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Optimization of Quantitative X-ray Phase Analysis by Monte Carlo Methods

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Abstract

Present methods for quantitative X-ray phase analysis make extensive use of multilinear regression. Practical application of these methods compels workers to make a choice among many different sets of experimental conditions such as the number, identity and relative concentration of the phases in the synthetic mixtures used for the solution of the regression problem; the number and extent of the angular regions within which X-ray intensities are to be measured; and so on. There are as yet no general criteria for this selection, and classical statistical experimental methods, even such effective ones as *SIMPLEX*, are very time consuming. In the present work a Monte Carlo method is proposed for optimization of the reproducibility and detection limit for a completely general quantitative X-ray phase analysis. A system of three computer programs to this end is developed and applied to X-ray phase analysis of laterites, illustrating the choice of a set of performing conditions among 20 of them.

Introduction

The development of X-ray diffraction led to several algorithms for quantitative phase analysis treatable by linear multiple regression methods (Bezjak, 1961; Naray-Szabo & Peter, 1964; Peter & Kalman, 1964; Karlak & Burnett, 1966; Fiala, 1972; Chung, 1974; Burova & Zhidkov, 1977; Zevin, 1977; Fuentes, 1982; Gonzalez & Roque, 1983). Most of these use a set of samples with known composition in the solution of the regression problem.

In practice the choice of the number of those samples and the concentrations of their components determines the precision of regression coefficients. The choice of angular regions within which X-ray intensities are to be measured is also critical. Other factors must also be taken into account.

At present no general criteria for optimization of the regression problem have been given. The problem refers essentially to the distribution of experimental points along the whole range of the independent variables in hyperspace. Nevertheless, some solutions have been proposed (Hartmann, 1972; Fiala, 1976).

Classical statistical experimental methods, such as *SIMPLEX* for instance, are very slow compared with potentially faster numerical ones. Monte Carlo methods permit the assay of an experimental option in a few minutes by a modern computer. In addition they avoid the necessity of measurements, and the distortion of results by non-statistical gross errors is therefore not possible.

In the present work a Monte Carlo method is proposed for the evaluation of a completely general quantitative X-ray diffraction method. Such procedures for simulating systems have been extensively used by engineers and economists but less by crystallographers.

The general quantitative X-ray diffraction method

The starting point for this method is the general intensity formula with correction for microabsorption (Leroux, Lennox & Kay, 1953),

$$I_{ij}=k_{ij}x_j/\rho_j(\mu^*)^{\alpha_j}\qquad i,j=1,\dots,N-1,\qquad(1)$$

where I_{ij} is the diffracted intensity by the jth phase in the ith peak; k_{ij} are constants; x_j are the weight fractions; ρ_j are the densities; μ^* is the mass absorption coefficient of the mixture and α_j are semiempirical constants introduced to correct the microabsorption (granularity) effects.† It may be expressed in the following form (Gonzalez & Roque, 1983):

$$I_{ij}=k_{ij}(\mu_j^*/\mu^*)^{\alpha_j}x_jI_{ij}^0\qquad i,j=1,\dots,N-1,\qquad(2)$$

where μ_j^* is the mass absorption coefficient of the jth phase and I_{ij}^0 is the intensity of the ith peak of the pure jth phase. The integral intensity in the ith region

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† The α_j's are really functions of several variables of the system but they can be considered as nearly constants (Gonzales, 1987).

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is then

$$I_i = \sum_{j=1}^{N-1} k_{ij} x_j I_{ij}^0 (\mu_j^*/\mu^*)^{\alpha_j} \qquad i = 1, \ldots, N-1. \quad (3)$$

Here, the Nth phase has been considered amorphous by X-ray methods or indeterminable (not detectable), *i.e.* $I_{iN}^0 = 0$.

We can write (3) in the form

$$I_i = \sum_{j=1}^{N-1} A_j M_{ji} \quad i = 1, \ldots, N-1 \quad \text{or} \quad \mathbf{I} = \mathbf{AM} \quad (4)$$

where

$$M_{ji} = k_{ij} I_{ij}^0 \qquad i, j = 1, \ldots, N-1 \quad (5)$$

and

$$A_j = x_j (\mu_j^*/\mu^*)^{\alpha_j} \qquad j = 1, \ldots, N-1. \quad (6)$$

Formula (4) has two aspects. On the one hand it expresses the inverse problem, *i.e.* the general regression problem, or determination of **M**. On the other hand it expresses the direct problem, *i.e.* the calculation of **A** knowing the intensities and regression coefficients.

