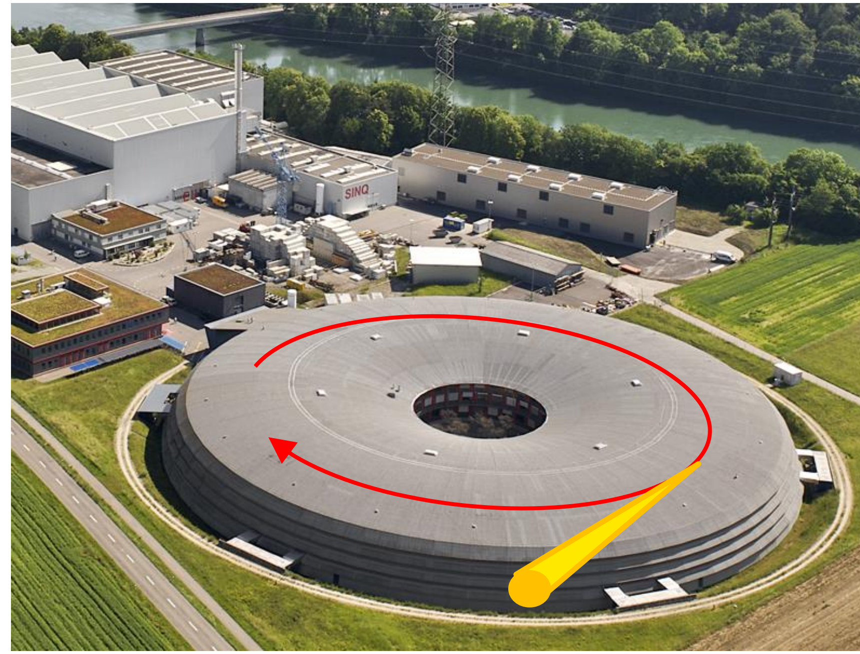
Dr. Nicola Casati :: Group Leader, Material Science :: Paul Scherrer Institut

High Throughput Powder Diffraction

The 2nd International Online Conference on Crystals

Synchrotrons as X-ray sources

- Tunable beam size (ideal for complex chambers or small samples)
- Tunable wavelength (Energy)
    - Short for more penetration, resolution
    - Long for higher cross-section
    - Move across elemental edges



Synchrotrons are also correctly associated to the highly intense radiation beam they produce, which can be exploited in several different ways

- Better $\Delta\lambda/\lambda$ (to select a highly monochromatic radiation)
- Larger signal/noise ratio (quality)
- Time resolved (quantity, or time resolution within an experiment)
- High throughput (quantity, more samples within time)

We will focus today on the last point, which is often neglected as a ‘brute force’ approach

Serial data acquisition (scanning)

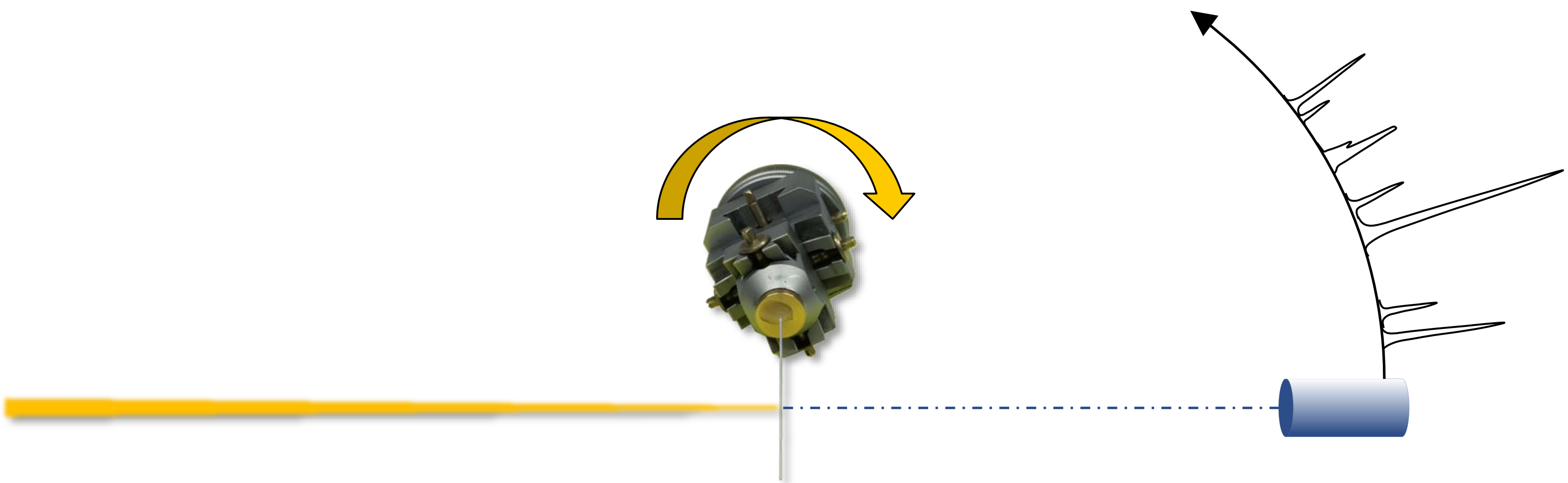
Transmission (Debye-Scherrer)

In powder diffraction, the traditional acquisition method, by scanning the detector angularly around the sample, has been progressively overtaken by more complex ones.

The single point-detector has progressively been substituted with several parallel ones, improving manifold the acquisition strategy.

