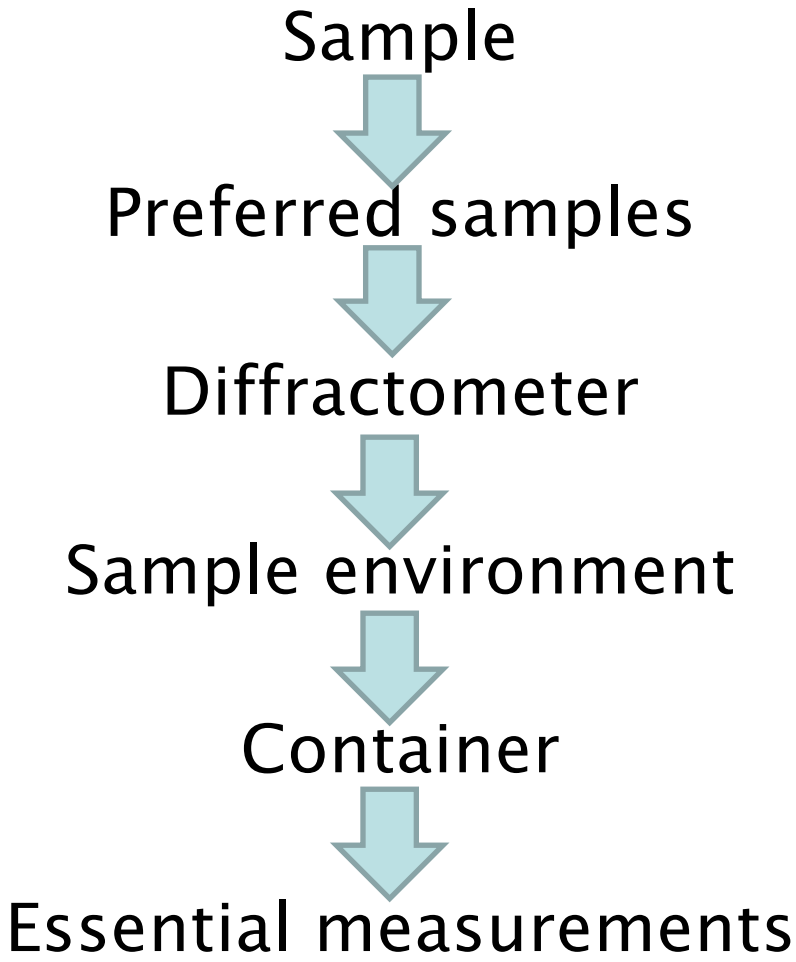
Experiment Design and Maximising Data Value

Sam Callear

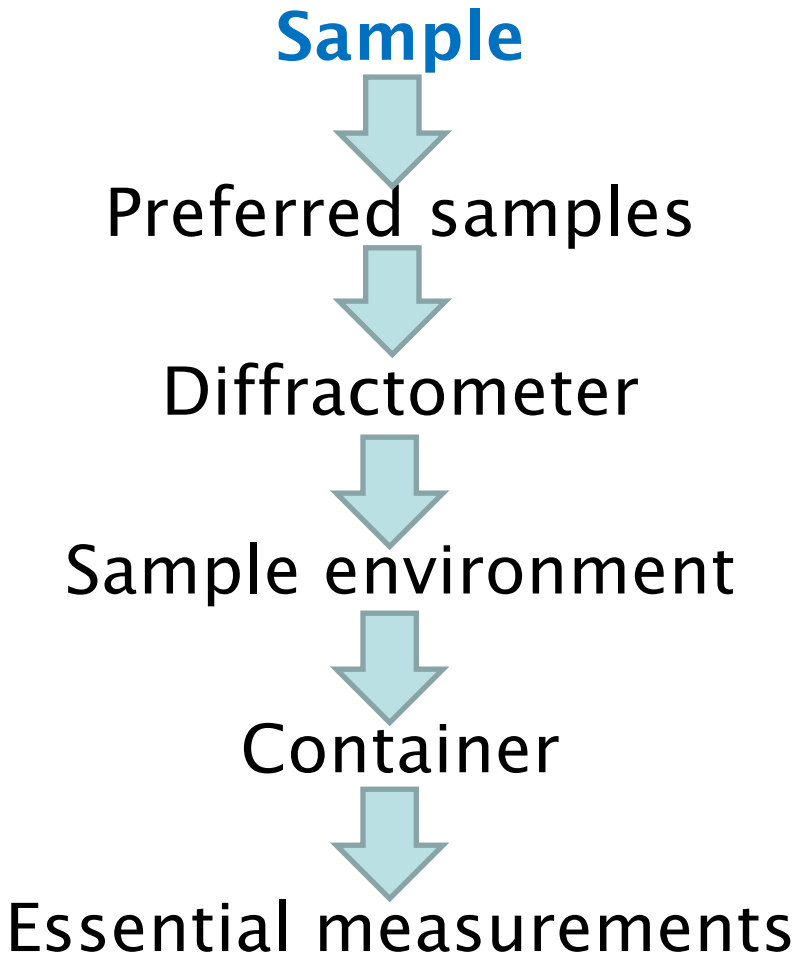
ISIS Facility, RAL

Experiment Design



Science & Technology Facilities Council
ISIS

Experiment Design



Science & Technology Facilities Council
ISIS

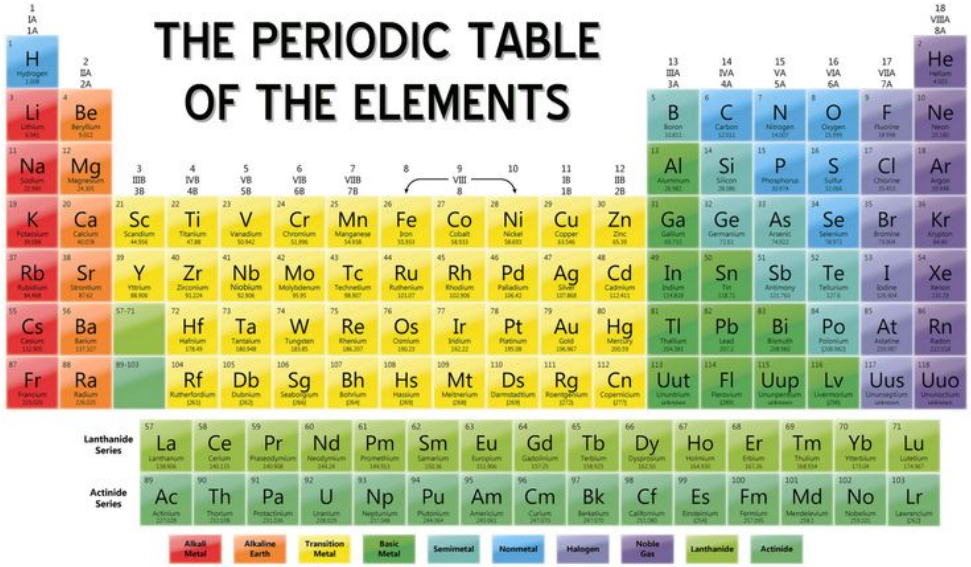
Sample

- Quantity
  - Enough to provide a measurable signal.
  - Affects choice of container, beam size and collection time.

- Composition
  - A precise elemental composition is required for data correction (the density of the sample is also required for data correction).
  - The quantity of the important molecule/atom in the sample needs to be large enough (in atom%) to give a measurable signal. The limit at which this occurs depends upon the sensitivity of the instrument which is affected by the instrument design, source stability, moderator stability, detector stability and statistical error.

