

# Experiment Design and Maximising Data Value

Sam Callear

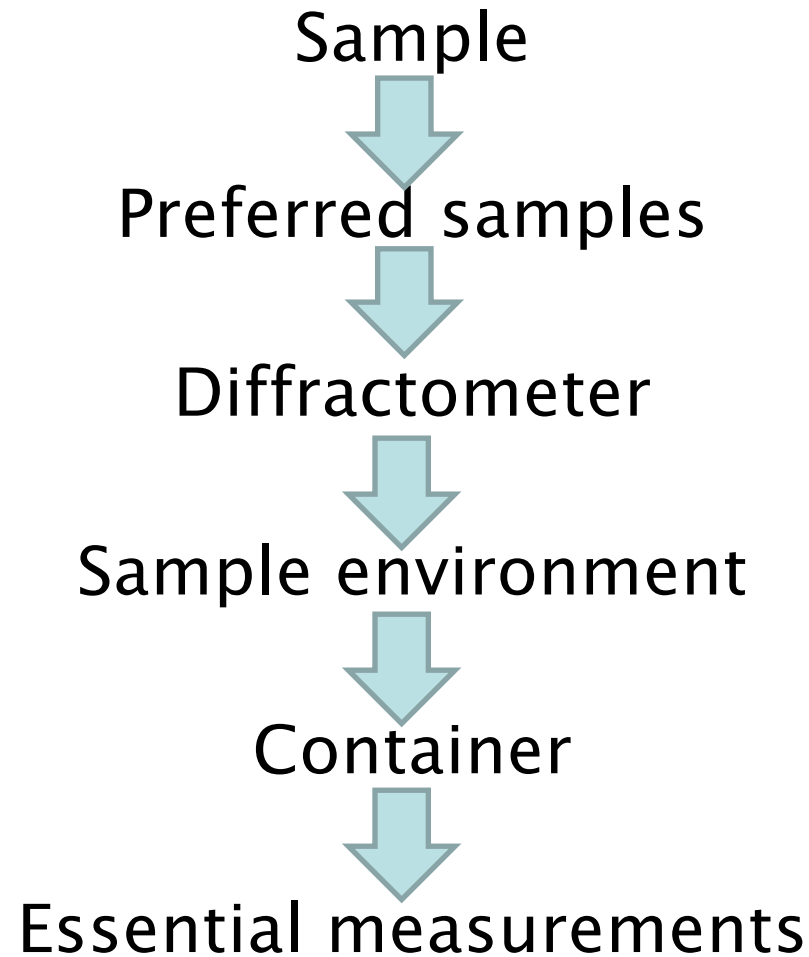
ISIS Facility, RAL



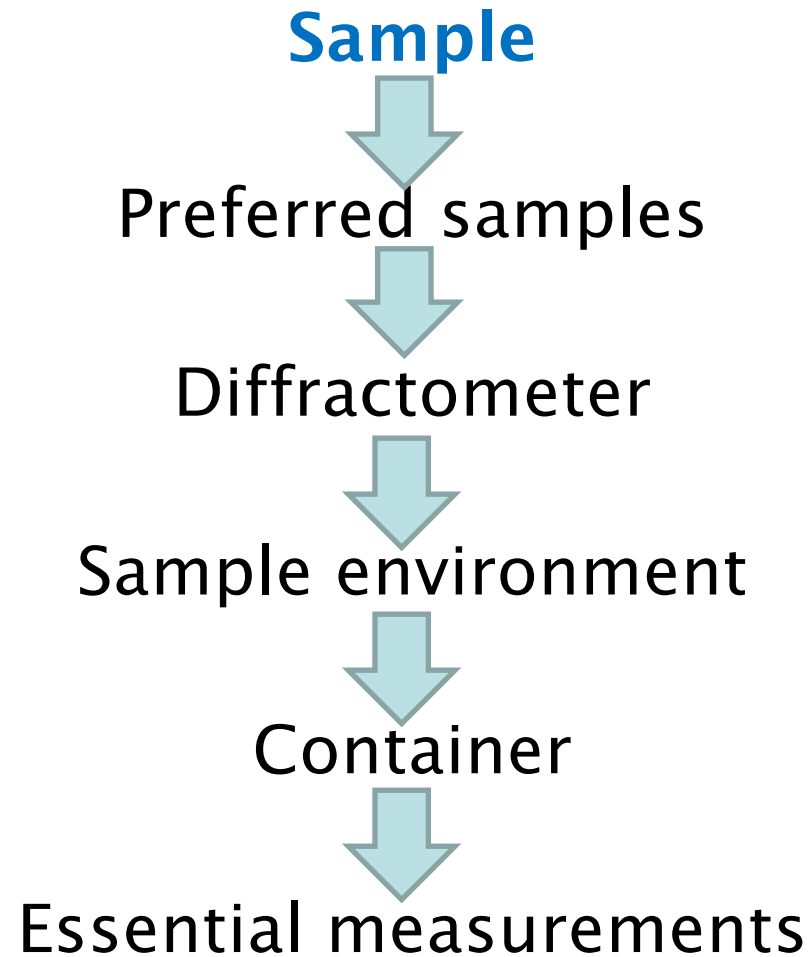
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# Experiment Design



