,) \,/\, (1\text{-}((I_{i,J})_D \,/\, I_{i,J}\,)]$$

Precision and accuracy

- Optimal dilution gives $(I_{i,J})_D \,/\, I_{i,J}$ approximately 0.33
- This gives precision of approximately 2%-3% with relative error of analysis of about 10%.

TECHNIQUE #5 Complete n-phase analysis

(relative class)

For analysis of all phases, an additional mass balance equation is available:

$$\sum_J x_J = 1$$

Two possibilities:

1. Determine weight fractions of each phase by technique #1, #2, #3, #4 etc. Then use mass balance equation to determine accuracy of analysis. ie deviation from a sum of 1 indicates either systematic error or misses phase(s).

2 The mass balance equation can be used to exclude one unknown (eg μ^*) from calculation of weight fractions.

e.g. Equation **… (1)** can be rearranged as:

$$x_J = \mu^* I_{iJ} / K_{iJ}$$

If both sides are summed over all the phases in the sample then:

$$1 = \mu^* \left(\sum_{J=1}^{n} I_{iJ} / K_{iJ} \right)$$

or:

$$\mu^* = \left(\sum_{J=1}^{n} I_{iJ} / K_{iJ} \right)^{-1}$$

By combining our rearranged equation **... (1)** with that for μ^* we can obtain an expression for any phase, let's say R, free of the absorption coefficient:

$$x_R = [\, I_{hR} / K_{hR} \,] \; / \; [\, \sum_{J=1}^{n} (I_{iJ} / K_{iJ}) \,]$$

$$x_R = 1 / \sum_{J=1}^{n} (\, \beta_{RJ} / S_{RJ}) \qquad \textbf{... (4)}$$

where: S_{RJ} is the ratio of intensities of peaks belonging to phases J and R respectively ie $S_{RJ} = I_{iJ} / I_{hR}$

and $\beta_{RJ} = K_{hR} / K_{iJ}$

- The feature of this method that makes it highly attractive is that equation **… (4)** contains only ratios and no absolute values of intensities and calibration constants. Thus the method can be considered independent of measurement conditions.
- Determination of β_{RJ} ratios by matrix methods (see Zevin, p136 ff).
- Also called **external standard method** (Hubbard C.R., Evans E.H, Smith, D.K., *J.Appl.Cryst*., **9**, 169-74, 1976) since the matrix analysis utilises a third phase K not found or doped in the sample in acquiring the β_{RJ} ratios.

TECHNIQUE #6 Whole Pattern Profile Matching

- Most useful where overlapping peaks are a problem .. Phase to be analysed may not have at least one clearly resolved peak.

Profile fitting Groups of overlapping peaks are separated into individual peaks and integrated intensities extracted. Knowledge of peak profiles, positions required but not crystal structure or composition.

Structure Refinement Either using the conventional methods developed for single crystal structural analysis (extraction of integrated intensities, refinement of derived structure factors against a model) or by continuous pattern Rietveld methods.

- Both structure refinement methods require knowledge of the crystal structure

- Numerous references on QXRD using Rietveld methods, with particular reference to work of Hill, Howard, Madsen (eg Hill, R.J., Howard, C.J., J.Appl.Crystallogr., 20, 1987, 467-74.)

$$I_k = S\, M_k\, LP_k\, |F^2|$$

S is the Rietveld scale factor

$$x_J = [\, S_J\, ZMV_J\,] \,/\, [\, \sum_{i=1}^{n} S_i\, ZMV_i\,]$$

Z = number of formula units per unit cell
M = atomic mass of the formula unit
V = volume of one unit cell

NOTES OF INTEREST

1. Absorption and Microabsorption

G. Cressey and M. Batchelder in IUCr Newsletter No. 20
http://www.iucr.org/iudr-top/comm/Newsletters/

Uses PSD … fits the mixed assemblage pattern with proportionally reduced 100% phase patterns of identified components.

Overcomes problems with preferred orientation, absorption and micro-absorption (from surface roughness).

2. Quantitative Analysis with Qualitative Control of Calibration Standards

T. Knudsen, X-Ray Spectrometry, 10 (2), 54-6, 1981

"Samples containing identical or very similar phases and differing in their contents of these can be used for calibration of a quantitative X-ray diffraction analysis without knowing their actual mineralogical composition. The method requires that at least one major peak for each phase is well isolated and that the number of calibration samples is equal to, or exceeds, the number of phases"

For a system of m phases and n samples (where $n \geq m$), and sum of weight % of all phases is 100%, a set of equations is derived of the form:

$$100 = K_1 I_{11} + K_2 I_{12} + \ldots + K_m I_{1m}$$

$$100 = K_1 I_{21} + K_2 I_{22} + \ldots + K_m I_{2m}$$

$$\vdots$$

$$100 = K_1 I_{n1} + K_2 I_{n2} + \ldots + K_m I_{nm}$$

ie this is a matrix of the form $L = IK$

with L and K being column matrices with the elements 100 and the K_J 's respectively, and I a rectangular matrix containing the I_{iJ} 's.

$$
\begin{bmatrix} 100 \\ 100 \\ \vdots \\ 100 \end{bmatrix}
\begin{bmatrix} I_{11} & I_{12} & \cdots & I_{1m} \\ I_{21} & I_{22} & \cdots & I_{2m} \\ \vdots & & & \\ I_{n1} & I_{n2} & \cdots & I_{nm} \end{bmatrix}
\begin{bmatrix} K_1 \\ K_2 \\ \vdots \\ K_m \end{bmatrix}
$$

$$
L \quad = \quad I \quad K
$$

A least squares solution for the calibration constants K_{iJ} is given by:

$$K = (I^{T} I)^{-1} I^{T} L$$

with the superscripts ^{T} and $^{-1}$ representing the transpose and inverse matrix.

This operation can be conveniently carried out using a spreadsheet (eg Microsoft EXCEL).

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