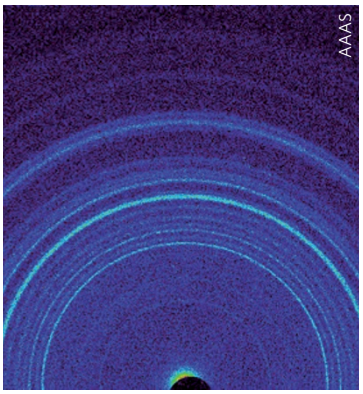
MILESTONE 15

Powder struggle

"The powder method has gained a new importance in neutron diffraction owing to the general lack of large specimens for single-crystal methods". With this brief opening sentence of his landmark paper in 1969, Hugo Rietveld had explained very clearly the scenario of solid-state crystallography at the time.

In a powder diffraction experiment, the sample is composed of a large number of randomly oriented crystalline grains, so that the peaks from scattering by diffraction of all lattice planes can in principle be detected at the same time. The technique originated several decades before Rietveld's work, when Peter Debye and Paul Scherrer performed X-ray diffraction experiments that led them to discover the structure of graphite in 1916 (Milestone 4). Around 30 years later, the first neutron powder diffraction experiments appeared. Although it had proved useful to solve relatively simple structures, by the 1960s it was realized that powder diffraction was unwieldy to use with structures of increasing complexity. The presence of multiple phases, different grain sizes, and reflections due to the experimental conditions, for example the sample or detector geometry, were generating a large number of overlapping and intermixing peaks that were difficult to separate.

Hugo Rietveld was a crystallographer at the Netherlands Energy Research Foundation, and one of his tasks was to unveil the structures of possible fuels for nuclear reactors, for which only powder samples existed. He had experience in using computer software to model diffraction patterns from single-crystalline samples, and he set off to extend his previous work to powder diffraction patterns. The software he generated used some of the parameters that could be extracted from the actual data, like the peaks' positions, intensities and widths, to calculate a theoretical diffraction profile. This was used as a starting point for an iterative least-squares fit to the measured spectrum. In Rietveld's method, a curve-fitting procedure for the whole diffraction pattern replaces a comparison of individual peak intensities.



Powder diffraction pattern of a sample of the soil of Mars, collected by the Curiosity rover. Figure reprinted with permission from D. L. Bish *et al. Science* **341,** 6153 (2013).

The first concept and results were published in 1967, and a second publication two years later provided a more comprehensive description of the procedure now known as the Rietveld refinement method. The 1969 paper is specifically about neutron diffraction but it speculates about extending the method to X-ray powder diffraction, which would eventually be achieved almost a decade later, and is still widely used today.

The secret of the method's longevity and widespread use is its strong computational nature. With time, ever-growing computational power has allowed increasing amounts of information to be obtained and analysed, well beyond the simple structure of a material. The method is widely used in metallurgy, mineralogy, forensic science, archaeology, condensed-matter physics, and the biological and pharmaceutical sciences, and it can provide information on quantitative phase analysis, strain and defect distribution. The technique also played a central role in the recent geochemical analyses carried out by the Curiosity rover on the surface of Mars.

As Rietveld himself put it in 2002, "I am totally amazed looking at the ever increasing use that is being made of the method. [...] What began as a solution for a particular problem, turned out to be a tool of much broader value."

Fabio Pulizzi, Chief Editor,
Nature Nanotechnology

ORIGINAL RESEARCH PAPERS Rietveld, H. M. Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Crystallogr.* **22,** 151–152 (1967) | Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2,** 65–71 (1969)
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