OPTIMISING PDF DATA QUALITY USING A LABORATORY POWDER DIFFRACTOMETER

An impressive comparison of $G(r)$ calculated with PDFgetX3 [1] from data of naphthalene taken at room temperature with a STOE STADI P powder diffractometer in Transmission mode, equipped with a Ag-tube, a Ge(111)-monochromator for pure Ag $K_{\alpha 1}$-radiation as well as the Dectris MYTHEN 1K detector with 1 mm chip thickness and from the synchrotron beam line X17A , NSLS Brookhaven with a wavelength of 0.1839 Å resulted into amazingly similar peak widths for both experiments.

Therefore the same powder diffractometer has been chosen to investigate the influence of the wavelength, sample volume, temperature and detector technique to optimise the data quality for laboratory PDF data acquisition.

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PDF calculation

STADI P with Dectris MYTHEN 1K detector

In the recent past, the calculation of the pair distribution function (PDF) became more and more common as a new method to obtain structural information from complex materials beyond the Bragg equation and crystallographic PXRD analysis [2].
The atomic PDF G(r) gives the number of atoms in a spherical shell of a normalised thickness at a distance r from an atom,

$$G(r)=4\pi r[p(r)-p_0]$$

it is the sine Fourier transform of the total scattering structure function S(Q)

$$G(r)=\frac{2}{\pi}\int_{Q=0}^{\infty}Q[S(Q)-1]\sin(Qr)dQ$$

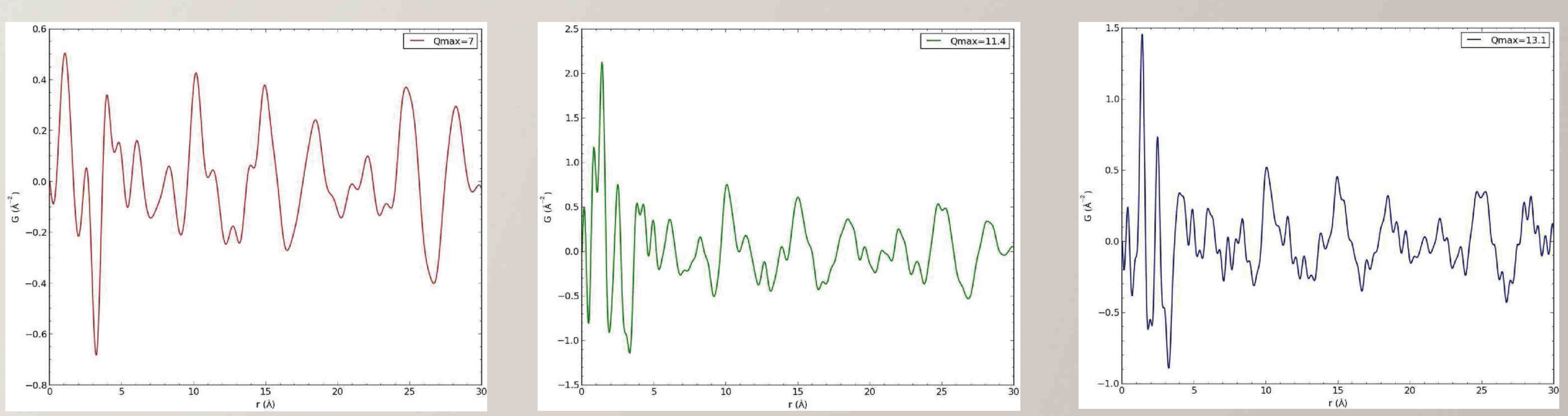
where Q is the magnitude of the scattering vector and S(Q) the corrected and normalised powder diffraction pattern of the material. S(Q) has to be measured to as high Q-values as possible to achieve the best resolution in real-space.