The inverse problem is solved by preparing L different synthetic mixtures which are placed in the diffractometer and their intensities measured on each of the $P = N-1$ integrated regions. Thus the following system of equations is obtained:

$$I_{ik} = \sum_{j=1}^{N-1} A_{kj} M_{ji} \quad k = 1, \ldots, L, i = 1, \ldots, P$$

or

$$\mathbf{I}_i = \mathbf{A}\mathbf{m}_i \quad (7)$$

where

$$(\mathbf{m}_i) = (m_j)_i = M_{ji} \qquad i = 1, \ldots, P.$$

The solution is (Draper & Smith, 1966)

$$\mathbf{m}_i = (\mathbf{A}^1\mathbf{W}^{-1}\mathbf{A})^{-1}(\mathbf{A}^1\mathbf{W}^{-1}\mathbf{I}_i) \qquad i = 1, \ldots, P \quad (8)$$

where $\mathbf{W}^{-1}$ is the inverse $L \times L$ matrix of statistical weights. It can be calculated from the residuals in analysis of variances, or postulated on the basis of several criteria. In practice no great error is introduced when the identity $\mathbf{W} \equiv \mathbf{1}$ is considered, where **1** is the unitary matrix.

The variance-covariance matrix of regression coefficients is

$$\mathbf{V}(\mathbf{m}_i) = (\mathbf{A}^1\mathbf{W}^{-1}\mathbf{A})^{-1}\sigma^2, \quad (9)$$

where σ^2 is the variance of the experimental measurements of intensities. It can be estimated from the residual sum of squares in the analysis of variances of regression.

In the solution of the direct problem several cases may be differentiated. In all cases it is necessary to calculate **A** from (4). But afterwards, if there are no X-ray amorphous phases or indeterminable ones, then $\sum x_j = 1$ and $\sum x_j \mu_j^* = \mu^*$ holds, and it is possible to calculate x_j. If there are such phases, but μ^* is known for each sample, then x_j is determinable too. One way of calculating μ^* is to follow a process of successive approximations (Engelhardt, 1955; Gonzalez, 1981; Gonzalez & Roque, 1983)

$$\mu^*(n) = \mu_N^* + \sum_{j=1}^{N-1} b_j [\mu^*(n-1)]^{\alpha_j} \quad (10)$$

where

$$b_j = (\mu_j^*)^{-\alpha_j} A_j (\mu_j^* - \mu_N^*). \quad (11)$$

$\mu^*(n)$ is the nth approximation to the mass absorption coefficient of the sample and $\mu^*(n-1)$ the $(n-1)$th one. Here all μ_j^*'s (μ_N^* included) are experimentally determined from clean phases.

Monte Carlo method for optimization

Now we have a rigorous mathematical algorithm for quantitative X-ray diffraction analysis. But there are several factors not fixed by the method, such as the number, identity and relative concentration of the phases in the synthetic mixtures used for the solution of the regression problem, the number and extent of the angular regions within which X-ray intensities are to be measured, and so on, which determine the effectiveness of the analysis.

The efficiency of any analytical method may be qualified by the reproducibility and detection limit of their results. These indexes can be determined by the stated algorithm supposing that the fluctuations of intensities are normally distributed with a known variance, as follows. We start from (4) in the form

$$\mathbf{A} = \mathbf{I}\mathbf{M}^{-1}. \quad (12)$$

Hence, according to (6), we obtain for the pure phases

$$\mathbf{1} = \mathbf{I}_0\mathbf{M}_0^{-1} \quad (13)$$

where $\mathbf{I}_0$ is the matrix of the pure-phase intensities and $\mathbf{M}_0$ is the matrix of regression coefficients unaffected by errors.