# Experiment Design



# 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

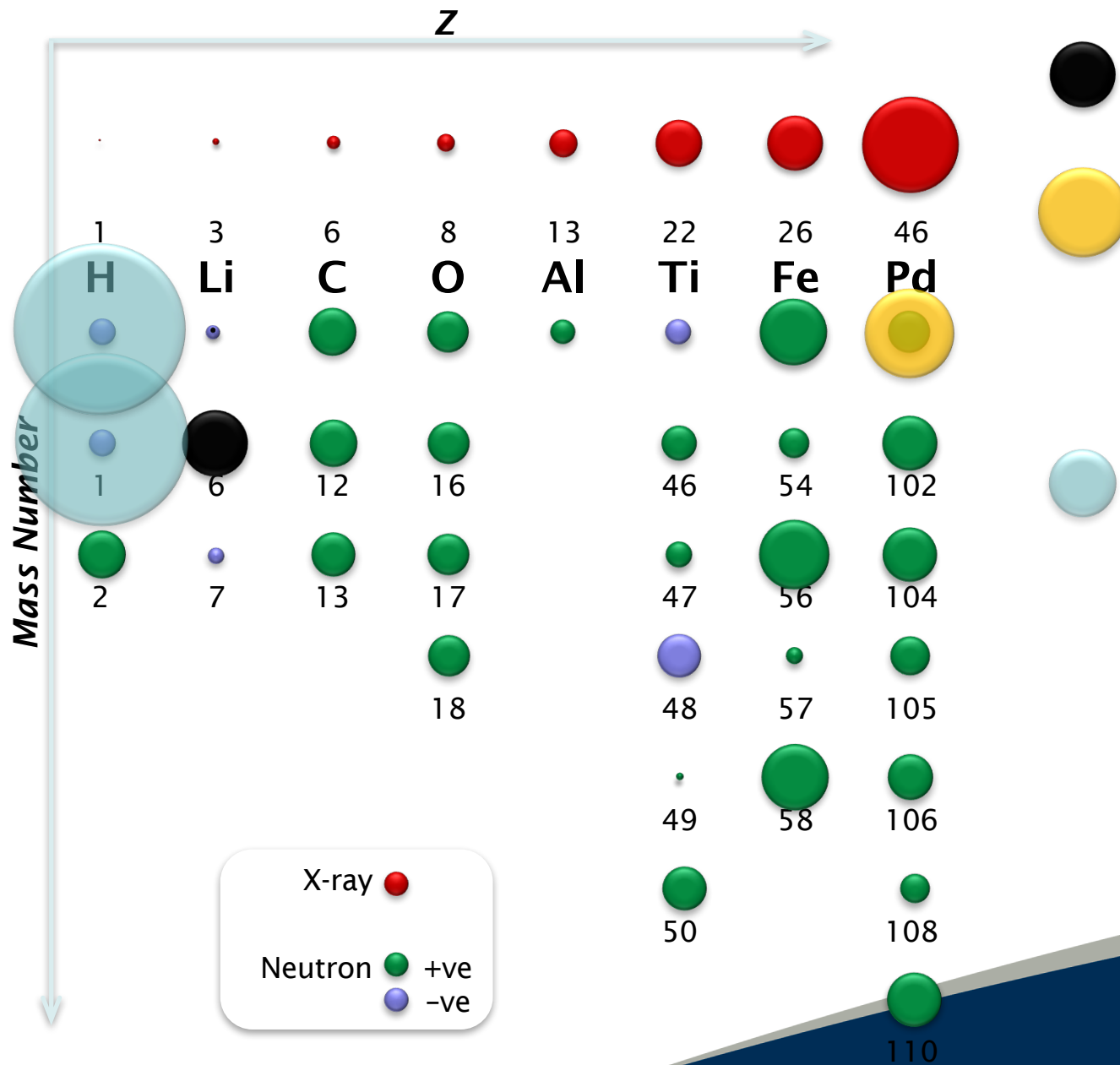
- Composition
  - Strongly absorbing elements?
  - Low coherent scattering cross-section/ high incoherent scattering cross-section?
  - Resonances (within the incident neutron energy range)?
  - Contains hydrogen (natural).