The influence of the wavelength

With $|Q|=\frac{4\pi\sin\theta}{\lambda}$

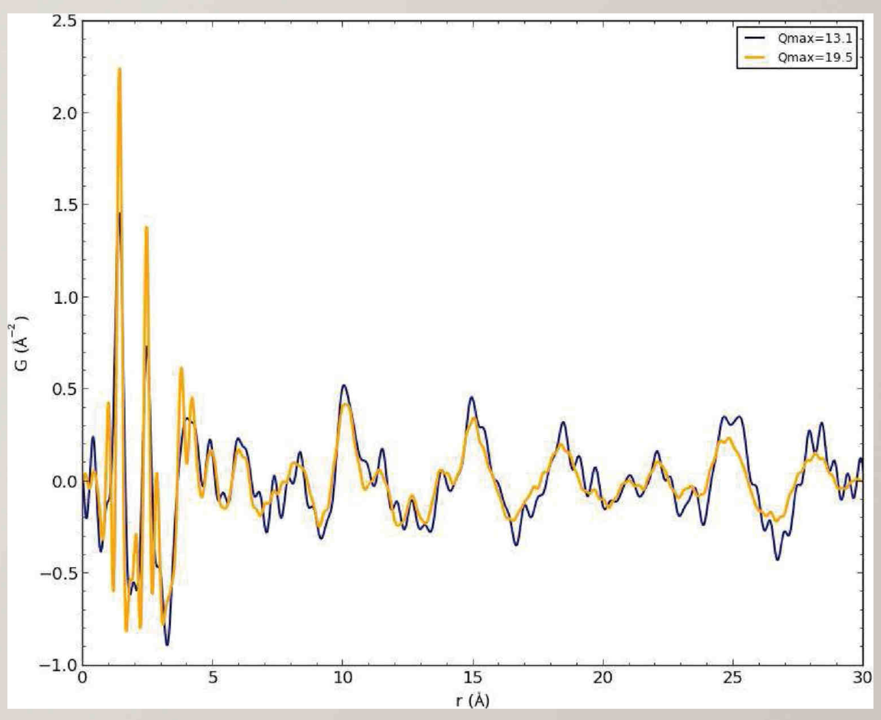
it is evident that synchrotron radiation with shortest wavelengths will be preferred to attain the best PDF data. Nevertheless, standard laboratory powder diffractometers can yield sufficient data quality in a reasonable measuring time when Mo $K_{\alpha 1}$- (0.7093Å) or Ag $K_{\alpha 1}$-radiation (0.5594Å) has been used.

Sealed in a 1.0mm capillary, the sample has been measured with 3 different wavelengths. PDF calculations yield a $Q_{(obs\ max)}$ for Cu- of 7.0 $Å^{-1}$, 11.4 $Å^{-1}$ for Mo-, 13.1 $Å^{-1}$ for Ag-$K_{\alpha 1}$-radiation and 19.5 $Å^{-1}$ for the synchrotron data (λ = 0.1839 Å).



G(r) for naphthalen measured with Cu- (red), Mo- (green) and Ag-radiation (blue)