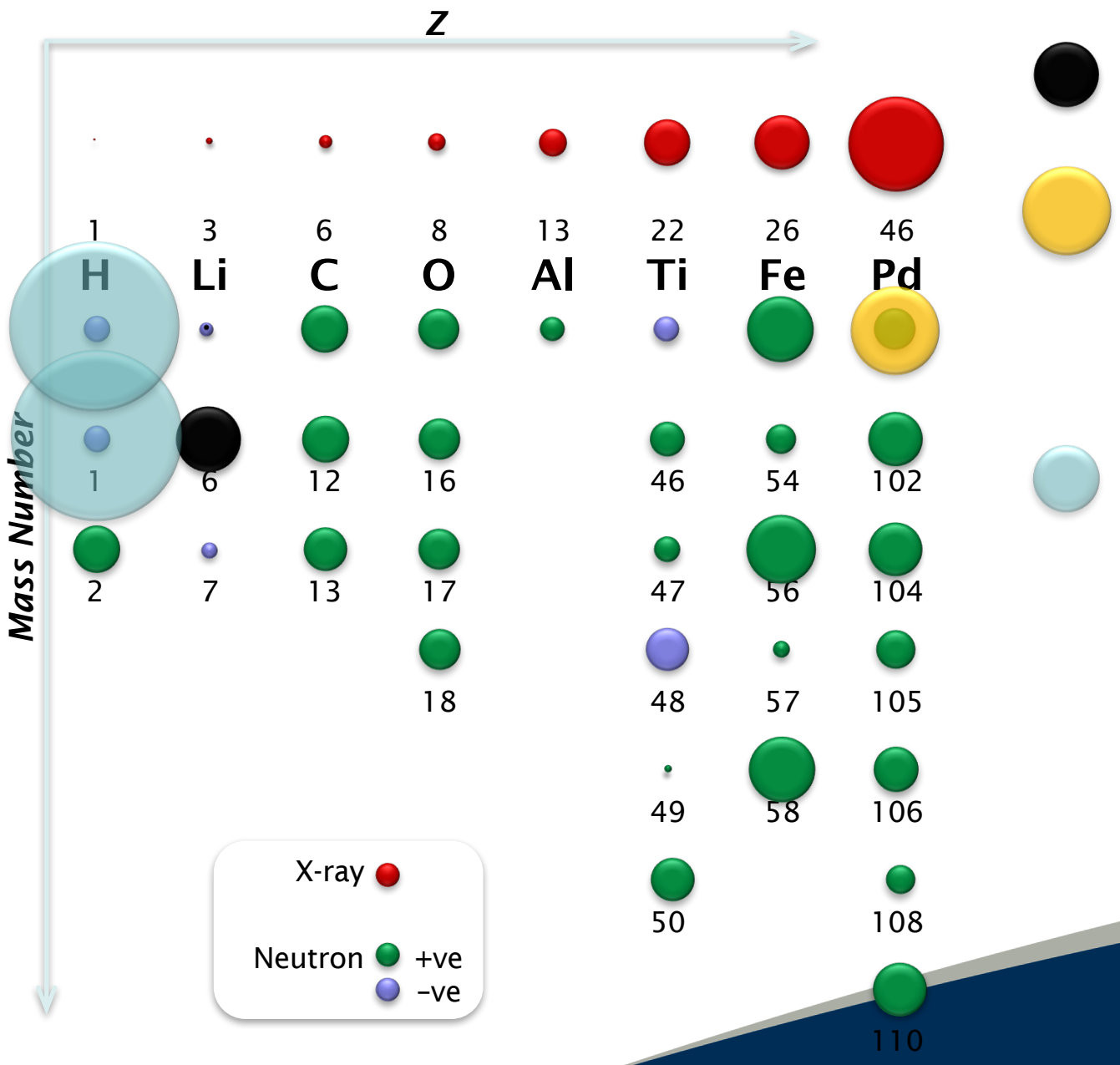
Sample

- Composition
  - Strongly absorbing elements?
  - Low coherent scattering cross-section/ high incoherent scattering cross-section?
  - Resonances (within the incident neutron energy range)?
  - Contains hydrogen (natural).



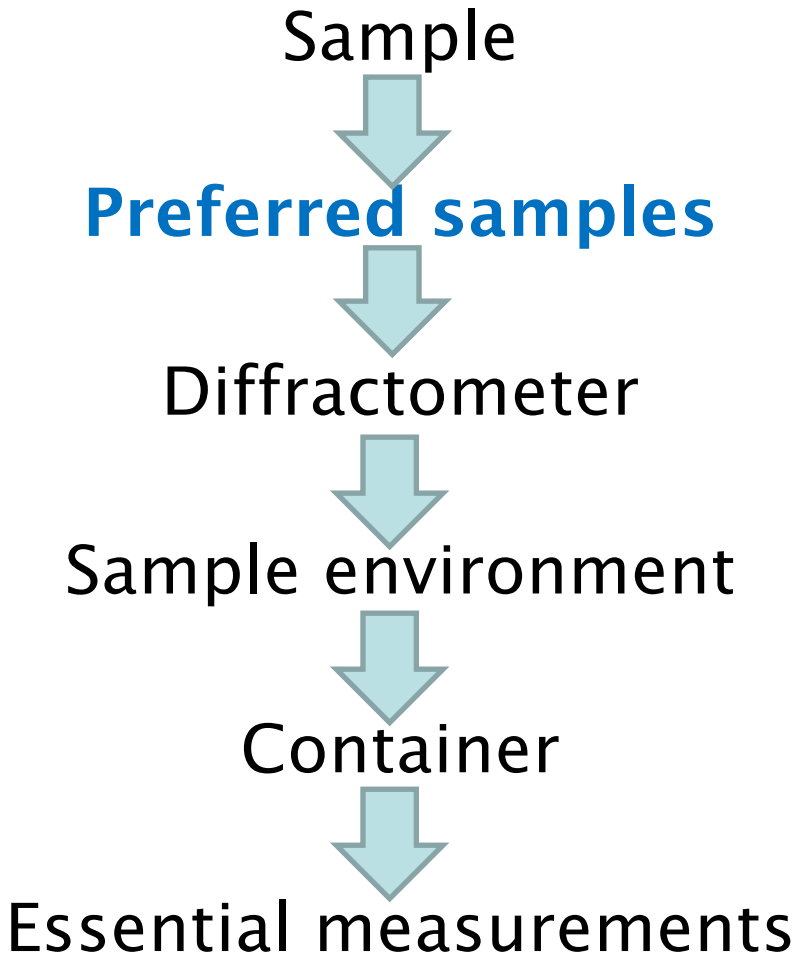
Science & Technology Facilities Council
ISIS

Isotopes



Science & Technology Facilities Council
ISIS

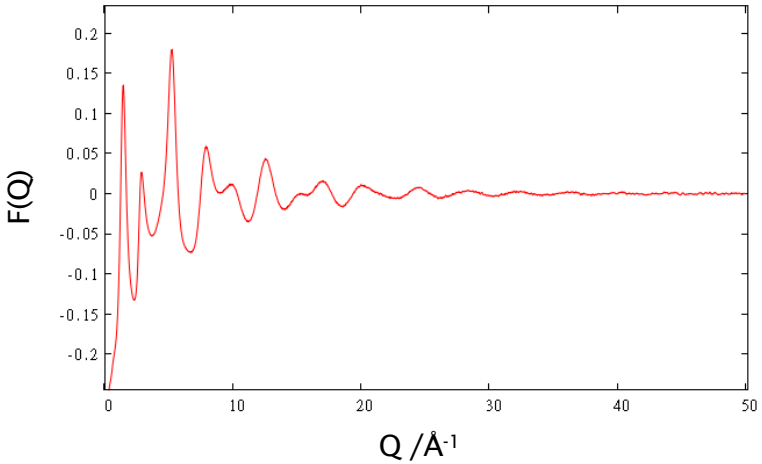
Experiment Design

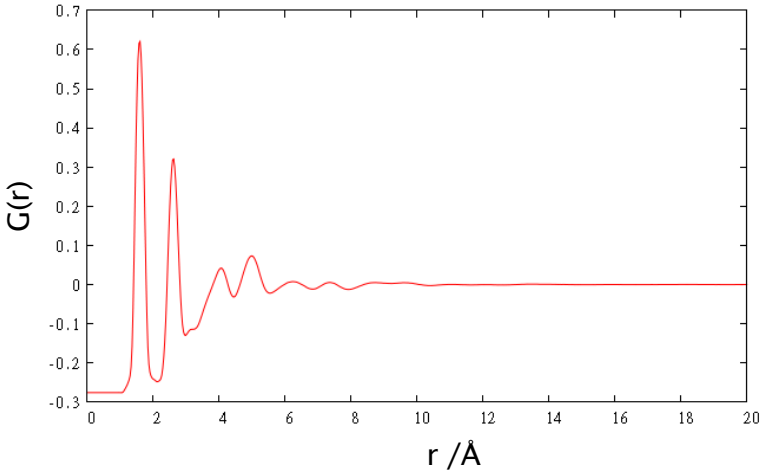


Science & Technology Facilities Council
ISIS

Maximising Data Value

- A single dataset contains information from the correlations between every pair of atoms present in the sample.
- For some simple samples, the peaks in the radial distribution function at low r do not overlap:





- But for more complex samples, the partial correlations overlap with other partial correlations, creating problems for analysing the data by inspection or through modelling.