Now, by considering that intensities are affected by errors, a new matrix **M** of regression coefficients is calculated from (8) and then

$$\mathbf{a} = \mathbf{I}_0\mathbf{M}^{-1} \quad (14)$$

where **a** is a matrix whose terms are numerically near to those of **1**. Therefore, from (13) and (14),

$$\mathbf{a} = \mathbf{M}_0\mathbf{M}^{-1} \quad (15)$$

in which the diagonal terms correspond to the pure-phase weight fractions (ideally 1), and the

Table 1. *Characteristic constants of pure minerals in laterites*

	Integrating angular regions												
Mineral	1	2	3	4	5	6	7	8	9	10	11	μ^* ($cm^2 g^{-1}$)	α
GO	0	0	0	62·8	0	4·9	0	0	0	0	3·0	60·5	0·81
HE	0	0	0	0	18·7	0	0	0	0	0	9·2	62·0	1·00
GI	0	0	0	0	0	11·0	0	0	0	4·0	5·8	49·4	0·84
LI	70·5	5·6	2·0	0	42·8	0	0	0	0	0	1·7	60·9	0·90
CR	0	2·3	0	0	0	0	9·6	0	19·2	0	0	105·7	0·57
CU	0	0	0	25·3	0	164·4	0	0	0	0	10·0	70·9	0·74
MG	0	0	0	0	0	0	14·4	0	14·0	0	0	109·2	0·90
CL	169·1	32·1	0	0	123·6	0	0	26·0	0	15·6	2·4	64·8	0·34

GO = goethite, HE = hematite, GI = gibbsite, LI = lizardite, CR = chromite, CU = quartz, MG = magnetite, CL = chlorite.

off-diagonal terms to the background (ideally 0). Thus

$$V_C = \sum_{i=1}^{N-1} (1-a_{ii})^2/(N-2) \qquad (16)$$

is the variance of concentrations, and

$$V_B = \sum_{i=1}^{N-1} \sum_{\substack{j=1 \\ i \neq j}}^{N-1} (a_{ij})^2/[(N-1)^2 - N] \qquad (17)$$

is the variance of background. The square root of (16) gives us the reproducibility, and twice the square root of (17) gives us the detection limit.

Table 2. *Angular intervals of chosen integrating regions for the measurement of intensities* [λ(Fe $K\alpha$)]

Region no.	Angular limits (°)
1	7·10–8·30
2	11·75–12·10
3	12·50–13·00
4	13·00–14·05
5	14·75–16·10
6	16·20–17·35
7	18·75–19·75
8	19·75–20·25
9	27·30–28·50
10	28·25–28·90
11	31·20–33·30

Program system

Programs were written in N-88 Basic for implementation on an NEC 9801 microcomputer. The system is composed of three independent programs with common files, *REG*, *INVER* and *SIMUL*. *REG* solves a general multiple linear regression problem. Data are supplied by the *INVER* program, and *SIMUL* allows initial conditions for simulation to be fixed. Fig. 1 is a block diagram of the program system. It runs fully automatically until the solution for a given case is reached.

The program *SIMUL* allows the system to be linked in order to solve a particular Monte Carlo problem. This program is able to read from keyboard or from file the simulation parameters, the range of matrices, mass absorption coefficients data, intensities data, and the relative concentration of the phases in the synthetic mixtures. It also computes A_j from (6) and I_i from (4) and transfers control to *INVER*.

INVER reads data from file, generates the simulated fluctuations of intensities from subroutine *NUMAL*, which in turn generates normal pseudorandom numbers with zero mean and unit variance. Control is then transferred to *REG* in order to solve the general multilinear regression problem in one of the integrating regions from (8), including the analysis of variances with the test of lack of fit. Control is again transferred to *INVER* for the next integrating region, and so on automatically until the solutions for all integrating regions are reached. Then the elements of the **M** matrix are read from file where they were stored, the inverse is calculated by a Gauss-Jordan method, and finally the reproducibility and detection limit are calculated from (16) and (17).

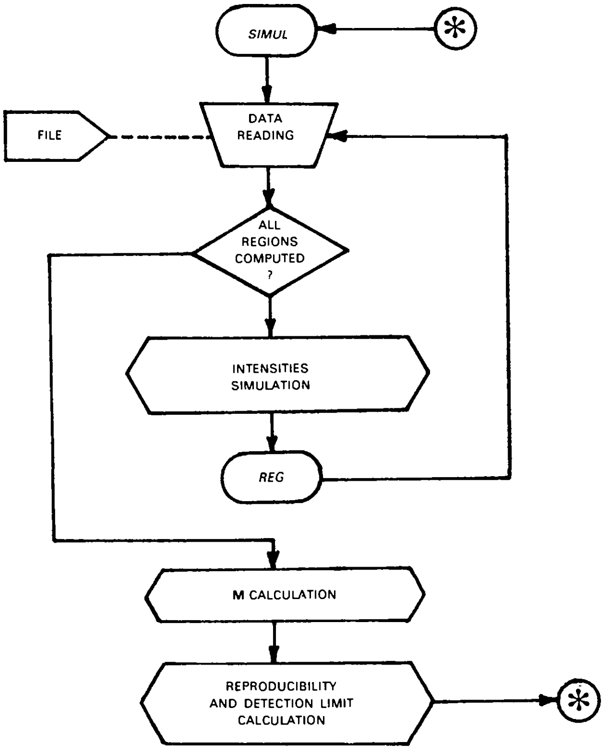

Fig. 1. Simplified block diagram of the program system.