Acquisition time

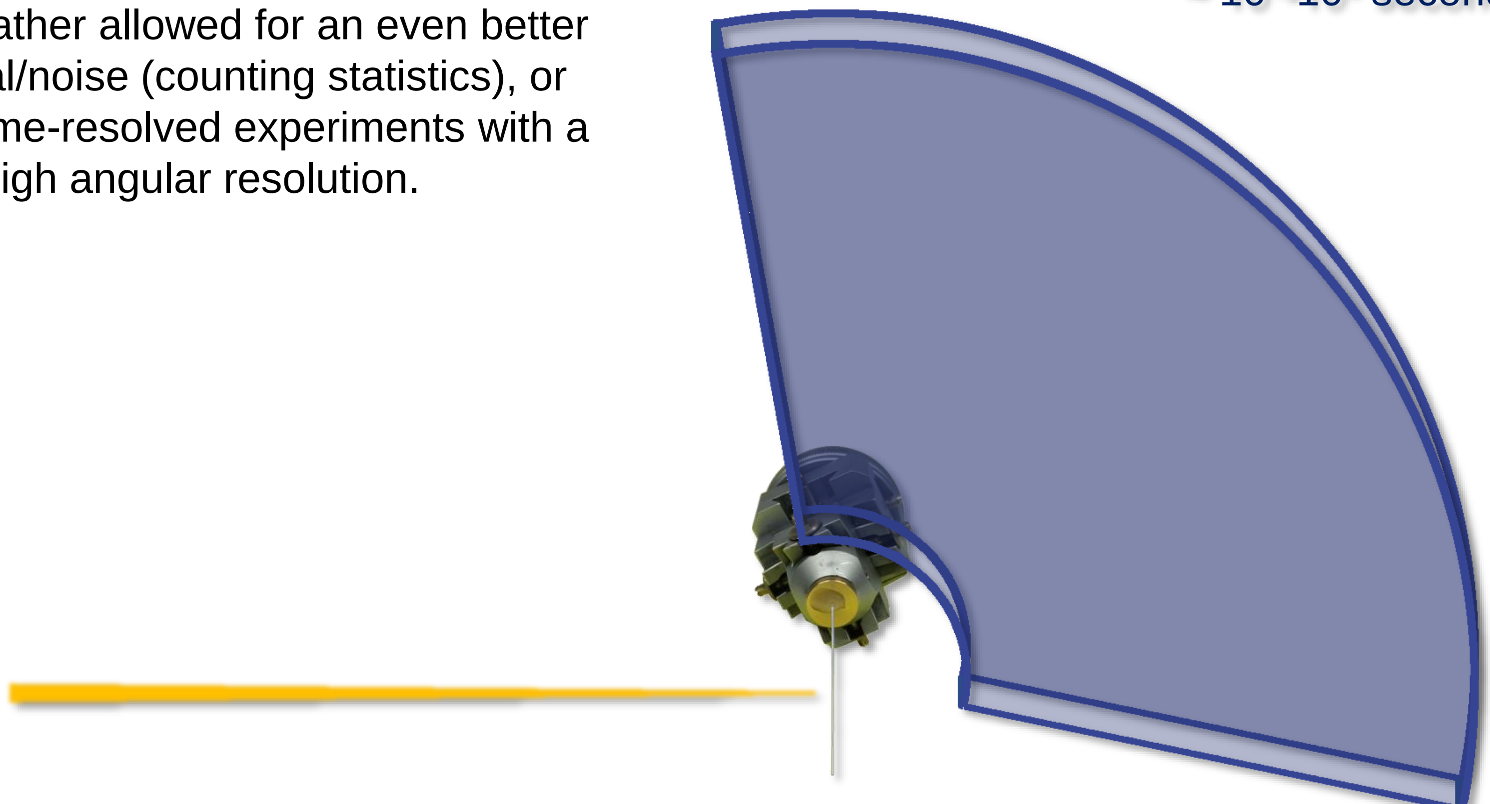
~ 10^3 seconds



Parallel data acquisition (1D)

Transmission (Debye-Scherrer)

Modern ‘stripe’ detectors, covering with 10^4 single counters a large angular range, have not improved the acquisition time correspondingly, but rather allowed for an even better signal/noise (counting statistics), or for time-resolved experiments with a still high angular resolution.



Parallel data acquisition (2D)

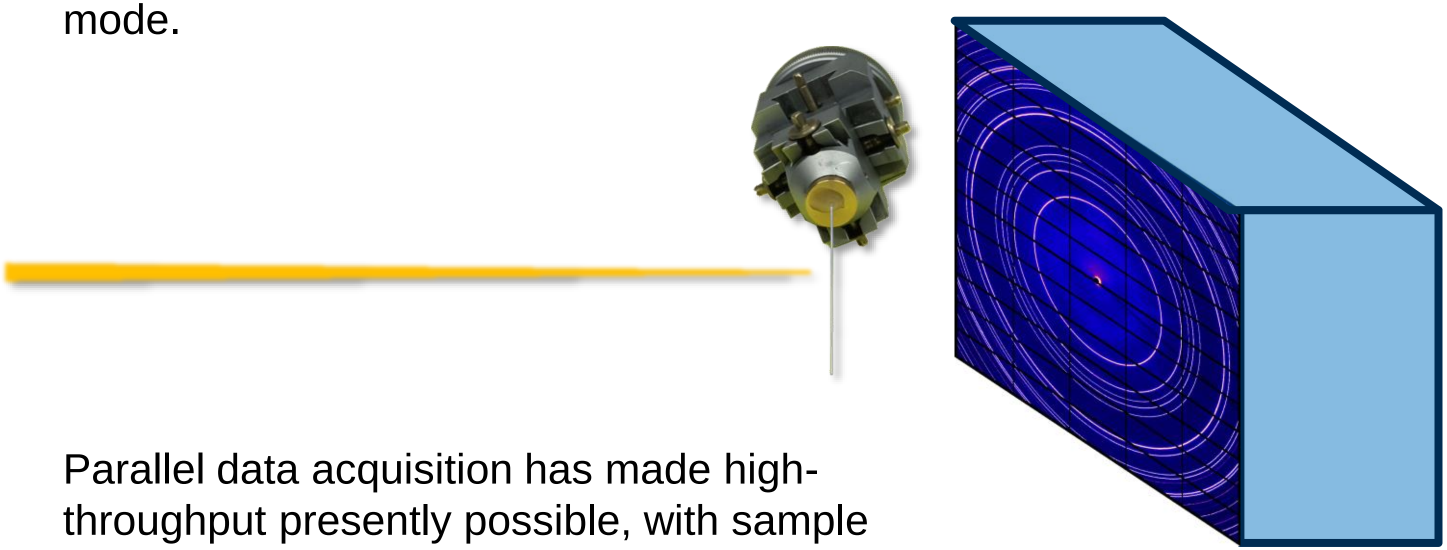
Transmission (Debye-Scherrer)

Area detectors offer a further advantage as they allow for integration of the full cone of diffraction, further increasing the signal/noise and/or decreasing the acquisition time possible.

These detectors are now capable of acquisition times of several 10s of kHz, running in continuous or pulsed mode.