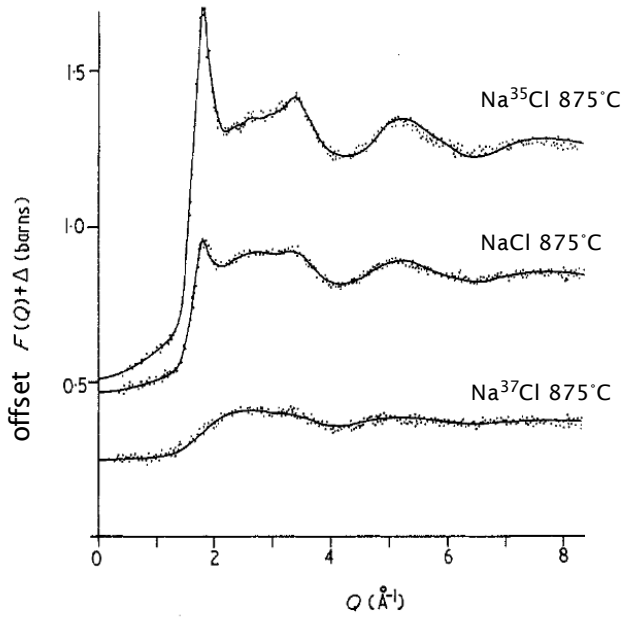
Isotopic Substitution

- First used by Enderby, North and Egelstaff to assess the partial structure factors of liquid Cu-Sn (*Phil. Mag.* **14** (1966) 961)

The structure of molten sodium chloride

F G Edwards†, J E Enderby†, R A Howe† and D I Page‡

Isotope	Enrichment	Coherent scattering length ($\times 10^{-12}$ cm)
^{35}Cl	99·3 %	1·18
^{37}Cl	90·4 %	0·349
Cl (mixture)	(37) 41 %–(35) 59 %	0·799
Na	(natural)	0·351



$$F(Q) = c_a^2 f_a^2 (S_{aa} - 1) + c_b^2 f_b^2 (S_{bb} - 1) + 2c_a c_b f_a f_b (S_{ab} - 1),$$

$$S_{\alpha\beta} = 1 + \frac{4\pi N}{VQ} \int (g_{\alpha\beta} - 1) r \sin Qr \, dr$$

J. Phys. C: Solid State Phys., Vol. 8, 1975.

Science & Technology Facilities Council
ISIS

Isotopic Substitution

The equations to be solved may be written in the matrix form:

$$[A].[X(Q)] = [F(Q)]$$

where

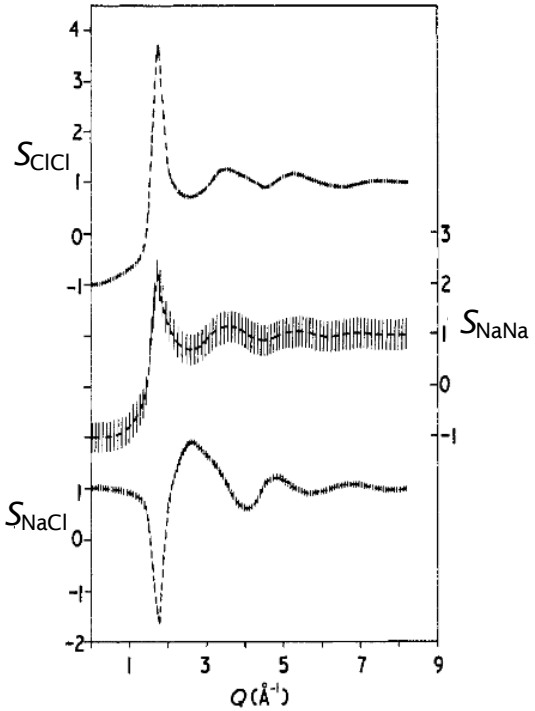
$$[A] = \begin{bmatrix} c_a^2 f_a^2 & c_b^2 f_b^2 & 2c_a c_b f_a f_b \\ c_a^2 (f'_a)^2 & c_b^2 f_b^2 & 2c_a c_b (f'_a) f_b \\ c_a^2 (f''_a)^2 & c_b^2 f_b^2 & 2c_a c_b (f''_a) f_b \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

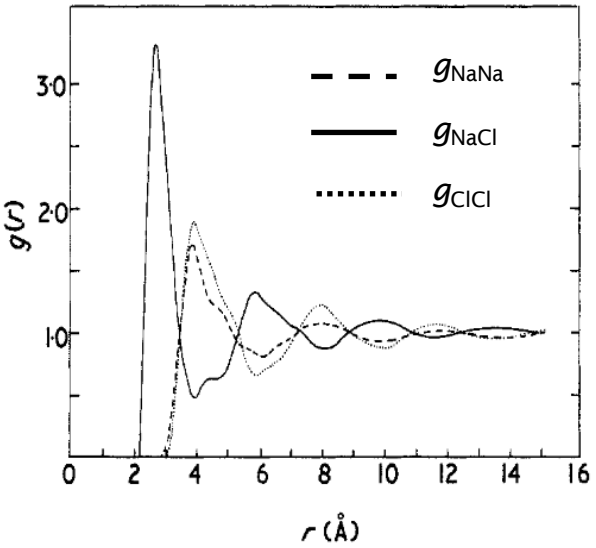
$$[X] = \begin{bmatrix} (S_{aa} - 1) \\ (S_{bb} - 1) \\ (S_{ab} - 1) \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix}$$

and

$$[F] = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}.$$

Indirect solution from $[X] = [A]^{-1}[F]$



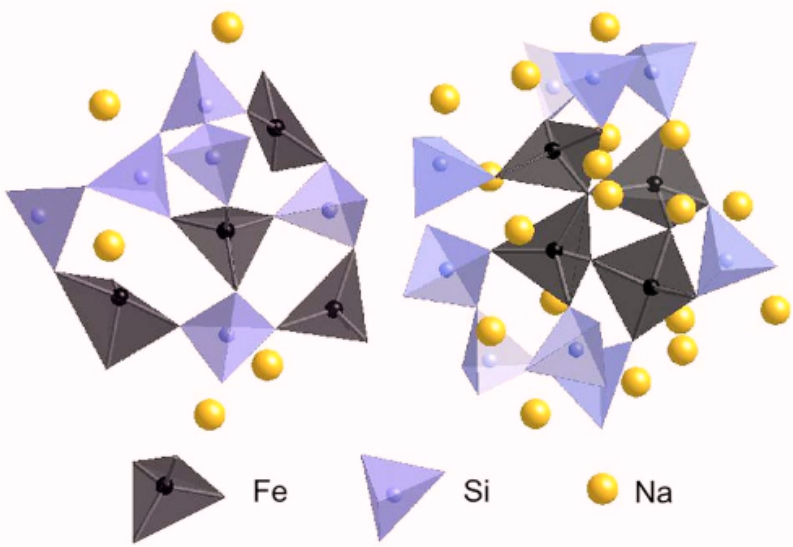


- Assumes the samples are isomorphic.
- Requires a significant scattering length difference between the isotopes (~1fm) and the isotopes to be stable.

