The Rietveld Method: a retrospection

by Hugo M. Rietveld

As a Ph.D. student, in the early sixties at the University of Western Australia, with my supervisor, the late Dr. Ted Maslen, I undertook the first single crystal neutron diffraction study in Australia on the compound p-diphenyl benzene. Automation, particularly by computer, was hardly known. At the Atomic Research Establishment in Lucas Heights (N.S.W.), the crystal orientation on the goniometer head had to be set by hand. The only automatic process was the theta-2theta scan, producing in one hour a piece of paper with approximately forty intensities per reflection. As a result, a continual personal attendance was required in twelve hour work shifts. Two hundred reflections were collected in this way, enough for two projections, one on the $(h\,0\,l)$ plane and the other on the $(0\,k\,l)$ plane (Clews *et al.*, 1961). These early experiences may well be why I vigorously embraced the possibilities of automation created by the introduction of computers. It also explains why I was convinced that good crystallographic work could only be done by means of single crystal diffraction: a Guinier film of the same compound would have consisted of many overlapping lines, which were frequently only to be used to determine the space group and the unit-cell dimensions.

After obtaining my Ph.D. (Rietveld, 1963), I joined the neutron diffraction group at the Reactor Centre Netherlands in Petten in 1964. There, for the first time, I was confronted with the use of neutron powder diffraction for structure determination and refinement instead of the determination of unit-cell dimensions only. In Australia, whilst conducting research on organic compounds, it had been relatively easy to grow large single crystals. In Petten, however, we were mainly interested in uranates as fuel for nuclear reactors. It was impossible to grow large single crystals from these compounds, so we were forced to work with powder specimens instead. In the beginning this proved to be quite successful, because only simple compounds with large unit-cells and high symmetry were studied. This produced well-resolved peaks in the powder diagram, giving a set of single structure factors to work with. Overlapping peaks could easily be graphically separated, as long as the overlap was not too severe. In order to increase the experimental resolution, the wavelength was further increased to 2.6 Angstrom. However the overlapping peaks became a real problem with lower symmetry compounds. A way to split these peaks analytically was by assuming Gaussian peak shapes and constant peak positions and halfwidths, followed by a least squares refinement with the amplitudes as parameters and the profile intensities as data. In the long run this also turned out to be unsatisfactory, because with severe overlap there was too much correlation between the amplitudes (*i.e.* the structure factors).

At that time in crystallography, it was customary to reduce, as much as possible, the amount of experimental data. The profile intensities obtained by step scanning were first summed over the peak to produce integrated intensities, thereby decreasing the amount of data by at least a factor of forty. To do this was a laborious necessity, because all subsequent calculations, first, from intensity to structure factor and then from there to the actual structure parameters, had to be done mainly by hand. In the beginning "Beever and Lipson" strips were used. Later mechanical desk calculators such as the "Facit" were introduced. No wonder no-one looked forward to substantially increasing the amount of experimental data by using the actual profile intensities instead of the integrated intensities. The arrival of computers with their immense comput-

ing power, gave me the idea that it should be possible to use the actually measured profile intensities instead of the derived integrated intensities. One obvious advantage of doing this was the proper handling of the statistics using statistically independent data. This was especially valid for powder data where overlap causes severe correlation between the extracted integrated intensities.

The functional relationship between *integrated intensities* and structure parameters was well understood. The next step therefore was to find a functional relationship between *profile intensities* and structure parameters. Having had experience in mathematically splitting overlapping peaks into separated integrated intensities, which in effect constituted a functional relationship between profile intensities and integrated intensities, it was obvious to go a step further and express the integrated intensities in terms of structure factors and these then in structure parameters. What helped me in particular to undertake this work, was the fact that the peaks were Gaussian and the relationship between halfwidth and diffraction angle was well known (Caglioti *et al.*, 1958). This functional relationship between *profile intensities* and structure parameters was expressed in the following formula:

$$y_i = \sum_k \omega_{i,k} F_k^2 ,$$

where the summation is over all reflections F_k^2 which can theoretically contribute to y_i on the basis of their position and their halfwidth (Rietveld, 1967).