**THE PERIODIC TABLE OF THE ELEMENTS**

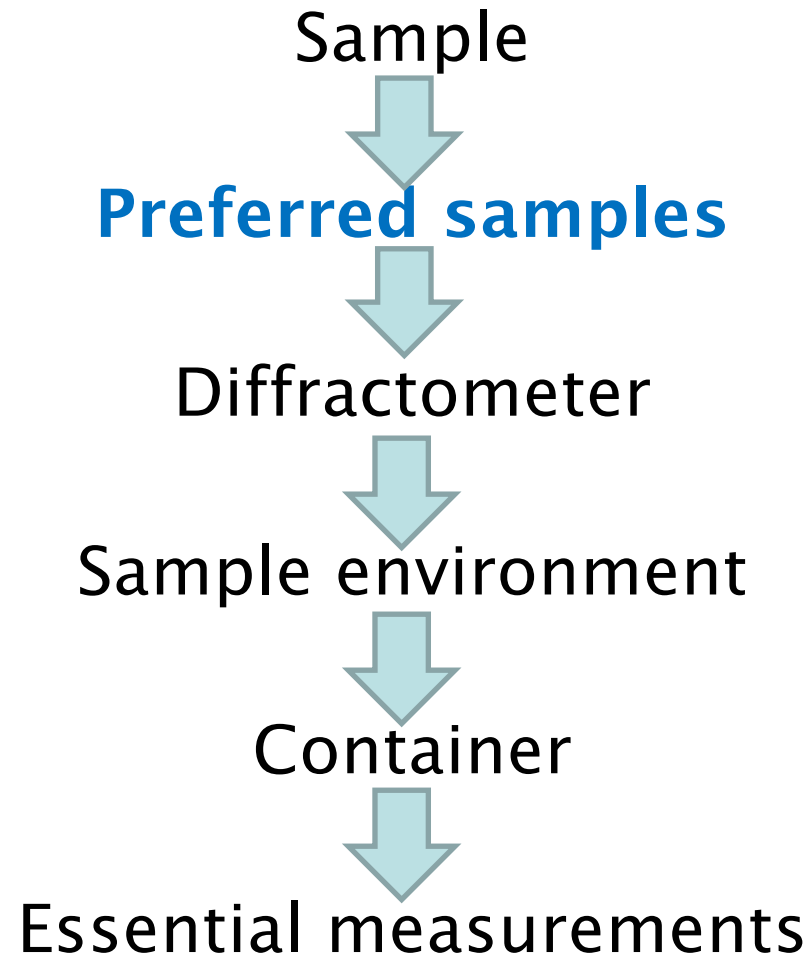
1 IA 1A	2 2A 2A											13 3A 3A	14 4A 4A	15 5A 5A	16 6A 6A	17 7A 7A	18 8A 8A	
1 H Hydrogen 1.008																	2 He Helium 4.003	
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 III 3B	4 IV 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8		9 VIII 9	10 VIII 10	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.80	
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29	
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222	
87 Fr Francium 223	88 Ra Radium 226	89-103 Actinide Series	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 267	111 Rg Roentgenium 268	112 Cn Copernicium 269	113 Uut Ununtrium 270	114 Fl Flerovium 271	115 Uup Ununpentium 272	116 Lv Livermorium 273	117 Uus Ununseptium 274	118 Uuo Ununoctium 276	
57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967				
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.08	99 Es Einsteinium 252.083	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium 262.10				
Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogens	Noble Gas	Lanthanide	Actinide									



