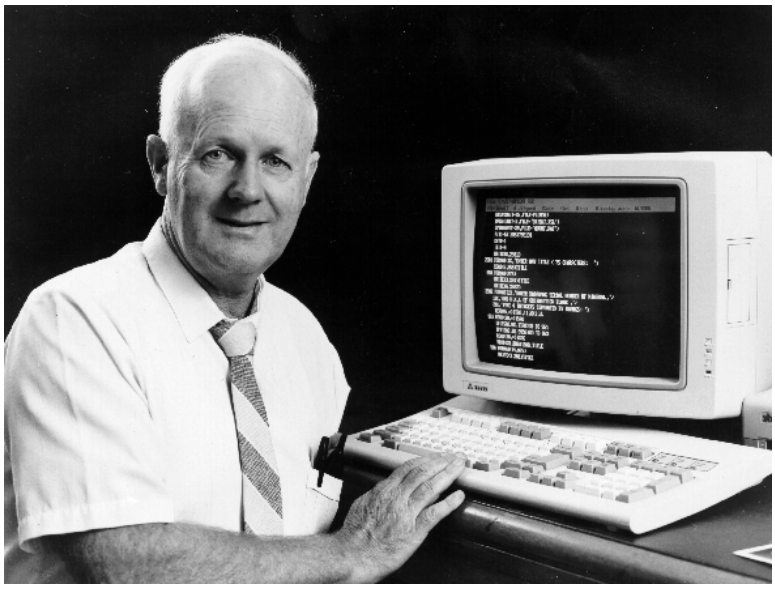
Rietveld Made Easy
A Practical Guide to the Understanding of the Method and Successful Phase quantifications.

The third printing of this book is dedicated in memory of John C. Taylor (1935-2002)



Published by:

Sietronics Pty Limited
Unit 3/22 Walder St
PO Box 3066
Belconnen ACT 2616
Email: spl@sietronics.com.au
Web: www.sietronics.com.au

First printing: October 2001

Second Printing (with minor corrections and dedication): June 2003

Third Printing (with foreword by Hugo Rietveld): September 2004

National Library of Australia Cataloguing-in-Publication data:
Taylor, J. C. (John Charles), 1935-2002.
Rietveld made easy : a practical guide to the understanding
of the method and successful phase quantifications.
ISBN 0 9750798 0 8.
1. Cement - Analysis. 2. Crystallography. 3. Rietveld method. 4. X-rays - Diffraction. I. Hinczak, Ihor. II. Title.
548.83

Printed and bound in Canberra, Australia

Foreword By Hugo Rietveld

Initially the Rietveld Method was developed to refine the structure of crystalline materials by means of powder diffraction. Over the years, this method has proved to be successful, whereby even the structure of proteins with thousands of atoms can be refined. Nowadays the structure of a molecule cannot only be refined but it can also be determined *ab initio* by this method.

An unforeseen application, at least by me, is in the field of phase analysis, where we can now readily determine, quantitatively and qualitatively, the components of a mixture of materials. Although initially the Rietveld Method was known only within the academic domain, such as universities and research laboratories, this new application has broad use also in industry, ranging from oil exploration to manufacturing cement. It is therefore no longer exclusive to crystallographers.

It is rewarding to see the method being applied in such diverse areas. I do hope, however, that it will not be treated as a “black box”, and that its users will always appreciate the underlying crystallographic principles.

The book “Rietveld Made Easy” will certainly contribute to this goal.

Hugo Rietveld

Introduction

Part I: Non-Rietveld : XRD Analysis using Integrated Intensities

The basic premise of this book is that Rietveld analysis, in particular refinement of Rietveld scales, using the full XRD profile, to produce mineral phase quantifications, becomes easy if some elementary crystallography is understood first. That is, a beginner need not see Rietveld analysis as a formidable black box, but should learn about unit cells (a, b, c, α, β, γ), Miller indices, the Bragg Law, and structure factors (F (hkl)), and preferably be able to calculate the angles and intensities of a simple powder pattern, e.g. Cu metal, on a hand calculator. Some elementary facts about crystal structure, morphology, symmetry and crystal structure space groups are given first. Then some other basics about X-ray production, diffractometers, absorption and intensity aberrations in XRD analysis are given, and finally a general formula is presented for quantification using integrated intensities.

Numerical examples are provided, worked out with a hand calculator. Progression is from simple to more advanced studies, in easy logical stages.

To finish Part I, a worked example of quantitative analysis of a two-phase mixture with integrated XRD intensities is given. Once the information in Part I is assimilated, then extension to the Rietveld formula is straightforward.

Part II: Rietveld: A Simple Extension to the XRD Profile from Non-Rietveld

Part II, Rietveld analysis, using the full XRD profile rather than line integrated intensities, follows as a simple extension of Part I. Refinement strategies, designed to avoid pitfalls often encountered by beginners in Rietveld, are described, in order that the Rietveld scales, necessary for quantification of minerals, are arrived at painlessly. A simple XRD pattern, from a quartz-ZnO mixture, is used to show in detail a general Rietveld refinement strategy for phase quantification.

The reader is then gently introduced to some more advanced Rietveld refinement topics such as amorphous content determination, extension to poorly crystallised materials (e.g. clays) and phases with no available crystal data. Split peak shape functions (for treating line asymmetry) and background level refinements with polynomials are described. It is shown how microabsorption, anomalous dispersion, irregular linewidths, extinction, preferred orientation, inadequate sample preparation, and poor particle statistics can limit the accuracy of a Rietveld quantification. The relation between program (calculated) and real errors in the weight percentages is given. Proper choice of radiation and intensity standards is emphasised.

Finally, a brief description of the relatively new GADDS (General Area Detector Diffraction Solution) X-ray diffractometer, and its use together with Rietveld refinement in quantifying trends of mineral weight percentages over the surface of a real unground rock surface is given.