Table 3. *Description and typical deviations obtained of peaks (SP) and background (SB) for each of the 20 sets of performing conditions*

Set	Number of mixtures	Phases considered										Regions considered											SP	SB
		CL	CR	AN	GO	HE	CU	MG	GI	LI	MA	1	2	3	4	5	6	7	8	9	10	11	(%)	(%)
1	20	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×			×	×	10	17
2*A*	17	×	×		×	×	×	×	×	×	×	×	×	×	×	×	×	×			×		15	23
2*B*	15	×	×		×	×	×	×	×	×	×	×	×	×	×	×	×	×			×		329	226
2*C*	15	×	×		×	×	×	×	×	×	×	×	×	×	×	×	×	×			×		118	109
2*D*	15	×	×		×	×	×	×	×	×	×	×	×	×	×	×	×	×			×		24	31
3*A*	15	×	×		×	×	×	×	×	×	×	×	×		×	×	×	×			×	×	14	31
3*B*	15	×	×		×	×	×	×	×	×	×	×	×		×	×	×	×			×	×	26	50
4*A*	15	×	×		×	×	×	×	×	×	×	×	×		×	×	×	×		×	×		38	36
5*A*	13		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		5	9
5*B*	15		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		10^5	10^4
5*C*	13		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		Diverges	
5*D*	10		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		Diverges	
5*E*	13		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		17	14
5*F*	14		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		11	13
5*G*	14		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		25	18
5*H*	10		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		15	12
5*I*	12		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		13	12
5*J*	12		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		16	9
5*K*	13		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		9	8
5*L*	11		×		×	×	×	×	×	×	×	×	×		×	×	×	×			×		7	7

CL = chlorite, CR = chromite, AN = antigorite, GO = goethite, HE = hematite, CU = quartz, MG = magnetite, GI = gibbsite, LI = lizardite, MA = amorphous material.

Table 4. *Weight fractions of lateritic minerals and absorption coefficients for each standard sample in sets 5L, 5A and 5K*

Mix. No.	GO	HE	GI	LI	CR	CU	MG	MA	μ^*(cm^2 g^{-1})
Set 5*L*									
1	0	0	0	0	0	0·2	0·4	0·4	81·9
2	0·3	0	0·3	0·2	0	0	0·1	0·1	62·1
3	0	0	0·2	0·5	0	0·3	0	0	61·6
4	0	0·3	0·1	0	0·3	0	0	0·3	73·3
5	0	0·2	0·4	0	0·2	0·2	0	0	67·5
6	0·1	0·1	0	0	0	0·8	0	0	69·0
7	0·4	0	0	0	0·6	0	0	0	87·6
8	0	0·45	0	0	0	0	0·55	0	88·0
9	0	0	0·5	0	0	0	0	0·5	54·7
10	0	0·5	0	0·5	0	0	0	0	61·5
11	0·6	0·4	0	0	0	0	0	0	61·1
Set 5*A*									
1	0	0	0	0	0	0·2	0·4	0·4	81·9
2	0·3	0	0·3	0·2	0	0	0·1	0·1	61·9
3	0	0	0·2	0·5	0	0·3	0	0	61·2
4	0	0·3	0·1	0	0·3	0	0	0·3	73·3
5	0	0·2	0·4	0	0·2	0·2	0	0	67·5
6	0·1	0·1	0	0	0	0·8	0	0	69·0
7	0·4	0	0	0	0·6	0	0	0	87·6
8	0	0·45	0	0	0	0	0·55	0	88·0
9	0	0	0·5	0	0	0	0	0·5	54·7
10	0	0	0	0·5	0·5	0	0	0	82·9
11	0	0	0	0	0·5	0	0·5	0	107·5
12	0	0·5	0	0·5	0	0	0	0	61·0
13	0·6	0·4	0	0	0	0	0	0	61·1
Set 5*K*									
1	0	0	0	0	0	0·2	0·4	0·4	81·9
2	0·3	0	0·3	0·2	0	0	0·1	0·1	61·9
3	0	0	0·2	0·5	0	0·3	0	0	61·2
4	0	0·3	0·1	0	0·3	0	0	0·3	73·3
5	0	0·2	0·4	0	0·2	0·2	0	0	67·5
6	0·1	0·1	0	0	0	0·8	0	0	69·0
7	0	0·45	0	0	0	0	0·55	0	88·0
8	0	0	0·5	0	0	0	0	0·5	54·7
9	0	0	0	0·5	0·5	0	0	0	82·9
10	0	0·5	0	0·5	0	0	0	0	61·0
11	0·6	0·4	0	0	0	0	0	0	61·1
12	0·4	0	0	0	0·6	0	0	0	87·6
13	0	0	0	0	0·2	0	0·8	0	108·5