Science & Technology Facilities Council
ISIS

J. Phys. C: Solid State Phys., Vol. 8, 1975.

Isotopic substitution – glasses

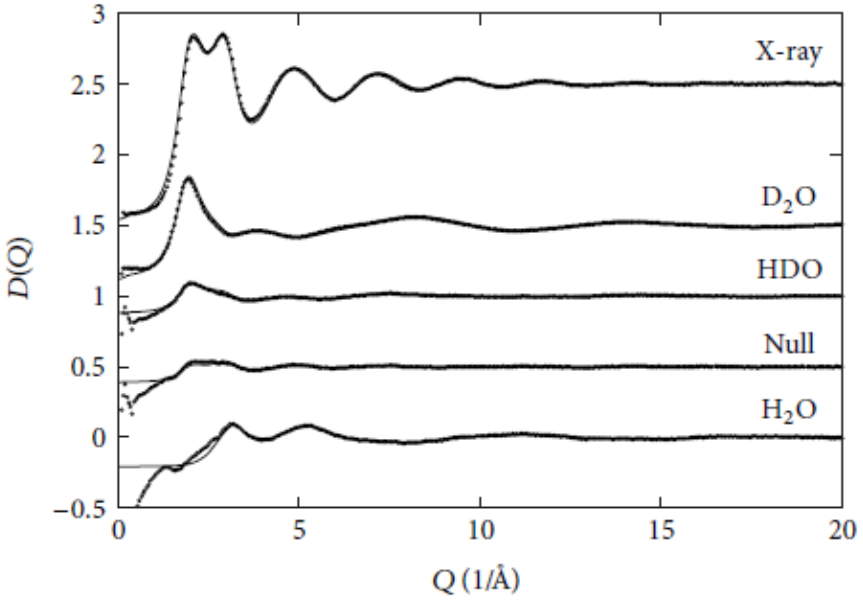


- Often contain overlapping partial correlations, particularly metallic glasses.
- Non-molecular glasses have no specified bonding patterns that can be used to constrain a model.
- Heavy atom isotopes can be prohibitively expensive.
- For elements with negative and positive scattering isotopes, the 'null scattering' method can be used where appropriate quantities of the negative and positive scattering isotopes are used so as the overall scattering from the particular element = 0.
- Ideally collect data from a sample containing the natural abundance of isotopes, an enriched isotope and where possible a null mixture.

Cormier et al. Appl. Phys. Lett. 89 (2006) 141911
DT Bowron, Procedia Materials Science, 7 (2014) 38-52

Isotopic substitution – molecular liquids

- Use of isotopic substitution with application to water containing solutions first noted by Enderby and Neilson in 'Water A comprehensive Treatise' in 1979 (ed Franks, Volume 6, p 1, Plenum Press, New York).
- Used extensively in the study of water using D_2O, H_2O, 50:50 HDO and 'null' 36:64 HDO isotopic mixtures.
- A very powerful technique owing to the large difference in scattering lengths between the isotopes and the large number of hydrogen atoms in organic liquids.
- Beware of hydroxyl and amine hydrogen atoms as these can exchange in solution therefore if a solution of D_2O and CH_3OH is prepared, the solution will actually contain HDO and $CH_3OH_{0.5}D_{0.5}$.
- For studies of a solute in a solvent, the technique was developed to show the solvent-solute correlations (2nd order difference).



$$F(Q) = c_X^2 b_X^2 [S_{XX}(Q) - 1] + 2c_X c_H b_X b_H [S_{XH}(Q) - 1] + c_H^2 b_H^2 [S_{HH}(Q) - 1]$$

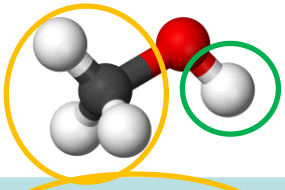
J. L. Finney, A. K. Soper, Chem. Soc. Rev., 1994, (1),1-10.

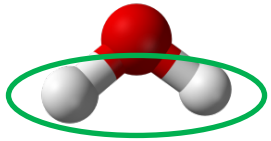
A.K. Soper, ISRN Physical Chemistry, 2013, 279463

D. T. Bowron, J. L. Finney, and A. K. Soper, *J. Phys. Chem. B* 1998, *102*, 3551-3563.

Isotopic substitution – molecular liquids

- For concentrated solutions where:
  - The number of non-exchangeable hydrogen atoms in the solute is more than ~10% of the total number of atoms in the system.





	Solute (non-exchangeable hydrogens)	Solvent (and solute exchangeable hydrogens)	
Solvent-solvent (1st order difference)	D	D	1
	D	HD	2
	D	H	3
	D	D	
Solute-solute (1st order difference)	HD	D	4
	H	D	5
	D	D	
Solute-solvent (2nd order difference)	HD	HD	6
	H	H	7

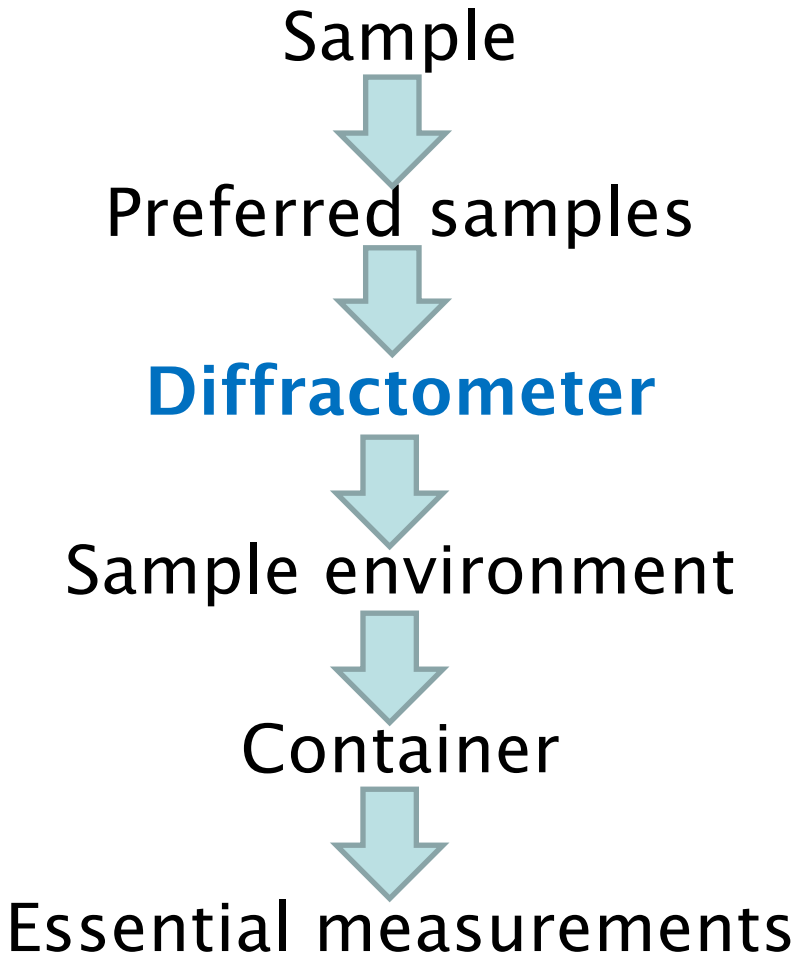
- For 3 component systems:
  - Maximise the amount of D in the sample.
  - Choose the combinations that give information about the important functional groups relevant to the experiment aim.

Isotopic substitution – molecular liquids

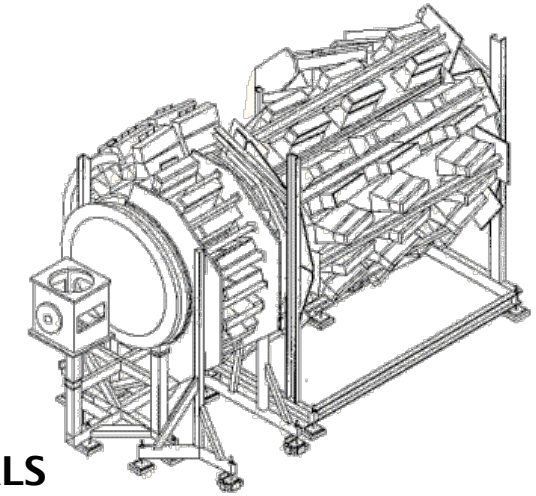
- For weak solutions where:
  - The concentration of the solute is 1-2 atom%
  - Or, the number of non-exchangeable hydrogens on the solute that can be deuterated is <10% of the total number of atoms in the system.