# Isotopes

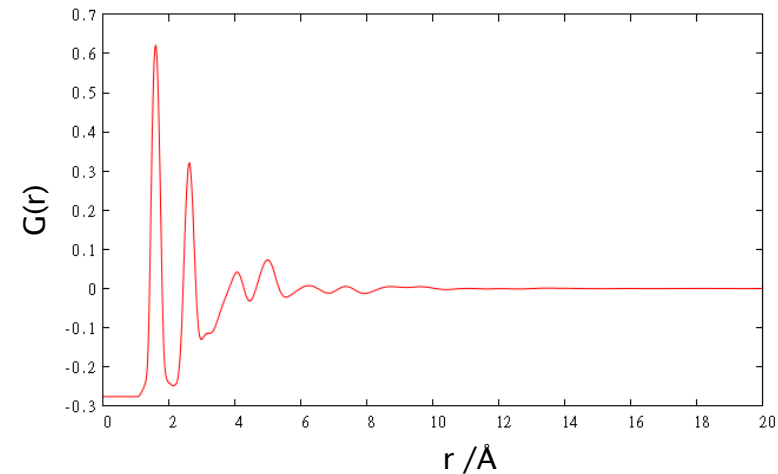
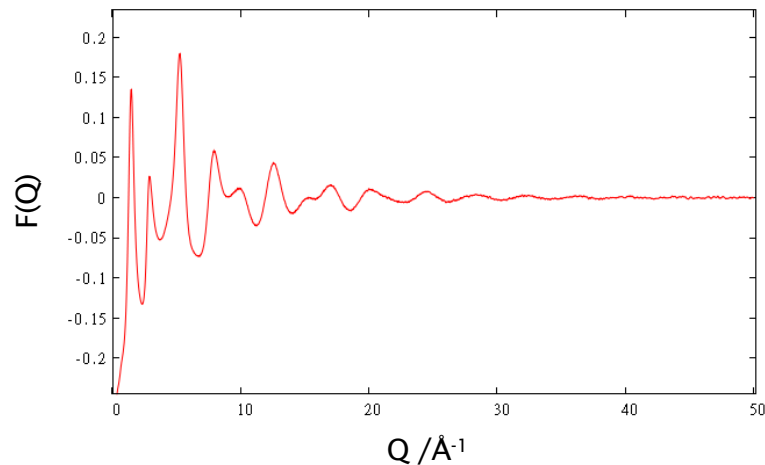


# Experiment Design



# 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.





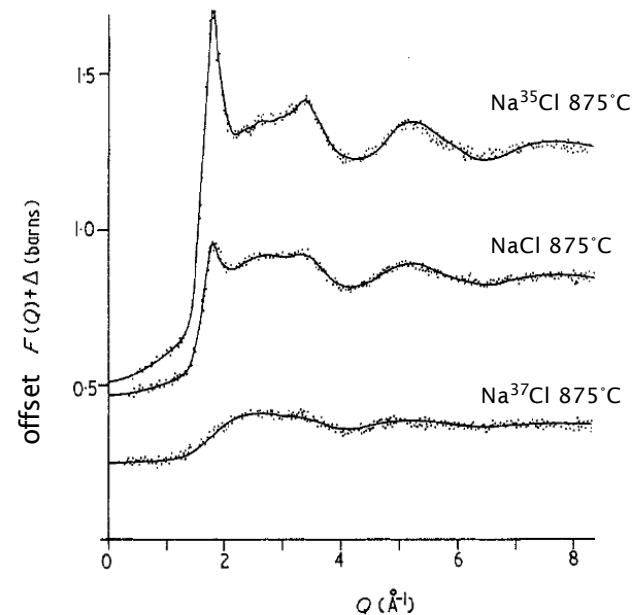
# Isotopic Substitution

- 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)
$^{35}\text{Cl}$	99.3 %	1.18
$^{37}\text{Cl}$	90.4 %	0.349
Cl (mixture)	(37) 41 % - (35) 59 %	0.799
Na	(natural)	0.351



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

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

# Isotopic Substitution

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

$$[A] \cdot [X(Q)] = [F(Q)]$$

where

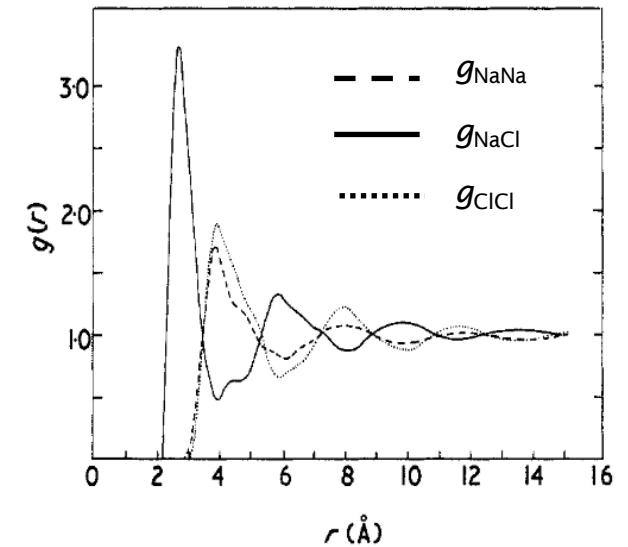
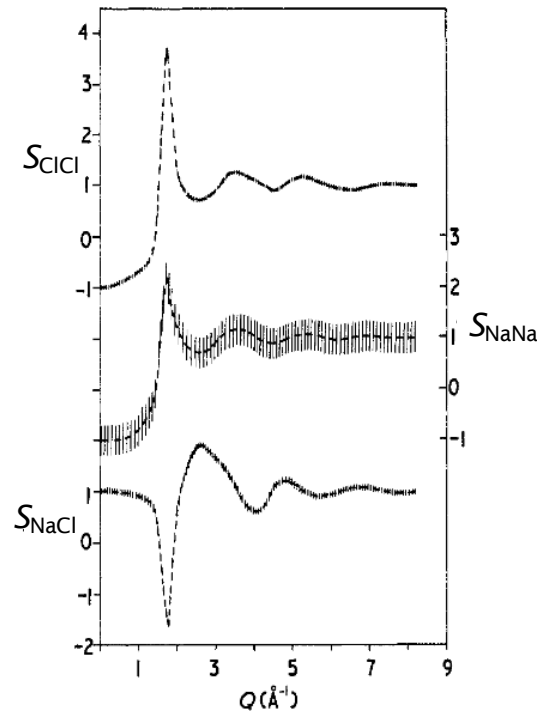
$$[A] = \begin{bmatrix} c_a^2 f_a^2 & c_b^2 f_b^2 & 2c_a c_b f_a f_b \\ c_a^2 (f'_a)^2 & c_b^2 (f'_b)^2 & 2c_a c_b (f'_a) f'_b \\ c_a^2 (f''_a)^2 & c_b^2 (f''_b)^2 & 2c_a c_b (f''_a) f''_b \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33}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