GO = goethite, HE = hematite, GI = gibbsite, LI = lizardite, CR = chromite, CU = quartz, MG = magnetite, MA = amorphous mineral.

Application to laterites

This general quantitative X-ray diffraction method was applied to Cuban laterites. With this aim mass absorption coefficients, microabsorption corrections and intensities of pure minerals were determined (Table 1). The mass absorption coefficients were measured by the direct transmission method in the common way (Zavyalova, Ivoilov & Denisova, 1964). The microabsorption corrections were determined in specially designed experiments in the manner proposed by Vlasov & Volkova (1974). Intensities of pure minerals were measured point by point in optimized instrumental conditions. All measurements were carried out in a DRON 2,0 diffractometer with rigorous Bragg–Brentano focusing, Fe $K\alpha$ radiation and scintillation detector. The angular intervals for each integrating region are listed in Table 2.

Twenty different sets of realization conditions were composed in order to optimize reproducibility and detection limit. In all cases a 5% coefficient of variation for the intensities was supposed. Test conditions and the results obtained are listed in Table 3. The most satisfactory conditions are those of 5*L*, but 5*A* and 5*K* are also acceptable. Weight fractions of standard samples in sets 5*L*, 5*A* and 5*K* are listed in Table 4.

Concluding remarks

The absence of general criteria for optimizing quantitative X-ray diffraction methods is no great disadvantage when simulated experiments are applicable. They can reduce the time necessary to achieve optimization by more than a thousand times. The experimental assay of an option may cause several months delay, but the results of a simulation are obtained in about 30 minutes.

If suitable indexes of efficiency are chosen then the same principles can be applied rigorously to other situations in X-ray crystallography with equal or greater profit.

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Deriving the Two-Component Description of Incommensurate Structures From the Superspace Group

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Abstract

McConnell & Heine [*Acta Cryst.* (1984), A**40**, 473-482] have shown that an incommensurate (IC) structure may be fully described as an average structure plus two pure component difference structures C_1 and C_2 modulated by $\cos(\mathbf{Q}.\mathbf{r})$ and $\sin(\mathbf{Q}.\mathbf{r})$ respectively, where the symmetries of C_1 and C_2 are related in a precise way. This result was derived from the conventional Landau theory where the symmetry is specified by an irreducible representation of the space group of the average or disordered structure. It has also been shown by de Wolff, Janssen & Janner [*Acta Cryst.* (1981), A**37**, 625-636] that an IC crystal has the symmetry of a four-dimensional space group; the papers discussing these superspace groups describe the modulation in terms of only a single component. It is proved here that the two descriptions are identical in content, showing that the structure of a superspace group implicitly requires the existence of both C_1 and C_2, and that their symmetries are uniquely related in this formulation as in the McConnell-Heine theory. Two one-dimensional examples are discussed and $NaNO_2$ is considered in detail. Although the McConnell-Heine theory was formulated in terms of the sinusoidal modulation which occurs just below the transition temperature, it is shown that the symmetry properties derived in that theory continue to be valid as the modulation 'squares up' at lower temperatures.

1. Introduction

In recent years it has become recognized that incommensurate (IC) modulated structures have very precisely definable symmetry. Since the IC modulation destroys the regular lattice periodicity, it had at one time been felt that the symmetry was essentially lost. But this is now seen not to be the case. Given the lattice structure and the modulation, the structure is determined throughout all space, implying a correlation of essentially infinite range. This situation is quite

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