	Solute (non-exchangeable hydrogens)	Solvent (and solute exchangeable hydrogens)
Solvent-solvent (1st order difference)	H	D
	H	HD
	H	H

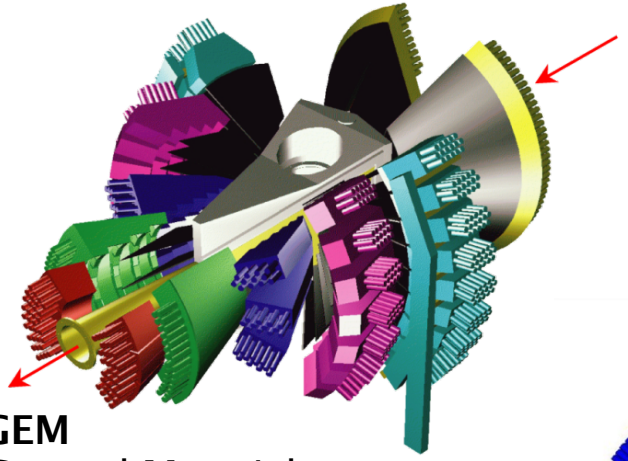
Experiment Design



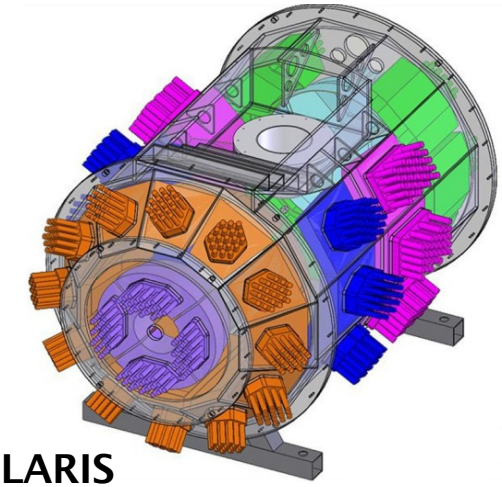
ISIS Diffractometers



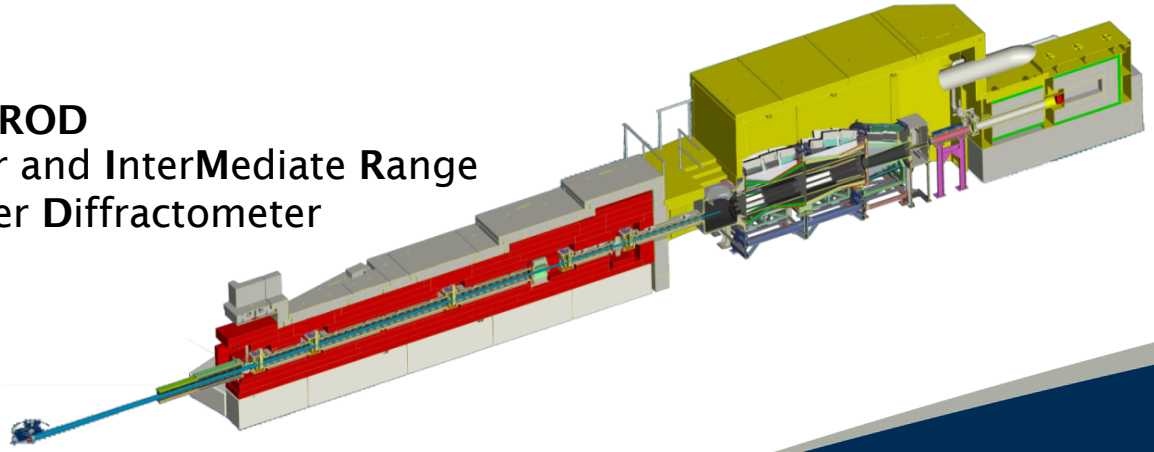
SANDALS
Small **A**ngle **N**eutron **D**iffractometer
for **A**morphous and **L**iquid **S**amples



GEM
General **M**aterials
Diffractometer



POLARIS
Medium resolution
powder diffractometer

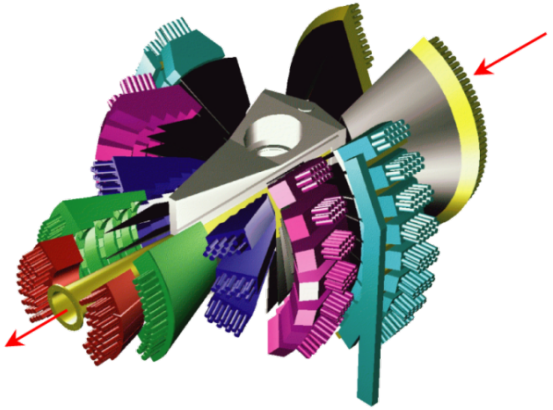


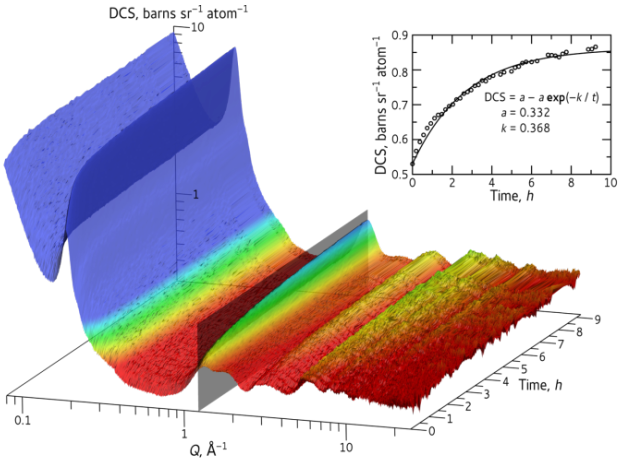
NIMROD
Near and **I**nter**M**ediate **R**ange
Order **D**iffractometer

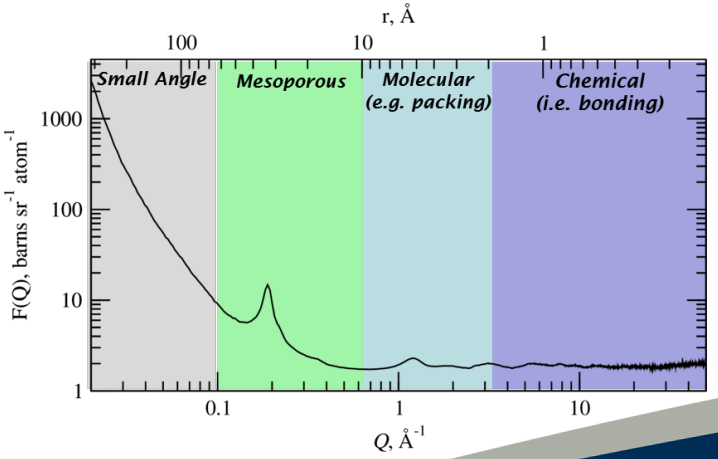
Science & Technology Facilities Council
ISIS

Diffractometer selection

- Depends on:
  - How disordered the sample is
  - If hydrogen is present
  - If any elements have resonances
  - The largest length scale to be probed
  - If the measurements are time-resolved