Acquisition time

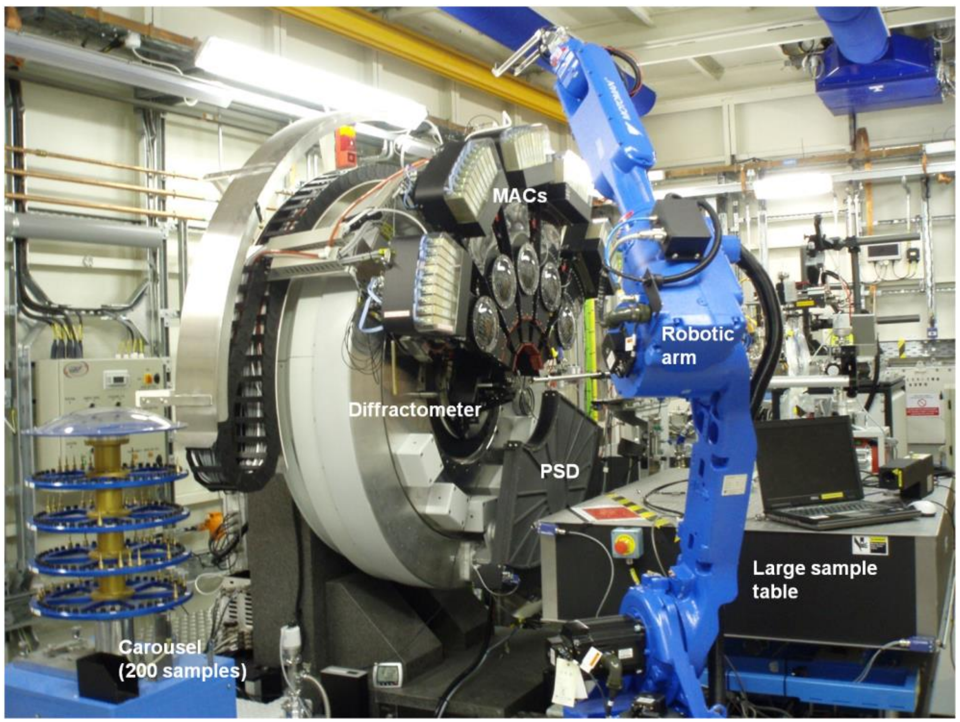
~ 10^{1}-10^{-4} seconds



Parallel data acquisition has made high-throughput presently possible, with sample delivery being presently the bottleneck

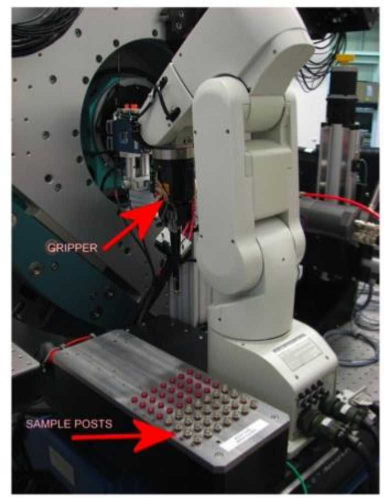
Automation

A robotic arm to automatically change samples is present in several beamlines around the word, equipped initially with multi crystal analyzers (MACs in the picture below) and with 1D 'stripe' detectors (PSD below).



https://www.diamond.ac.uk/Instruments/Crystallography/I11.html

Sample changing robot:



Capacity: 152 samples (56 individual and 96 in magazines)

Small footprint allowing easy access to sample area

Integrated with Cryostream 700+ for combined use of robotic operation with temperature control

Proven reliability of industrial Mitsubishi robot

Locally designed Robot-Human Safety System (RHSS) to ensure safe operation

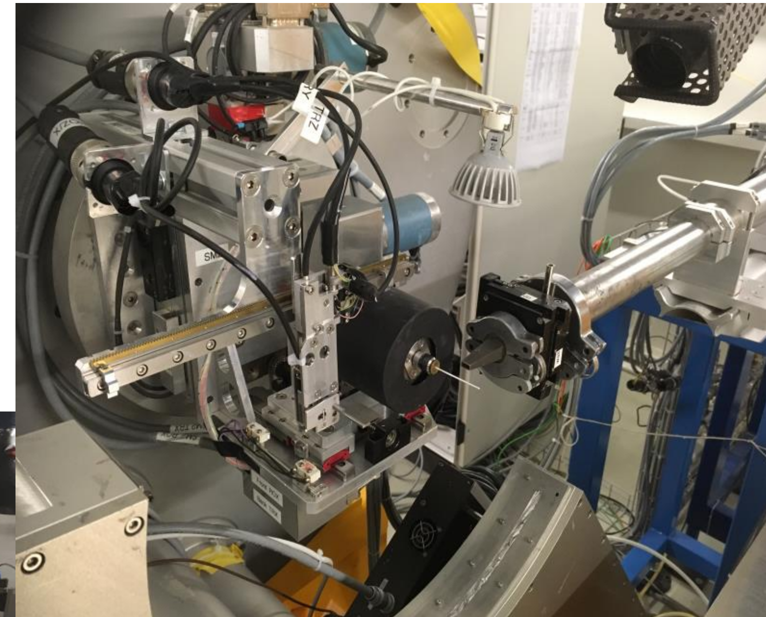
https://11bm.xray.aps.anl.gov/images/RobotDetail_large.jpg

