EXPO&*more* International Workshop

Crystallographic Software for Powder Diffraction Data

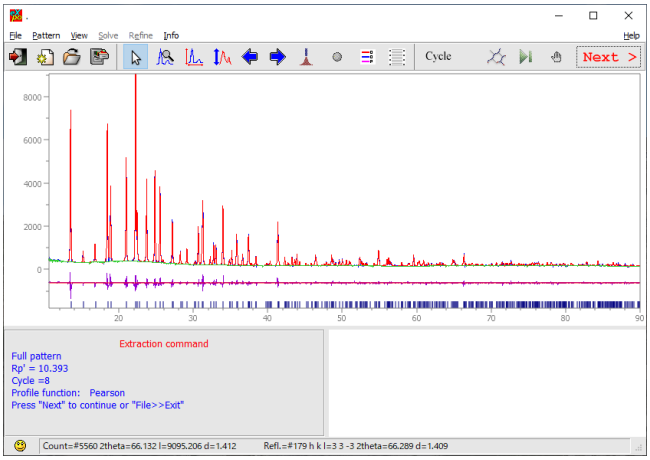
30 September – 3 October 2019 | Bari, Italy

Reported by Akito Sasaki & Akihiro Himeda,
XRD Application & Software Development Dept.

The EXPO&more International Workshop was held at Polytechnic of Bari, Italy, from September 30th through October 3rd, 2019. Angela Altomare *et al.* at IC/CNR (Istituto di Cristallografia/Consiglio Nazionale delle Ricerche) have been developing EXPO crystal structure analysis software for over 20 years, applying direct methods and direct space methods to powder X-ray diffraction （PXRD） data. Typically, single crystal diffraction data is used for structure analysis. However, when high-quality single crystals cannot be obtained for some reason, scientists would like to perform crystal structure analysis using PXRD data. EXPO is the only program that incorporates direct methods for crystal structure analysis from PXRD data. Over 80 people attended the workshop from many countries, learning a lot about EXPO.

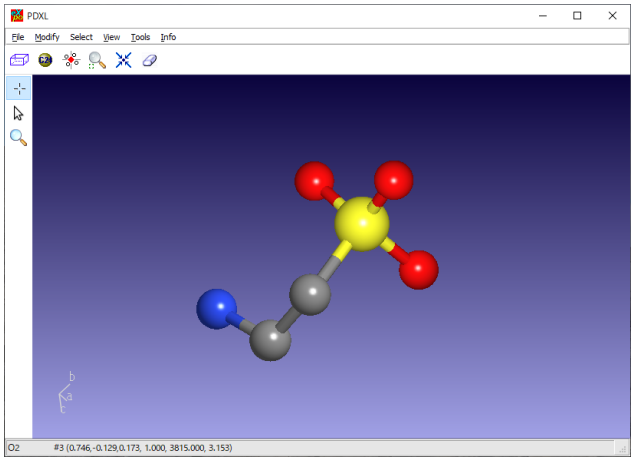
The Powder XRD plugin of Rigaku's SmartLab Studio II software contains functions for crystal structure analysis from PXRD data, in addition to general PXRD applications such as phase identification, quantitative analysis, *etc.* The relationship between EXPO and Rigaku software started in 2009, when we were selling PDXL. EXPO's functions can be used seamlessly in a series of structure analysis procedures both in PDXL and in the SmartLab Studio II Powder XRD plugin. For example, indexing will be done using Rigaku software, space group determination and initial structure determination will be done using EXPO, and structure refinement by the Rietveld method will be performed using Rigaku software again. In this workshop, we made a presentation on the relationship with EXPO. (You can download several presentation files from the EXPO&more Workshop > Scientific Programs page.) In this document, we briefly introduce EXPO and the other three programs presented at the workshop.

1. **EXPO**
   EXPO performs the initial structure determination using direct methods and/or direct space methods from PXRD data. Actually, all the functions required for crystal structure analysis are available in EXPO—from peak search and indexing through structure refinement using the Rietveld method. Academic users can use EXPO for free after registration. Therefore, EXPO is strongly recommended if you are going to try crystal structure analysis from PXRD data. Please note that EXPO can only handle data from a single crystalline phase sample. If peaks derived from impurities are observed in the PXRD pattern, a good solution cannot be obtained.