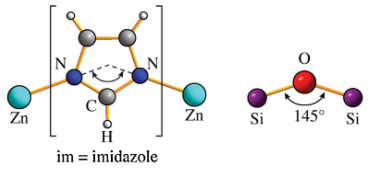


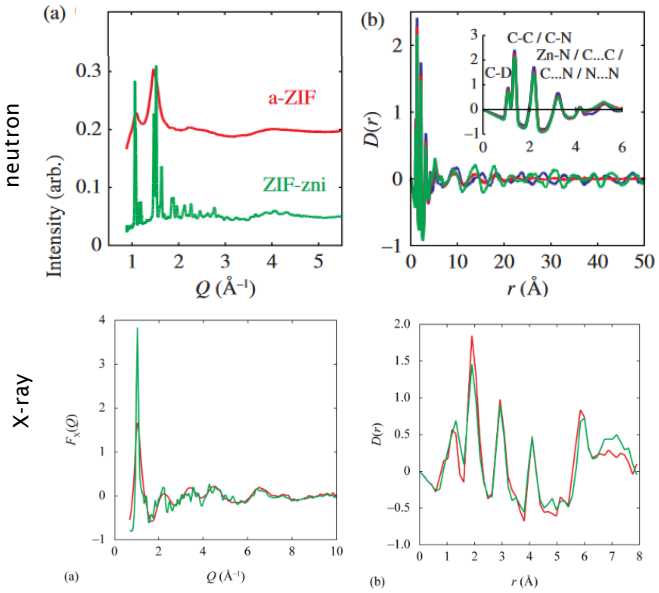


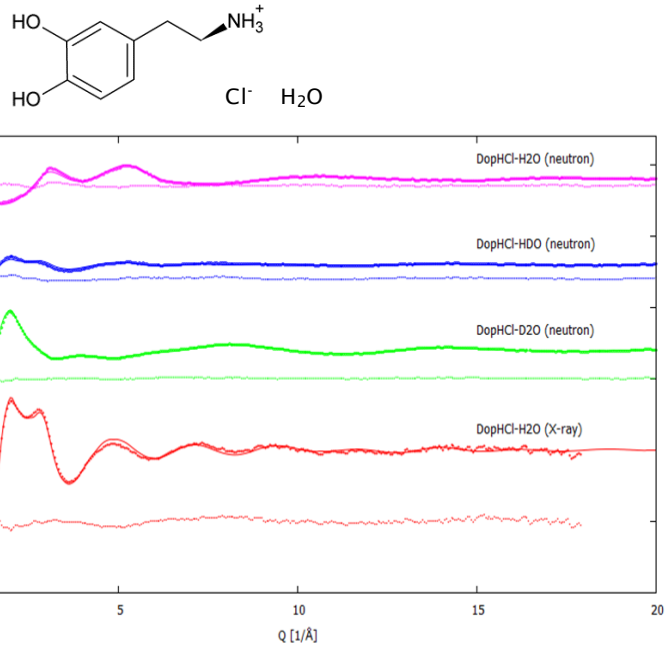
Science & Technology Facilities Council
ISIS

X-ray diffraction

- Highly complementary to neutron diffraction.
- Acts as an additional contrast which can be used to constrain a model.
- Particularly useful when isotopic substitution is not possible.

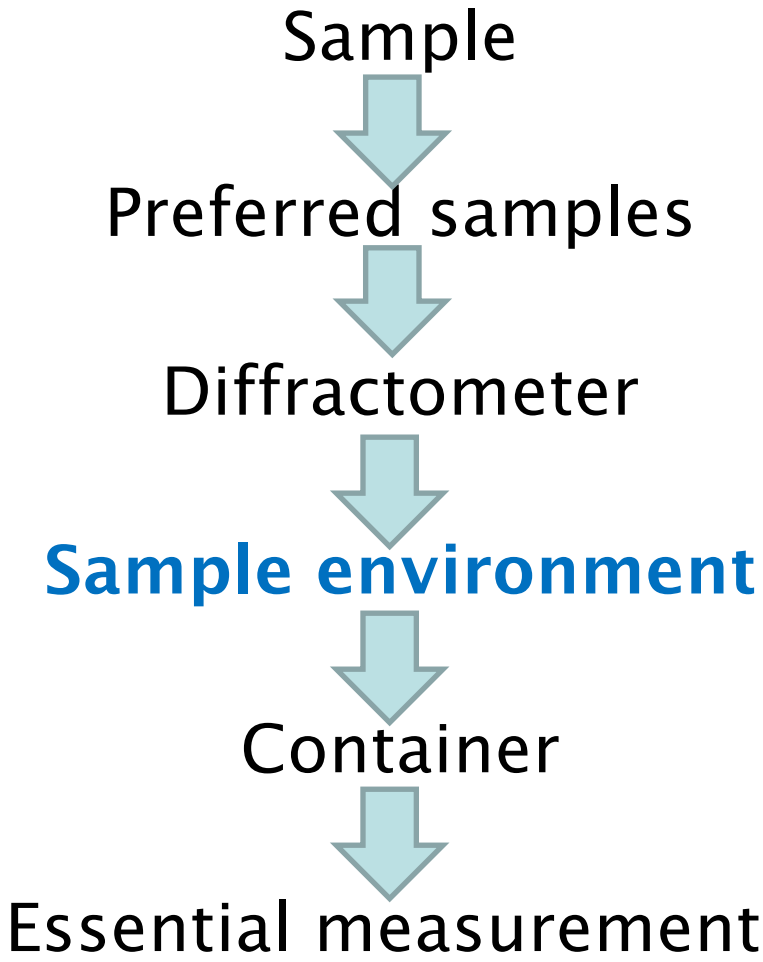






Science & Technology Facilities Council
ISIS

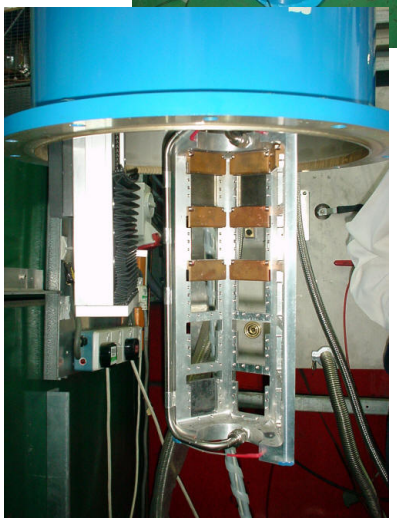
Experiment Design



Sample environment

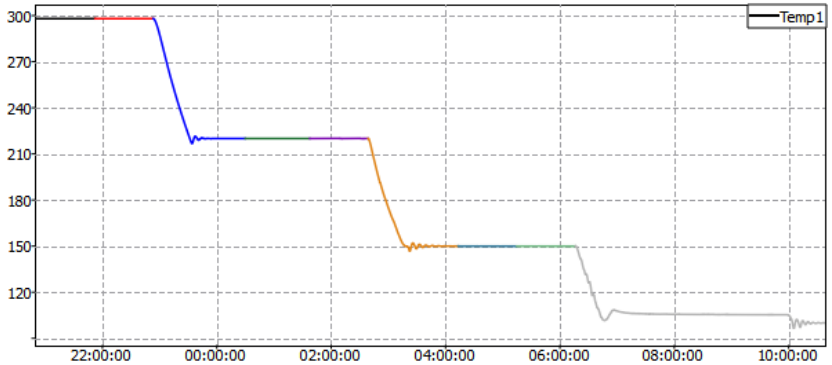
- Ideally contribute as little as possible to the overall scattering
  - Windows as thin as possible.
  - Made of a low scattering material that operates under the conditions of the kit.
  - Minimise the amount of kit in the beam.
- Know construction of the sample environment
  - Wall thicknesses
  - Atomic compositions
  - Density



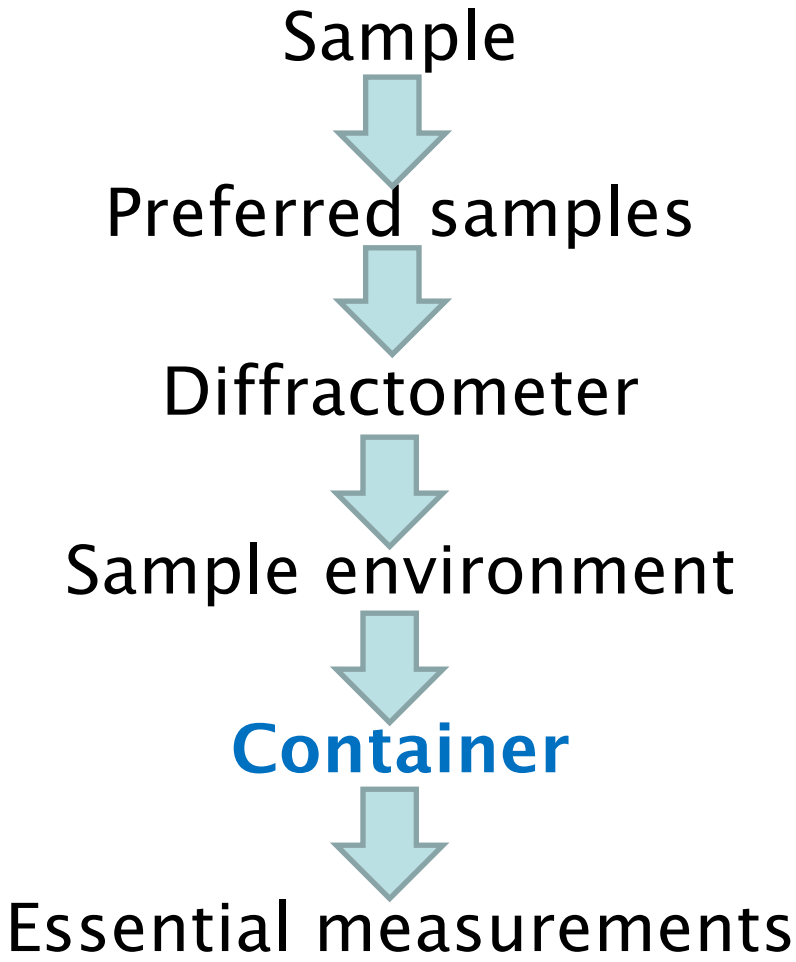



Sample environment

- Collect neutron data for the empty sample environment kit in the same state that the sample will be measured.
  - E.g. if a sample will be measured at 50K and 300K, the following measurements should be collected at each step:
    - empty sample environment
    - empty cell in sample environment
- Reproducibility and stability
  - The kit should produce the required condition reliably and with good stability.