This method was first reported in 1966 to the IUCr congress in Moscow, with little response. The following year I wrote a more comprehensive program in Algol 60 for magnetic and nuclear structures. This consisted of two parts. The first part calculated the contribution each reflection can make to the profile intensity and the second part refined the profile and structure parameters. When the refinement program was originally written, I left out all the profile parameters, such as halfwidth parameters, unit-cell dimensions and the background contributions. The reason this was done was not to introduce into the refinement, parameters such as these halfwidth parameters and background parameters in order to avoid "fudging factors". For most of these parameters had no direct physical meaning and the only reason to introduce them was to make a more perfect fit to the observed data: a perfect fit can always be achieved by introducing enough parameters, or degrees of freedom. In the first runs on WO_3, using neutron diffraction data, an improvement in e.s.d.'s of a factor two was obtained over the results by refining integrated intensities. Introducing the profile parameters decreased the e.s.d.'s of the structure parameters even further by a factor four. So while most of the profile parameters did not really contribute to a better understanding of the structure of the material, refining them gave a better-defined structure (Loopstra and Rietveld, 1969). In the original paper (Rietveld, 1969) it was suggested that the method could also be used for X-ray diffraction with the appropriate modifications. Because there was no need to do this, it was not until 1977 that these modifications were made, thereby opening up the use of the method to a much larger group of crystallographers (Malmros *et al.*, 1977).
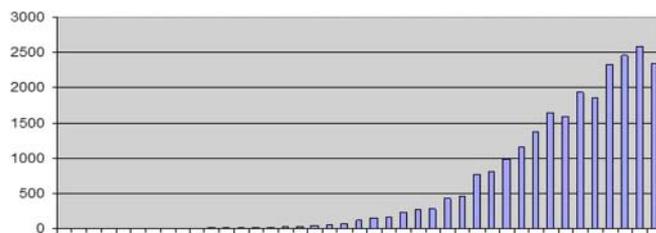

Fig. 1. Number of hits per year on "Rietveld Method" and synonyms in Google Science between 1967 and 2007.

Figure 1 shows the increase in the number of publications using the method.

In my first publication (Rietveld, 1967) I named this method 'The Profile Refinement Method'. This was a misnomer, because the profile was not refined but the crystal structure. In 1978 during the Neutron Diffraction meeting in Cracow, it was proposed by Ray Young and Terry Sabine to call the method the Rietveld Method to avoid ambiguity. This proposal was endorsed by all participants present. Over the years many more Rietveld programs have been written, such as RIETAN by Fujio Izumi, GSAS by Bob Von Dreele, DBWS by Ray Young, and FullProf by Juan Rodriguez-Carjaval. The addition of Graphic Users Interfaces to these programs greatly facilitates the tedious job of handling input data and evaluating parameters. While the first structures I refined, such as $MnTa_4S$, consisted of five atoms in the asymmetric unit, it was reported by Bob Von Dreele that he had managed to refine, from powder data, a protein structure with 1401 atoms, albeit with many constraints, in thirty minutes per cycle.

From mid seventies the method was also applied to quantitative analysis. While it was originally designed to refine a single structure from powder data, it turned out that the Rietveld scale factor could also be used in a multi phase powder. Here the objective is not to refine the constituent structures but, knowing the structures, to refine the scale factors. This then leads to the following formula,

$$W_p = c_p(ZMV)_p \Big/ \sum_{i=1}^n c_i(ZMV)_i,$$

where W_p is the relative weight fraction of phase p in a mixture of n phases, and c, Z, M, and V are respectively, the Rietveld scale factor, the number of formula units per cell, the mass of the formula unit, and the unit cell vol-
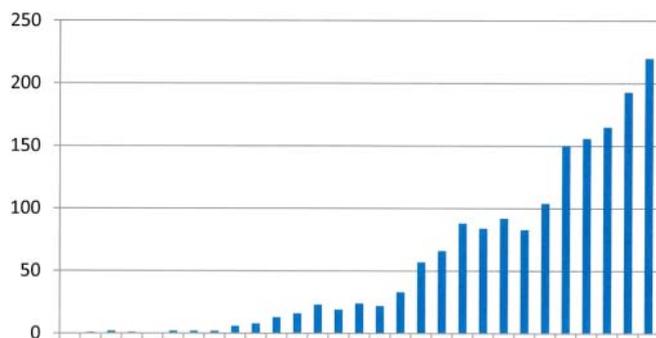

Fig. 2. Number of hits per year on "Rietveld Quantitative Phase Analysis" in Google Science between 1982 and 2009.

ume. This method has become increasingly important as can be seen in Fig. 2.

I am totally amazed at the ever increasing use that is being made of the method. Yearly, hundreds of publications use or refer to the method. What began as a solution for a particular problem, turned out to be a tool of much broader use. Now it is not only applied to structure refinement, but also to such diverse fields as quantitative phase analysis, measurement of strain and size, and the analysis of time-resolved data. I am deeply gratified that I have been instrumental in reviving this powder diffraction method.

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