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

and

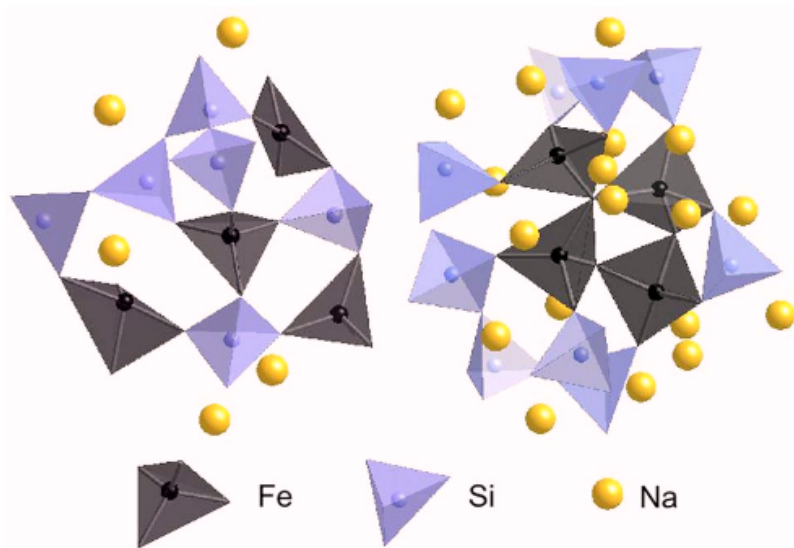
$$[F] = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}$$

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



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

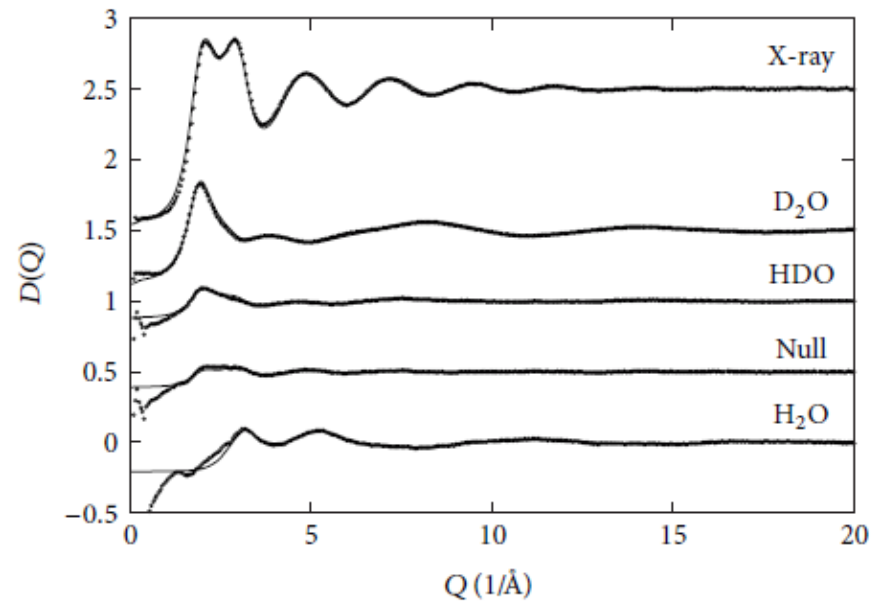
# Isotopic substitution – glasses



- 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.