Synchrotron versus sealed tube

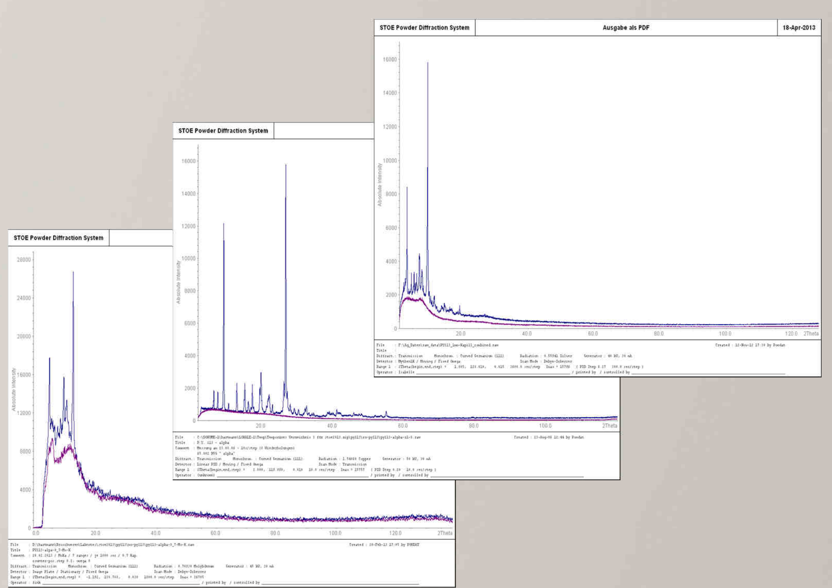


Comparison of the laboratory setup (blue) and the synchrotron experiment (yellow)

The direct comparison of the PDF curves of the synchrotron- (yellow) and the Ag-experiment (blue), shows that the resolution of the Ag-data is amazingly similar!

Taking into account that $\lambda_{(synchrotron)}$ has been approximately 50% of Ag-$K_{\alpha 1}$, the measuring time (Ag-experiment 18h, synchrotron 10min) is more than reasonable for this laboratory setup making the STOE STADI P with Ag-tube and Dectris MYTHEN 1K an impressive alternative to the expensive synchrotron experiments.

The right detector technique



Background and powder pattern of PY213 measured with Cu- and lin. PSD, Mo and IP PSD as well as Ag-radiation and MYTHEN 1K

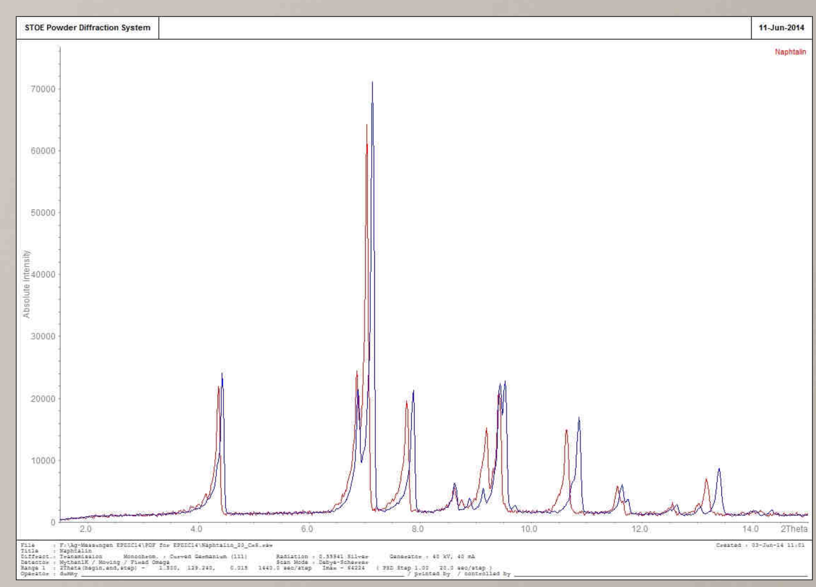
Pigment Yellow 213 [3] has been chosen as the test sample to compare different detector types, a STOE IP-PSD imaging plate (below), STOE´s linear PSD (middle) and the Dectris MYTHEN 1K (top).

Regardless the wavelengths they have been measured with, only a short view on the background of the powder diffraction patterns of pigment yellow 213 (blue) and the empty capillary (red) is enough to conclude that the MYTHEN 1K should be the detector of choice!