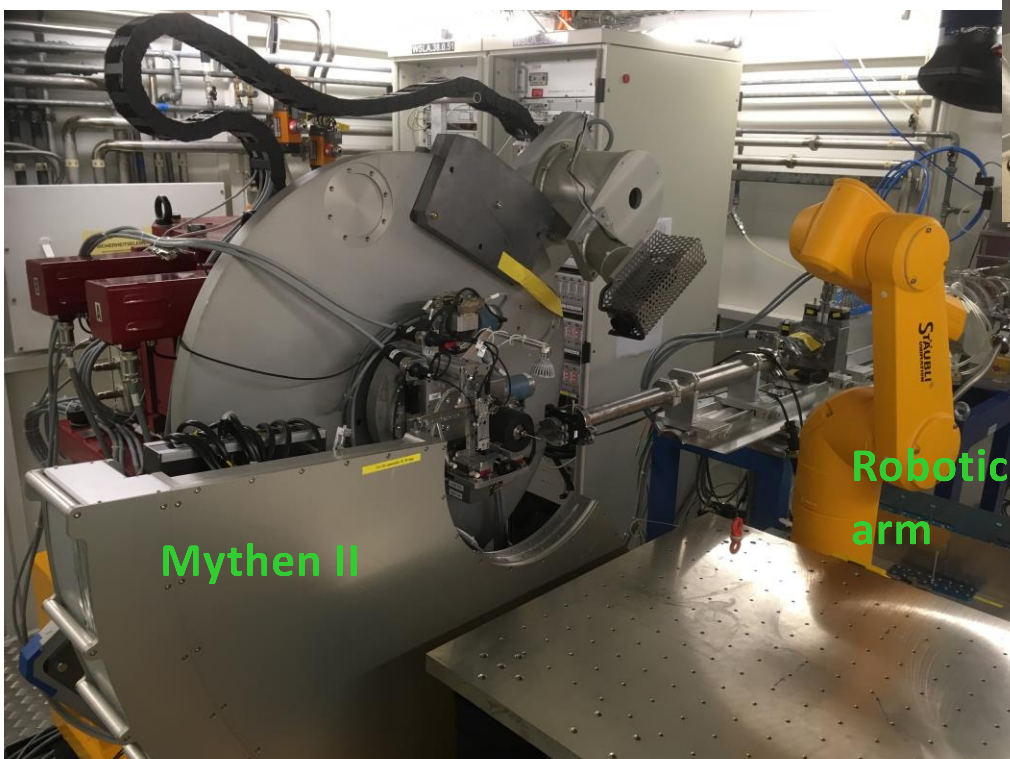
Typically hundreds of samples can be loaded in a dedicated holder.

Acquisition times can be as low as 100 s

Automation with 1D detectors

The challenge given by capillary samples for 1D detector is that a small offset of the capillary axis with respect to the rotation axis (spinning is necessary for particle statistics) leads to an apparent peak broadening.





For this reason, at the Swiss Light Source, where stripe detectors were pioneered, an automatic sample alignment is present.

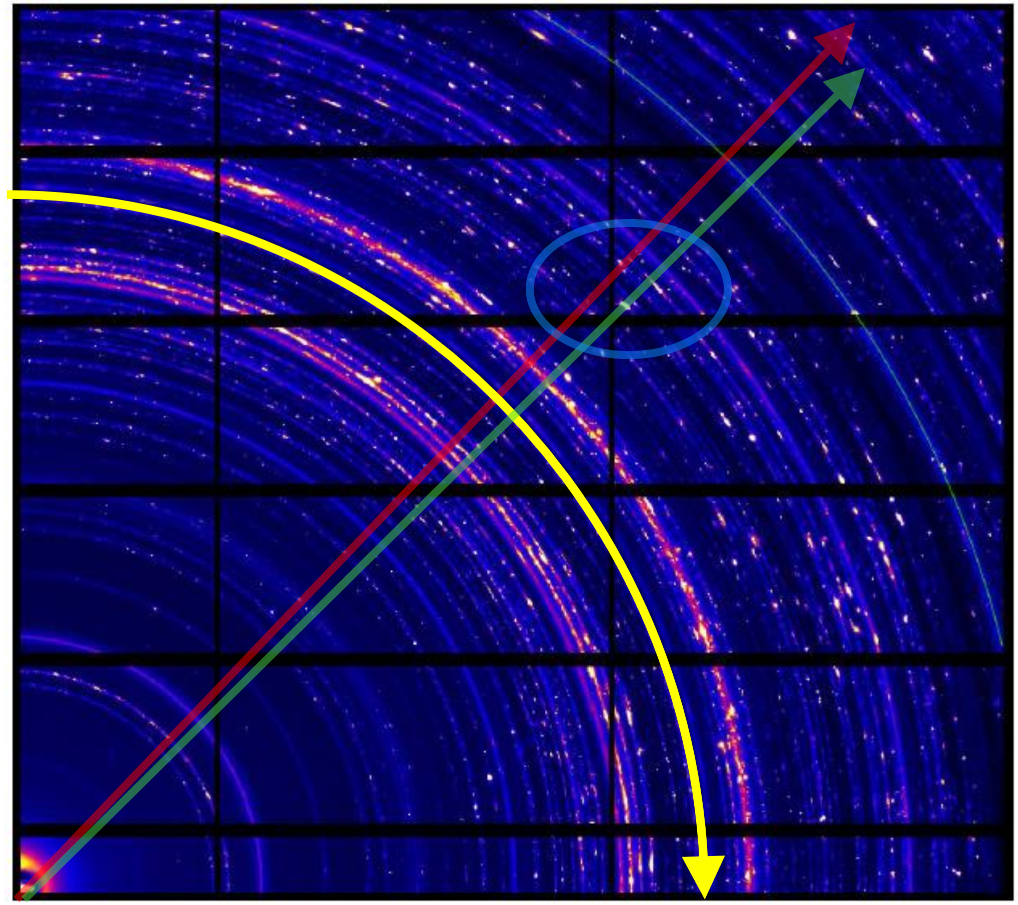
This operates a 4 degrees of freedom motorized head coordinated by a camera observing the sample while spinning.

Automation with 2D detectors

Spinning is necessary especially with 1D detectors, as particle statistics may dominate counting statistics.

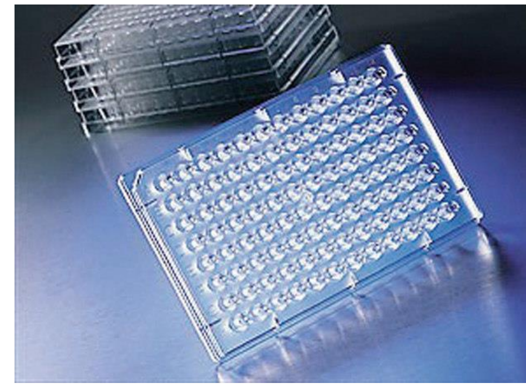
In this section of a 2D image it is clear that positioning a 1D detector along the red or green arrows would not produce the same intensities.

Better result than a simple radial integration are obtained with an azimuthal one, here following the yellow line. This approach is better but not satisfactory, still.