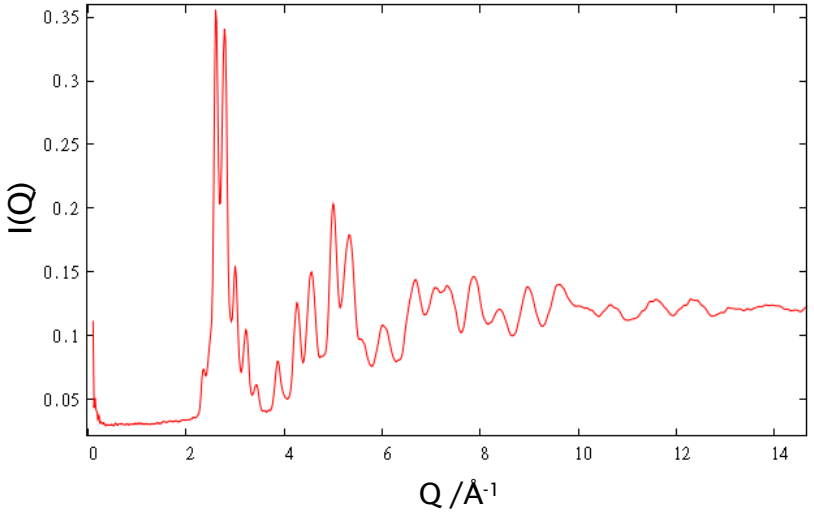


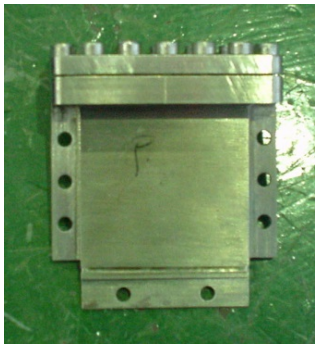
Experiment Design



Sample containment

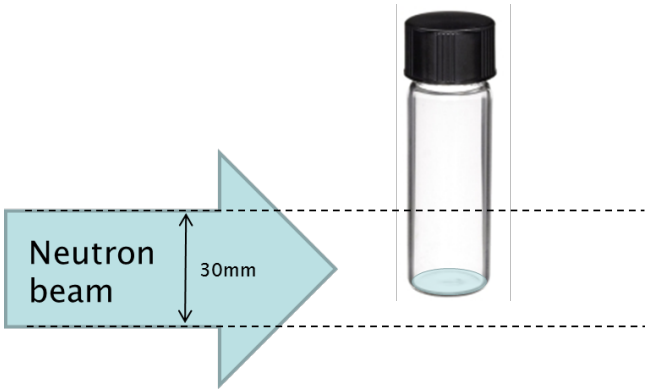
- Ideally ‘invisible’ neutrons, therefore only scatters incoherently e.g. V or is a null scatterer e.g. TiZr.
- Must be inert to sample.
- Must be appropriate to sample environment.
- Flat plate or cylindrical sample geometries
- Sample thickness (and choice of container geometry) depends on the sample composition and/or experiment conditions.

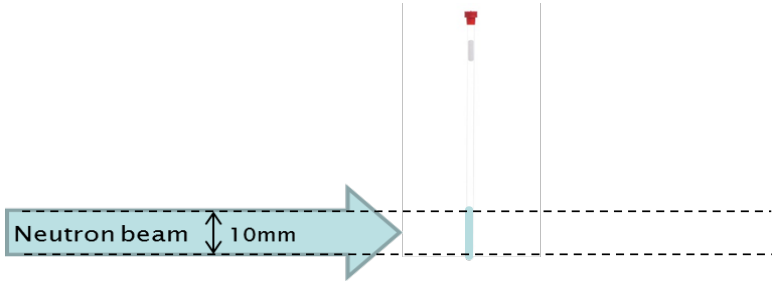




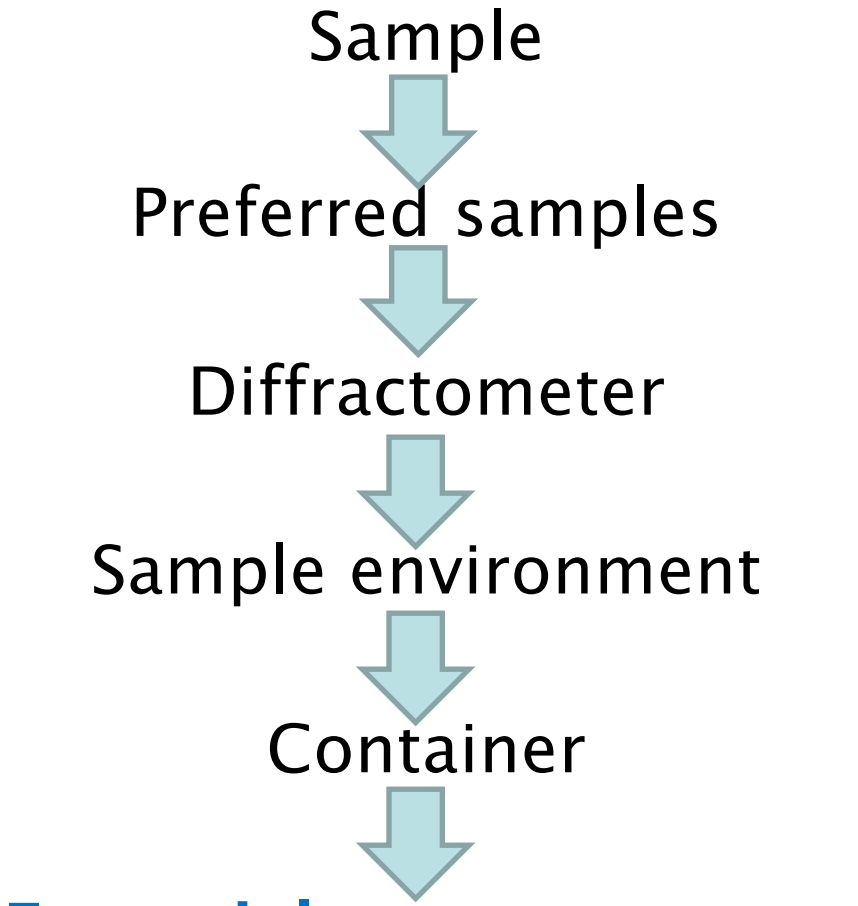
Sample containment

- The amount of sample available can determine the sample geometry/thickness.
- This also determines beam size.
- Often a measurement of each container used is taken – this is not necessary for very thin walled, very low scattering containers (across the whole Q range) that are nearly identical.
- Measure the container for a length of time that is equivalent to the level of its scattering compared to the sample. E.g. a thick walled quartz cell should be measured for as long as the sample while a thin foil vanadium pocket can be measured for half of the time of the sample.
- Container geometries, wall thicknesses, atomic compositions and densities are required for data processing in Gudrun
- Sample mounting must be:
  - Reproducible in position.
  - Stable throughout the measurement.