# 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<sub>2</sub>O, H<sub>2</sub>O, 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<sub>2</sub>O and CH<sub>3</sub>OH is prepared, the solution will actually contain HDO and CH<sub>3</sub>OH<sub>0.5</sub>D<sub>0.5</sub>.
- For studies of a solute in a solvent, the technique was developed to show the solvent-solute correlations (2<sup>nd</sup> 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.

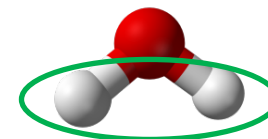
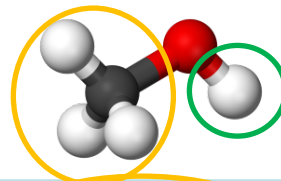


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# Isotopic substitution – molecular liquids

- 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 (1 <sup>st</sup> order difference)	D	D	1
	D	HD	2
	D	H	3
Solute-solute (1 <sup>st</sup> order difference)	D	D	4
	HD	D	5
	H	D	6
Solute-solvent (2 <sup>nd</sup> order difference)	D	D	7
	HD	HD	
	H	H	

- 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.



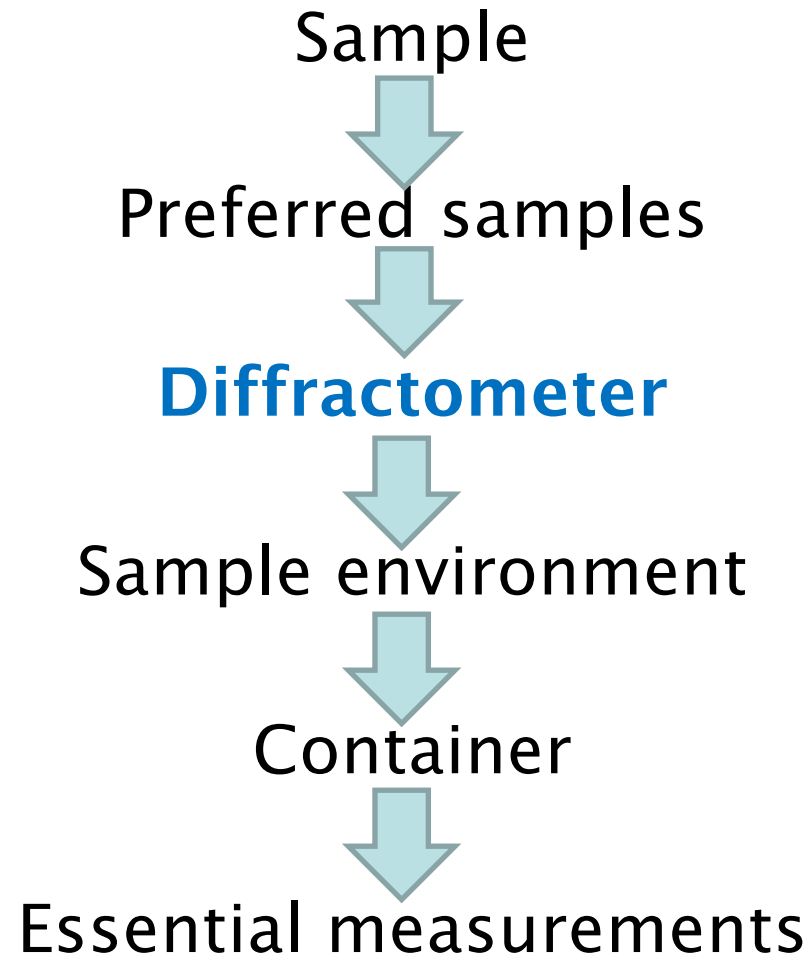
# Isotopic substitution – molecular liquids

- 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.

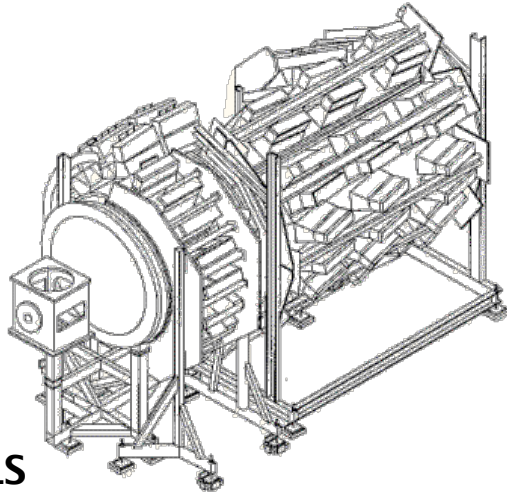
	Solute (non-exchangeable hydrogens)	Solvent (and solute exchangeable hydrogens)
Solvent-solvent (1 <sup>st</sup> order difference)	H	D
	H	HD
	H	H