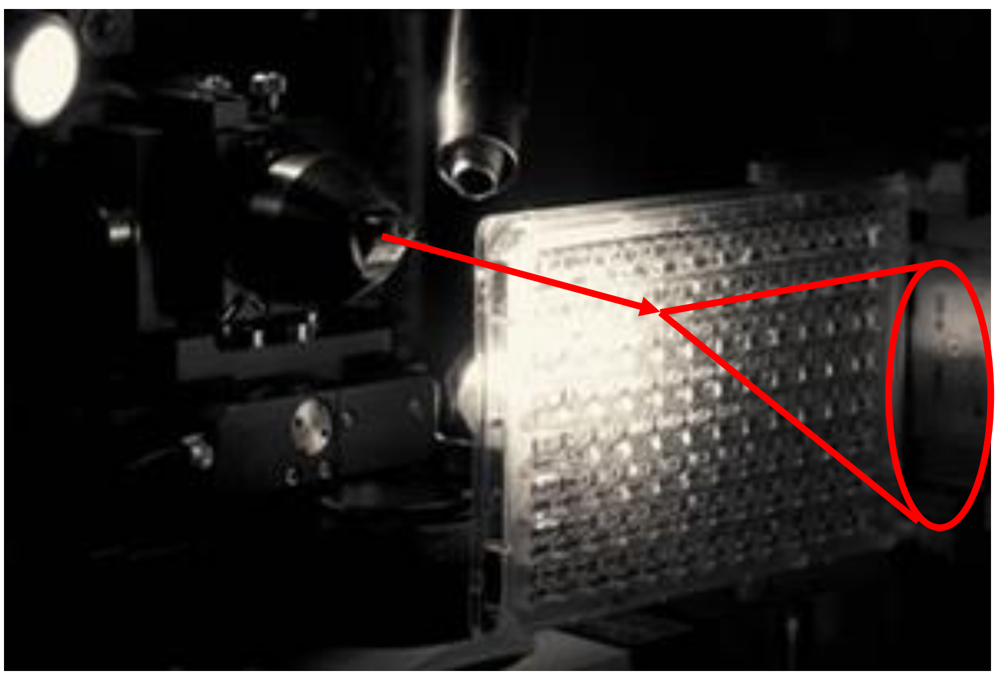


Sample delivery: plates

Static samples are easy to deliver to an area detector, For example in the form of a plate with several holes and X-ray transparent windows. This is the case for example of commercially available solutions for monitoring protein crystallization, adapted today to the general chemical environment.



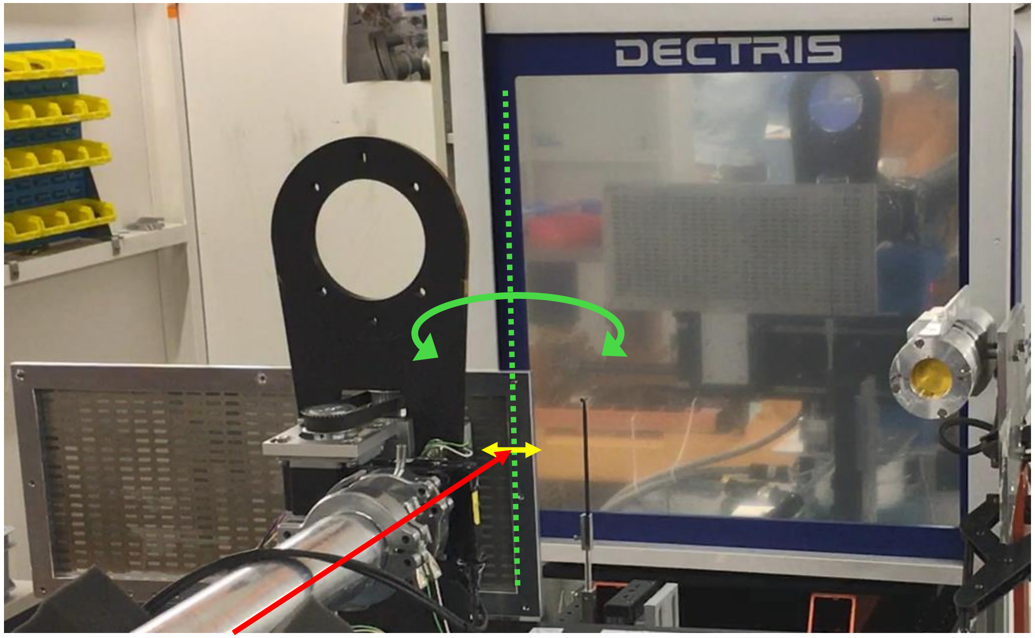
From Sigma-Aldrich



X-rays can penetrate through them, interact with the sample and be observed in transmission by a 2D detector positioned on the other side of the plate. Including sample change ~10 seconds per sample are possible in this way.

Plates + rotation + translation

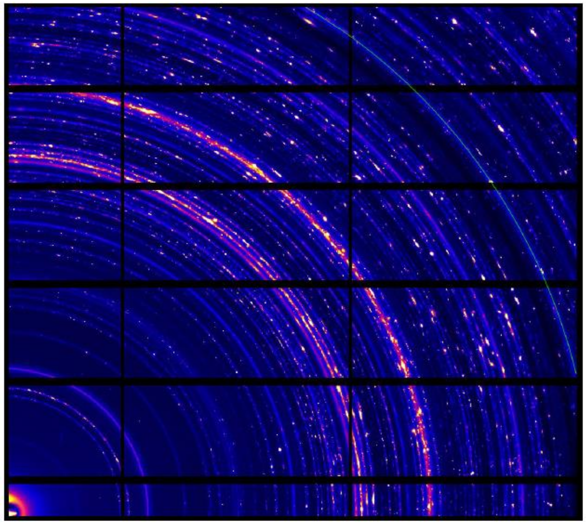
Moving the sample, anyway, is mandatory for high-quality results. A more limited movement applicable to a full plate is translation, a further one being rotation at the sample position. Such an approach does not produce the best quality but a significant and simple improvement, perfectly acceptable in many cases.