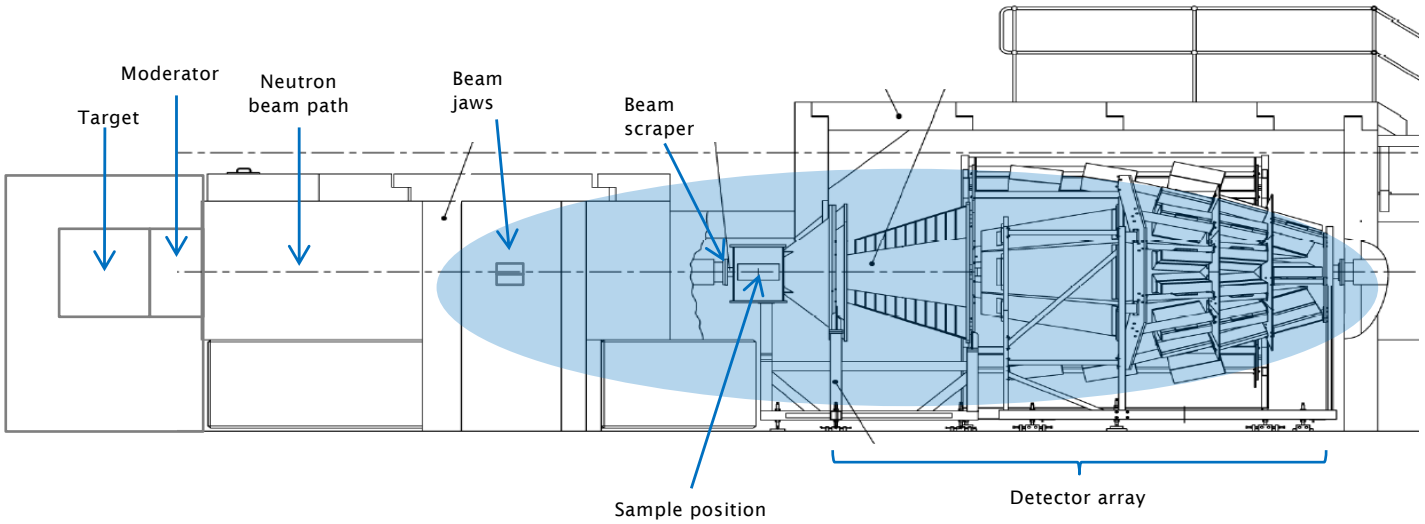




Experiment Design



Essential Measurements

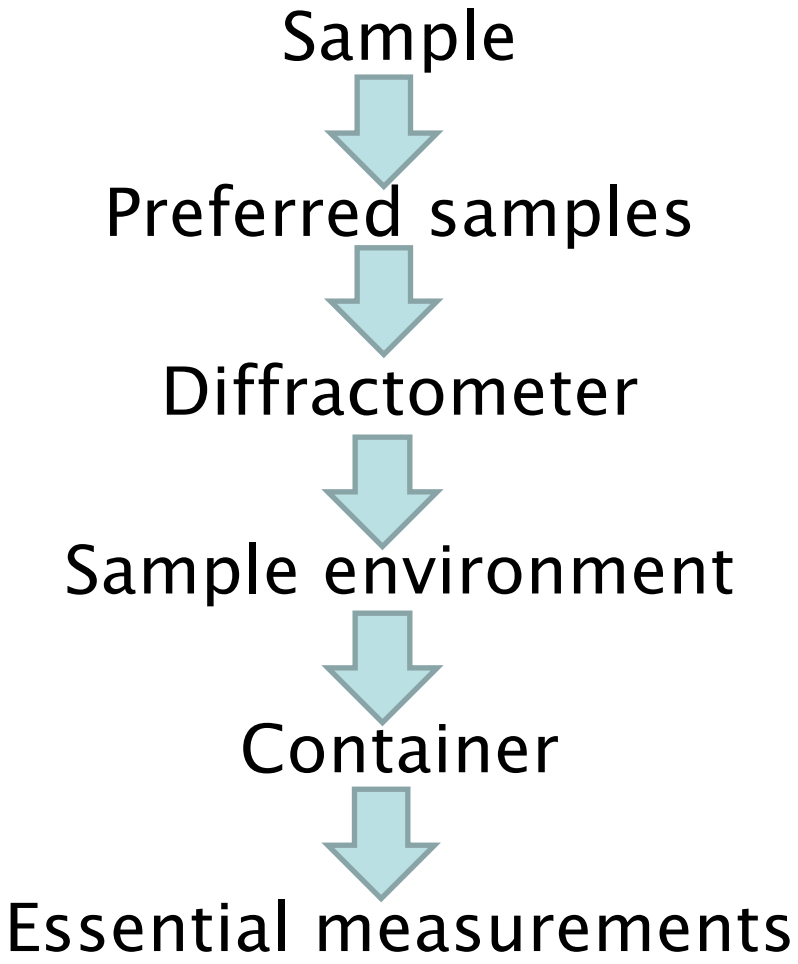


- Set beam size according to sample, container and any sample environment
  - Maximise amount of sample in beam
  - Minimise contribution from container, sample environment and instrument to scattering.

- Empty instrument
  - To capture the background scattering of the instrument.

- A standard material of the same geometry as the sample (cylindrical or flat plate)
  - To calculate useful quantities from the data regarding the structure of the material, the scattering level of the data must be normalised to a standard material.
  - Ideally a completely incoherent scatterer, e.g. V or VNb, so as there are no Bragg peaks.

Summary

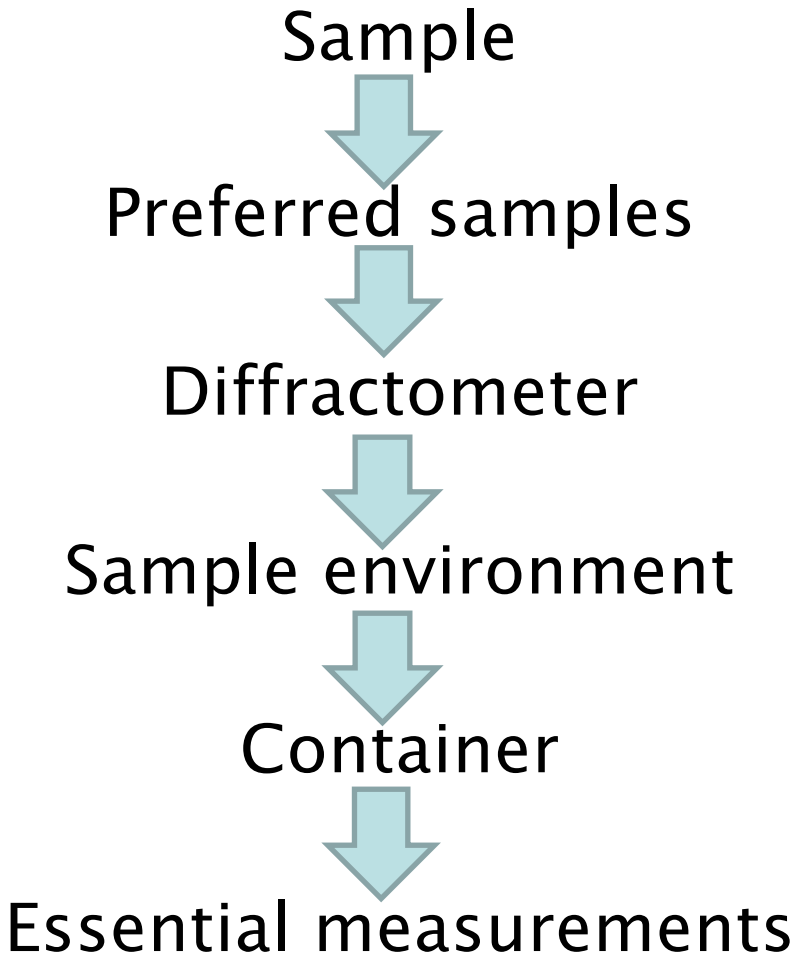


Identify any potential problems with the sample and adopt methods to alleviate these.

If possible, maximise the amount of information obtained from the experiment by using isotopic substitution to pick out key interatomic distances.

Consider using X-rays too.

Summary



Experiment Plan

1. Set the beam size.
2. Measure empty instrument and a standard for normalisation.
3. Measure the empty sample environment (if required) under the conditions the sample will be measured.
4. Measure the empty container (in the sample environment if being used) under the same conditions.
5. Measure the sample under the same conditions.