Temperature dependent measurements

To observe the temperature dependence of the data quality, the STOE STADI P has been equipped with an additional Oxford Cryosystems Cobra and a STOE furnace

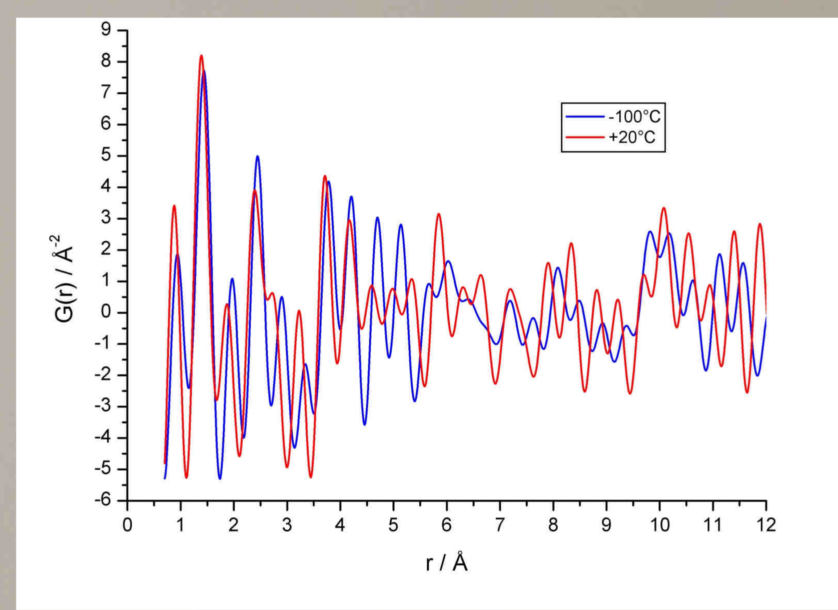
Naphthalene at low-temperature



Room-temperature (red) and -100°C (blue) measurement of naphthalene measured with Ag-$K_{\alpha 1}$-radiation

hkl	2θ (RT)	2θ (-100°C)	FWHM (RT)	FWHM (-100°C)
001	4.374	4.444	0.039	0.040
110	6.869	6.894	0.032	0.031
-111	7.053	7.155	0.042	0.041
-201	7.771	7.887	0.053	0.051

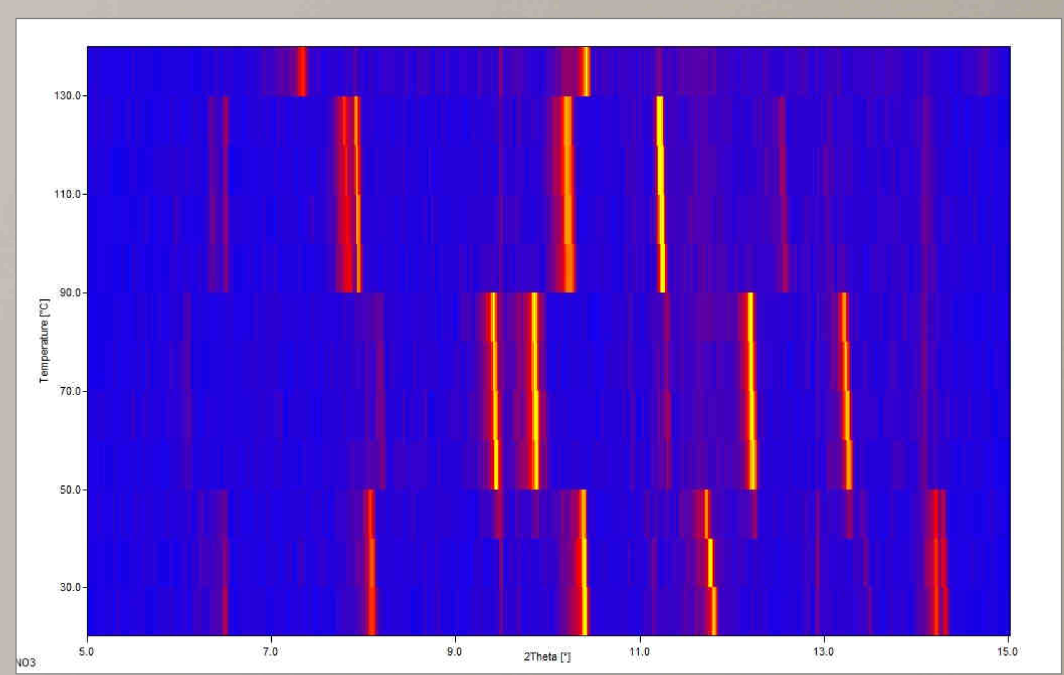
The low-temperature experiment of naphthalene has been carried out at -100°C.
The comparison with the measurement at room temperature shows the expected shift to higher 2θ-values, yet the influence on the FWHM is nearly neglectable.