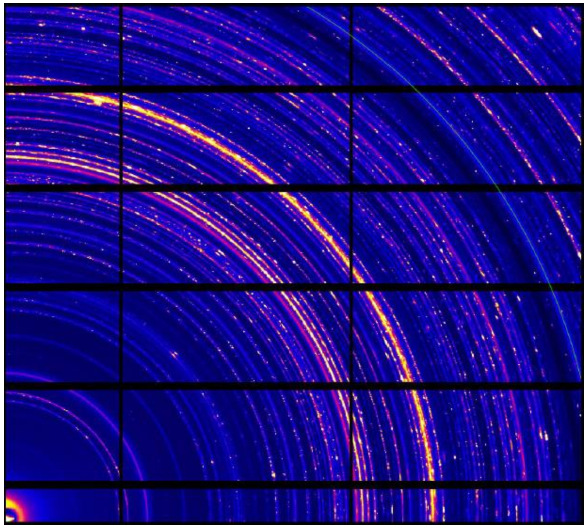
In our case a small ± 3° rotation on the sample (green) axis was coupled with a ± 8 mm horizontal translation (yellow). Each plate contained 500 samples, time per sample is below 13 seconds including plate changing.

Plates + rotation + translation

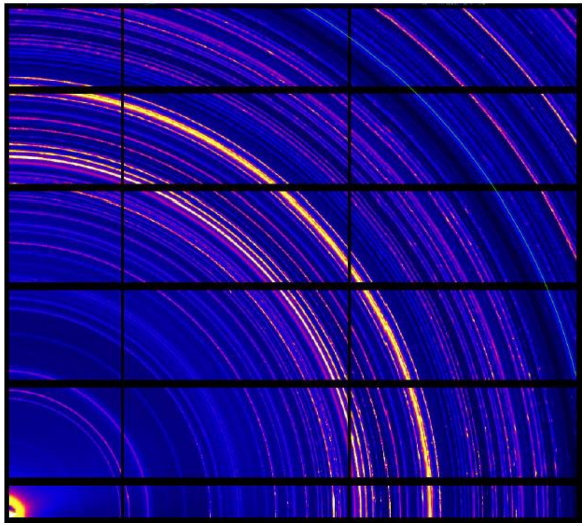
While motors can be accelerated it is clear such an approach is a compromise between simplicity, quality and time constraints. On the other hand results are meaningful even in the case of a non-ground sample.



Static sample



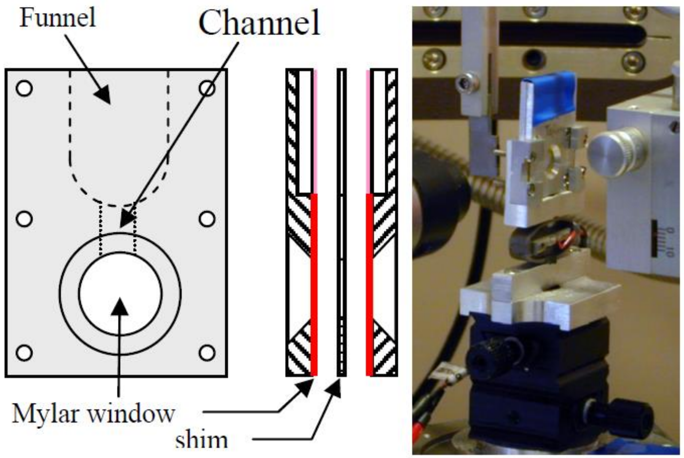
Rotation + Translation



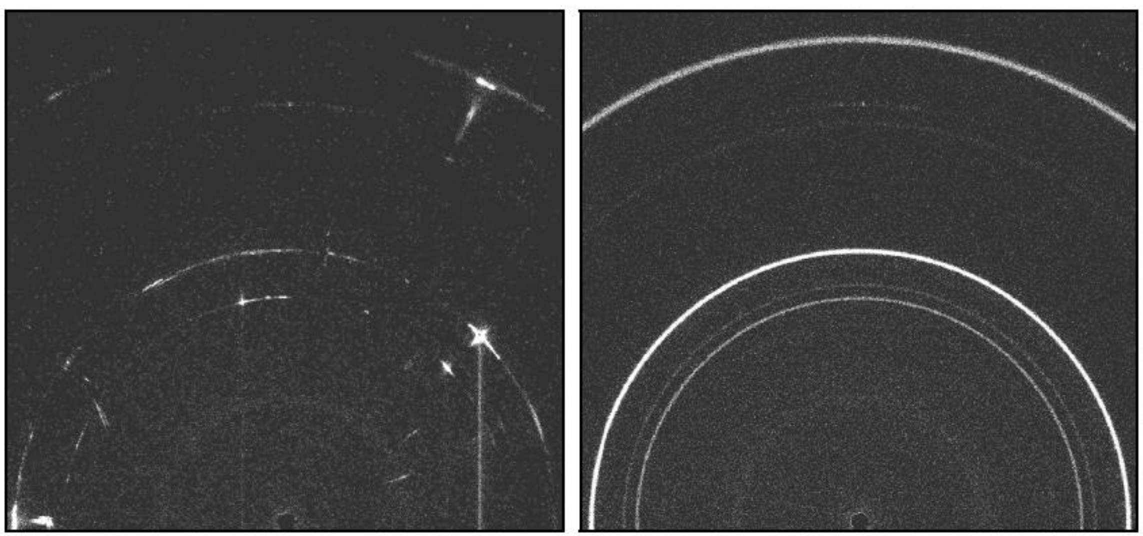
Ideal

Different ways of moving samples are a bit more complex, but not impossible.

Vibrating/shaking samples



Images from P.C. Sarrazin et al., Vibrating sample holder for XRD analysis with minimal sample preparation, International Centre of Diffration Data 2005, 48, 156-164