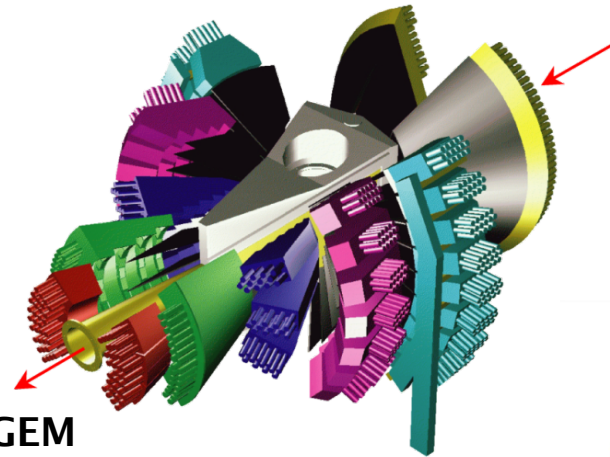
# Experiment Design



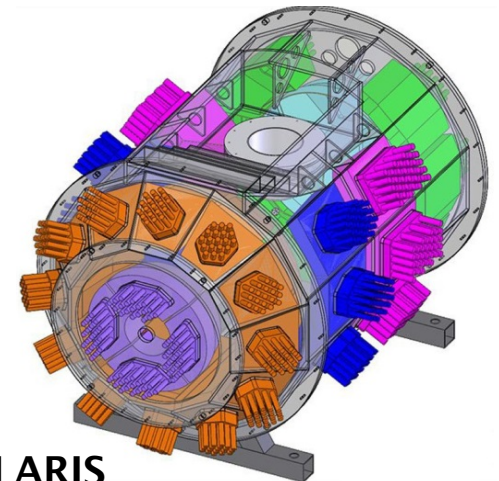
# ISIS Diffractometers



**SANDALS**  
Small Angle Neutron Diffractometer  
for Amorphous and Liquid Samples

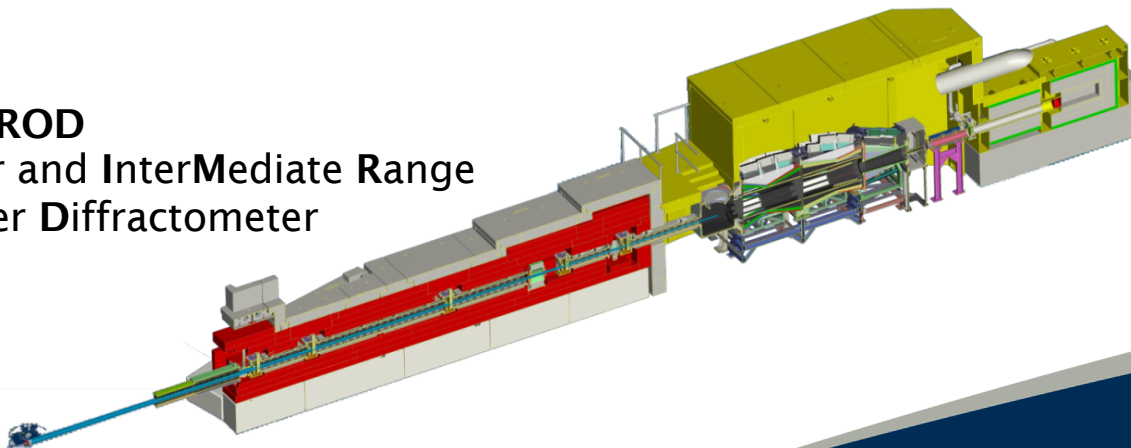


**GEM**  
General Materials  
Diffractometer