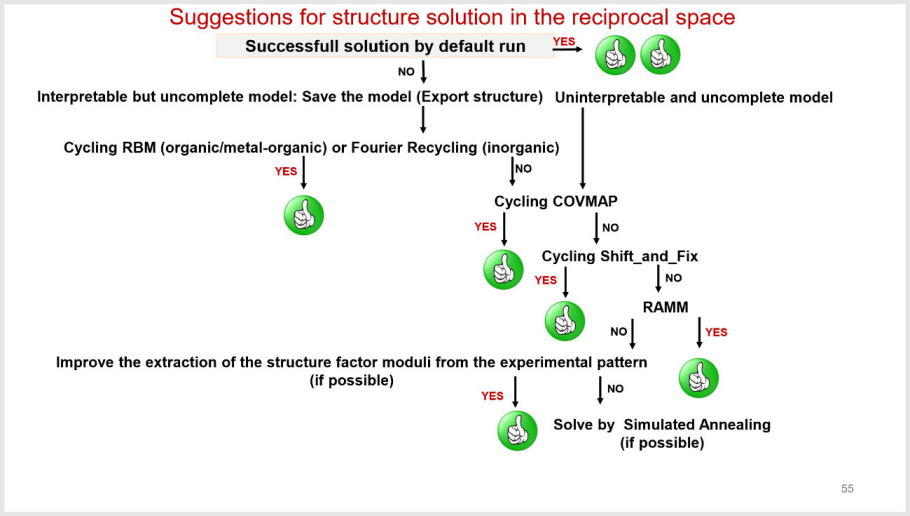


Lecturers elaborated on each step of structure analysis from its basic theory to how to use the software in the workshop setting. Tutorial documents and sample data were prepared so attendees could easily learn how to use the software. What is noteworthy is that several supportive functions are provided in EXPO because direct methods do not always provide a probable initial structure. These functions include “Explore Trials,” which allows you to explore all the direct methods phasing trials, “RBM (Resolution Bias Modification),” which corrects errors in electron density maps due to the truncation effects of Fourier transform, “COVMAP,” which helps to add new atomic positions based on the covariance concept, and so forth. In addition, although it takes a long time, “RAMM” is also implemented: it starts with randomly-set atomic positions, which are cyclically improved by Fourier transform and LSQ (weighted least-squares). It is difficult to determine the initial structure of, in particular, an organic compound consisting of light atoms; therefore, the above supplementary tools should be tried until a satisfactory result is obtained.

In EXPO, direct space methods using a simulated annealing algorithm are also implemented. In the case of molecular crystals such as organic compounds, better results are often obtained using direct space methods than direct methods, depending on intramolecular DOF (degree of freedom). Direct space methods do not require high-angle data compared to direct methods. Good analysis results will often be obtained if you collect data in the 2θ range less than 60-70° with CuKα X-rays. This is a big advantage of direct space methods.

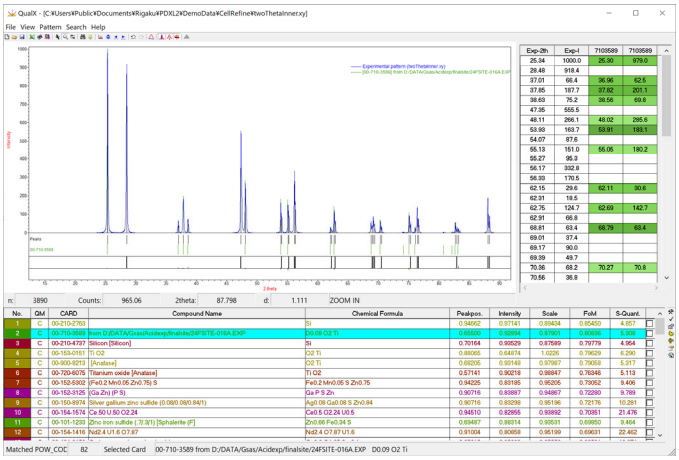


As described above, several methods to determine an initial structure are implemented in EXPO. Even if the sample consists of a simple compound, crystal structure analysis from PXRD data sometimes fails, while single crystal structure analysis usually succeeds. Please make full use of the functions and methods prepared in EXPO, and if a possible initial structure can be obtained, you may be able to achieve structure analysis by subsequent structure refinement using the Rietveld method. For the initial structure determination, please refer to the following approach.