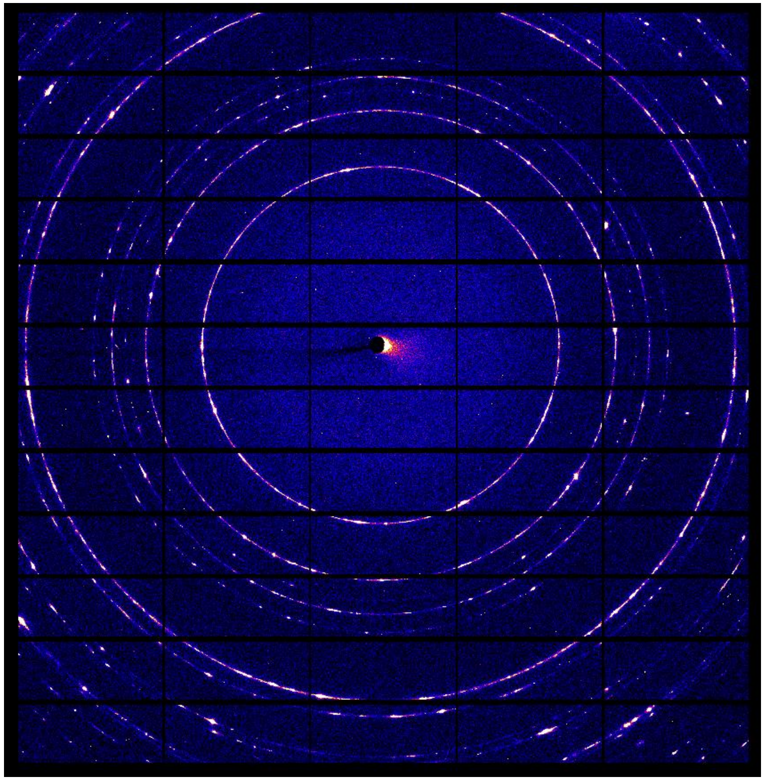
High frequencies induce a fluxional motion in the samples, which reorient particles in all possible ways. This approach was successfully pioneered in the CheMin instrument of the Mars Curiosity Rover.

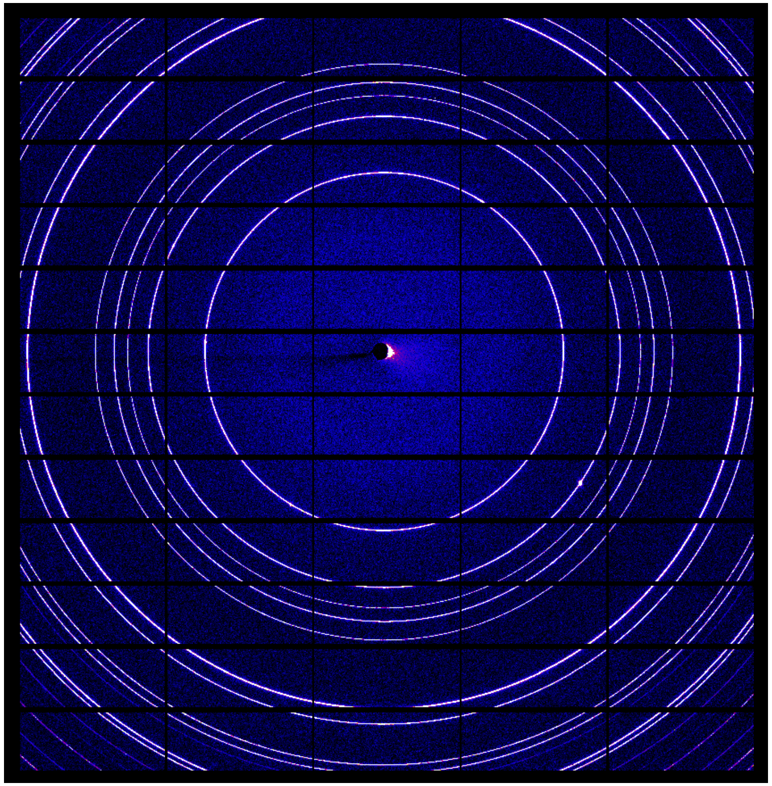
It is important to note that the sample does not require any preparation, i.e. unground powders can be used.

However, vibrating large plates is not an option, given the high energy that would be required. Single samples have to be quickly exchanged.

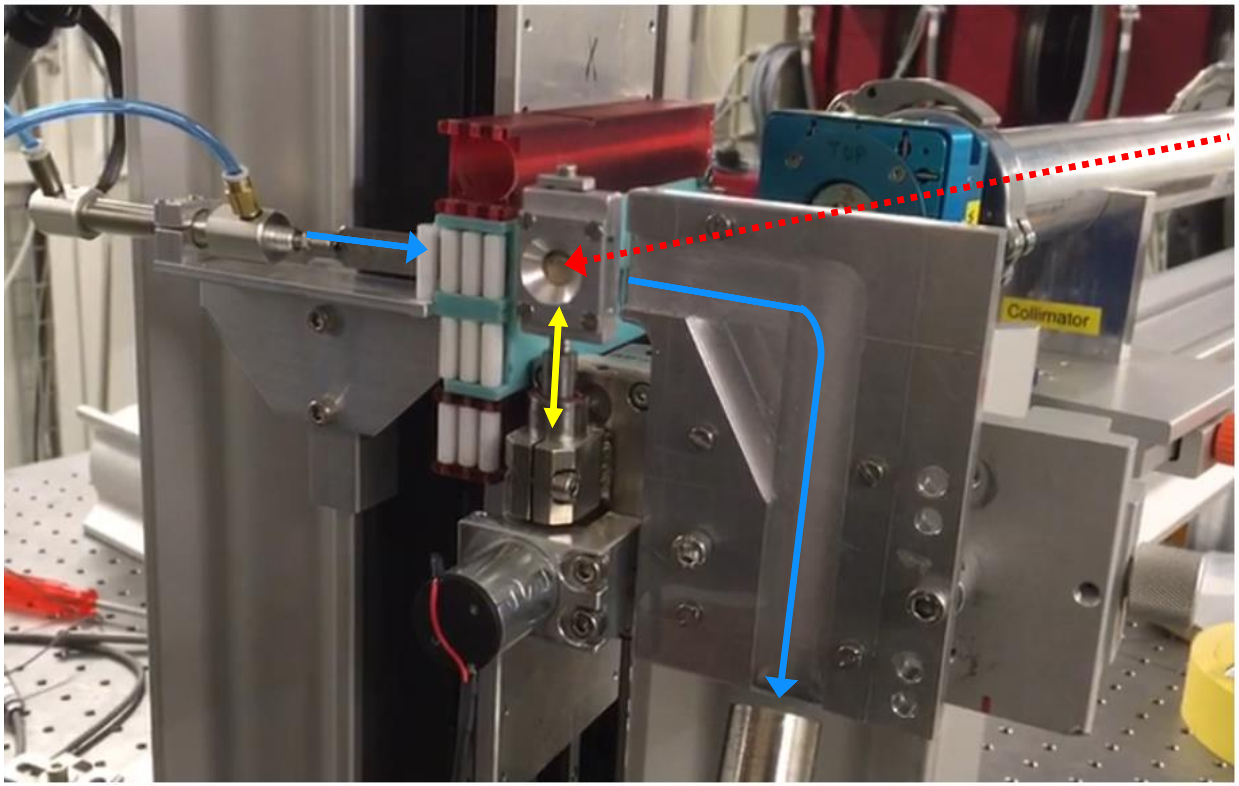
Vibrating/shaking samples

A similar approach was recently developed within our laboratory, specifically devoted to high-throughput. As piezo elements tend to be more fragile a different lower-frequency shaker was employed, allowing for more robust operations including a fast sample exchange.