G(r)-plot of naphthalene at RT (red) and -100°C (blue)

Ammonium Nitrate at high temperatures

With its 4 phase transitions at moderate temperatures NH_4NO_3 seemed to be the right compound for HT PDF experiments. For all measurements a 0.5 mm capillary has been used, the beam spot has been 1 mm² yielding an illuminated volume of only 0.5 mm³!

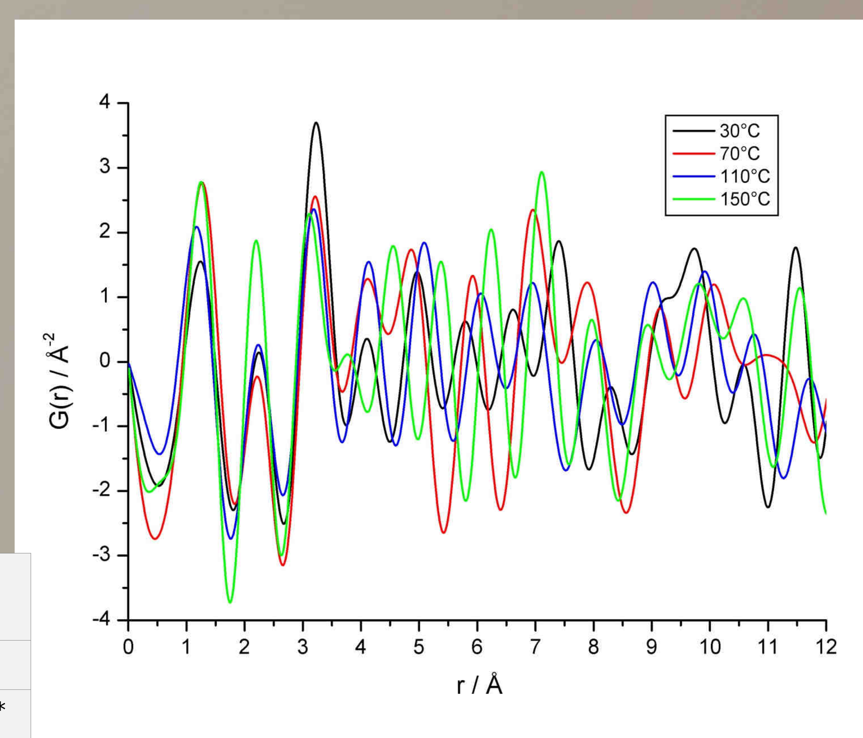


Guinier plot of a rapid T-resolved measurement of NH_4NO_3

The comparison of the PDF curves of all 4 phases shows a similar slope up to about 4 Å. Only the 6-fold coordination of N2 yields a remarkable high intensity at r = 2.2 Å in the PDF curve of phase I. For r values greater than 4 Å, the different structural details of the polymorphs are represented in the PDF curves.

Polymorph	N1 – H [Å]	N2 – O [Å]	N1 – O [Å]	N1 – N2 [Å]
I		2.2	3.1	3.8
II	1.0	1.2-1.25*	2.9-3.1*	3.7-3.8*
III		1.3	2.8-2.9	2.6
IV	1.0	1.3	3.0	3.5

Selected distances for all crystalline NH_4NO_3-Phases (ICSD data)
*: disorder



G(r)-plot of the NH_4NO_3 polymorphs I - IV

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