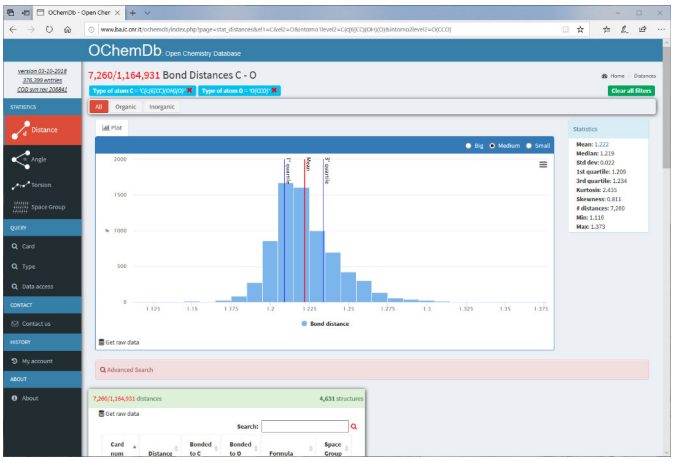
2. **QUALX**

   Angela Altomare *et al.* have developed several programs other than EXPO, distributing them mainly to academic users. One of them, QUALX, is a phase identification (phase ID) program. “Phase ID” determines which crystalline materials are included in a sample based on a PXRD pattern. Normally, the included materials are retrieved by pattern matching using material databases. The phase ID software sold by Rigaku, other X-ray analysis instrument makers, and X-ray analysis software vendors all use commercial databases such as ICDD-PDF, while QUALX retrieves materials using a free database called COD. The number of entries in COD now exceeds 400,000, and two types of index files for phase ID are available from QUALX: one consists of all the entries, the other consists of inorganic compounds only. If you are going to try phase ID, how about using QUALX?



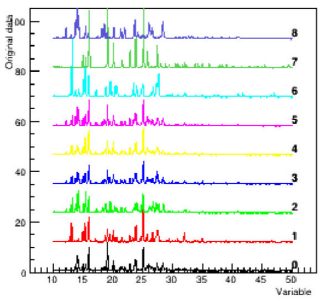
3. **OChemDb**

OChemDb is a web-based application that provides statistical values of bond lengths, bond angles and torsion angles of certain structures based on the crystal structure information in COD. There are a huge number of organic compounds in COD; therefore, these statistical values calculated from OChemDb are considered to be highly reliable. Sometimes, attempting to refine all the structural parameters in structure analysis using PXRD data is unsuccessful. Because of that, some restraint conditions are set on the basis of chemical grounds. In the crystal structure analysis of molecular crystals represented by organic compounds, it is reasonable to set restraint conditions to the molecular structure based on the statistical values obtained from databases. However, it is not easy to set up the restraint conditions. Even for taurine, which has a simple molecular structure, it is necessary to apply restraints to 13 bond lengths and 24 bond angles. That means you need to obtain the statistical values for these 37 parameters. It is not advisable for a user to type all these values. We are currently investigating if it is possible to send/receive conditions and values to/from OChemDb.

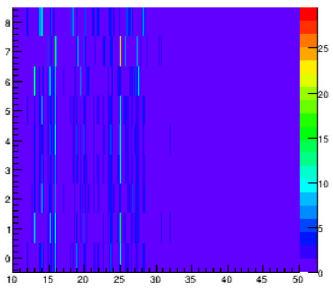


4. **RootProf**

In the last few sessions of the workshop, we had a lecture and training on RootProf multi-data analysis software. RootProf allows you to analyze a number of data sets quickly under the same conditions and to analyze correlations between data sets. The possible analyses are basic data processing (such as smoothing and background subtraction), phase ID, quantitative analysis, crystallite size analysis, cluster analysis, PCA analysis, *etc.* Recent advances in analytical instrumentation have enabled fast data collection, producing a large number of data sets in a short period of time. Individual data analysis is not realistic. Screening analysis and a massive amount of data analysis are sometimes needed instead of precise analysis. RootProf is a very useful program for this situation.



Original data shifted



Data matrix

We attended the lectures and training sessions on the above four programs for 4 days. We first learned about EXPO in the workshop 5 years ago, and realized that new functions and improvements have been made since then. Now EXPO is a very strong tool in our SmartLab Studio II. We occasionally give seminars and training courses on crystal structure analysis from PXRD data, and we plan to introduce the EXPO functions that we learned in these workshops. (The next training course will be held in January 2020 at SPring-8, a synchrotron radiation facility in Japan.)