Sample changing



Few s acquisitons

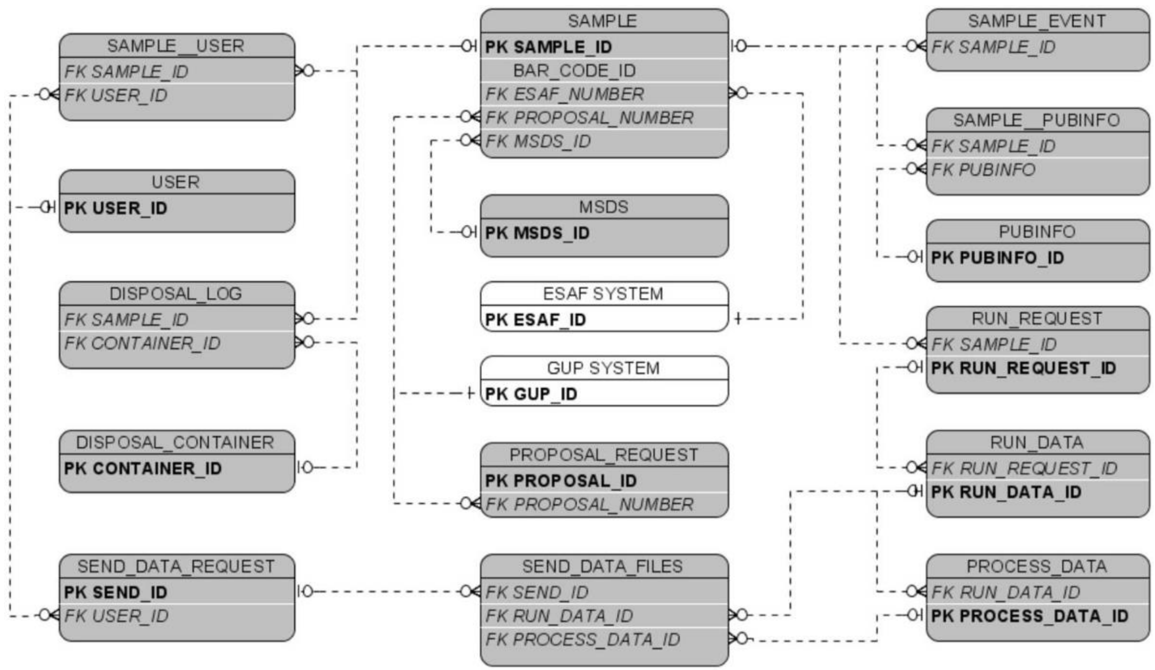
High quality

Automatic operation

Several washer-shaped sample holders are contained in long cartridges. Each holder can be quickly exchanged by a pneumatic drive into a vibrating seat. The sample is then vibrated and then expelled again by the arrival of a new one.

Full operation management

When operations are so large clearly a full organization is needed. This was very well pointed out in Toby, B. H., *et al.* (2009). J. Appl. Cryst. 42, 990-993, which were anyway dealing with hundreds of samples per day



PK = primary key FK = foreign key ≯O = one-to-many relationship possible between entries

At 5-10 seconds per sample operations exceeding 10.000 samples per day can be accomplished, making data management even more valuable.

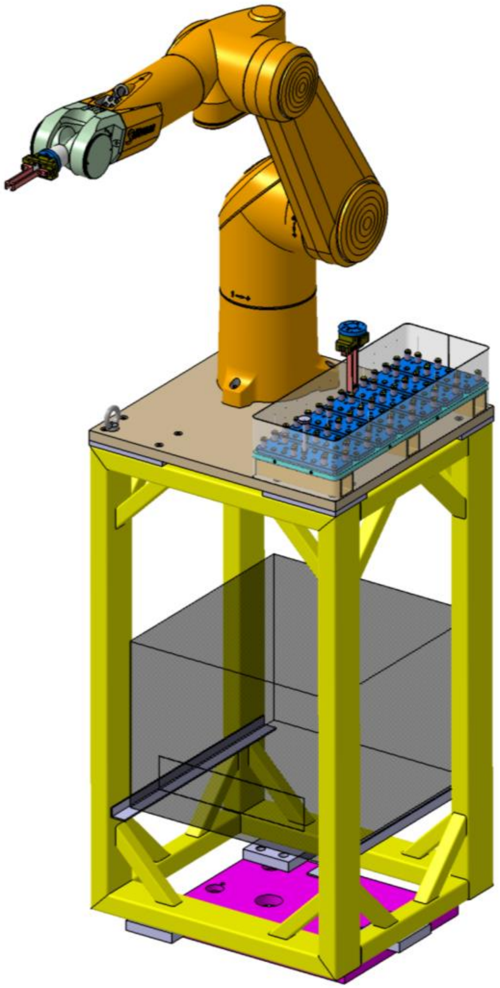
Is it worth it?

Combinatorial approaches are growing, with the availability of more robotic ways of performing synthesis, sampling and every other aspect of the full scientific chain, including data analysis and interpretation.

It is worth noting that the problem was raised for us by a company commissioning the measurement of more than 50.000 samples, showing that the interest is not an academic oddity or a showcase of capability, but rather a need already present in our society.

While this remains a ‘brute force’ approach, it couples well with the trend to employ ‘big data’ and the ability to process them in novel ways.

It is also worth noting that at the number of samples that can be measured presently a synchrotron is already cheaper, per sample, than a tube-based diffractometer.



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Conclusions

- Synchrotron high photon flux can be exploited for high throughput powder diffraction, on top of the more in depth studies
- Several detector geometries/quantities are available, ranging from hundreds to tens of thousands samples per day
- Fast sample delivery is possible coupled with enough movement to ensure good homogeneity even for unground samples