**POLARIS**  
Medium resolution  
powder diffractometer

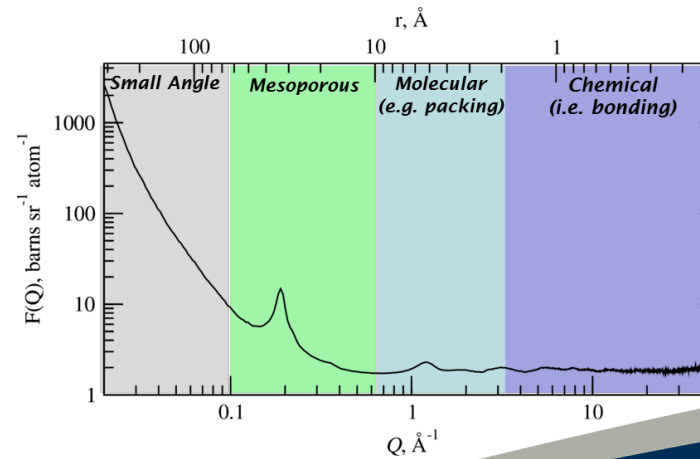
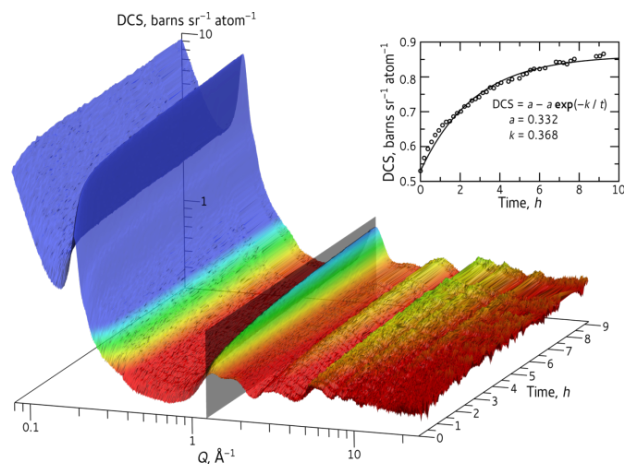
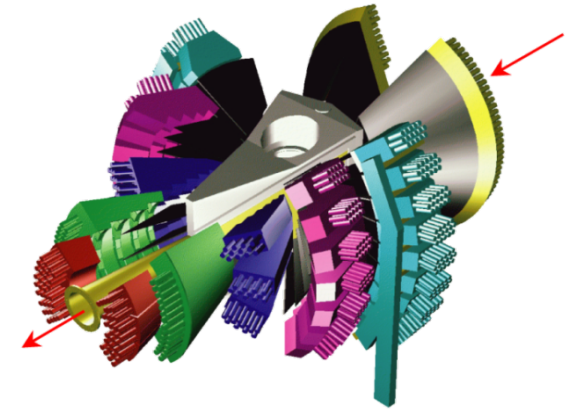
**NIMROD**  
Near and InterMediate Range  
Order Diffractometer





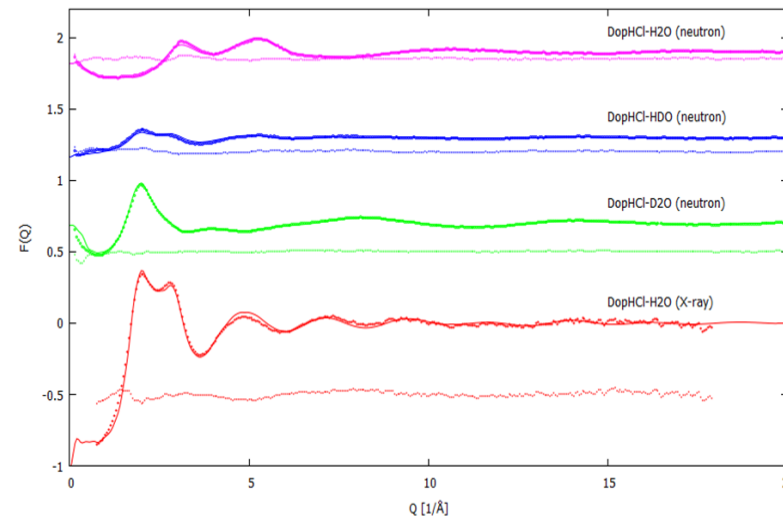
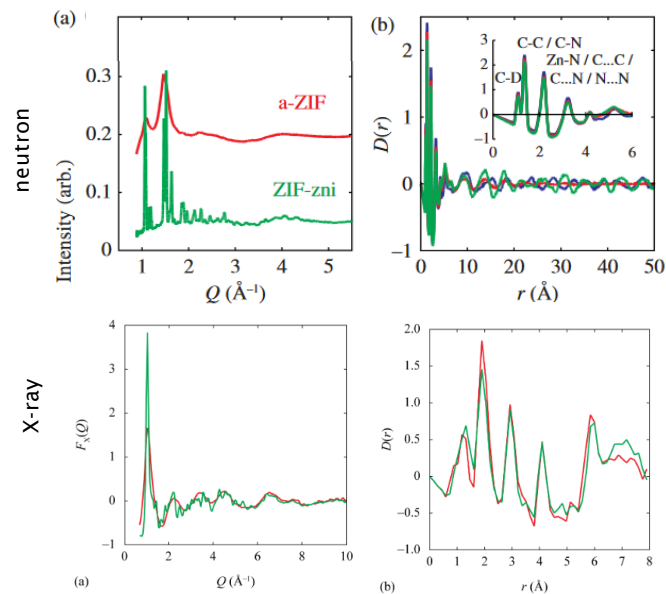
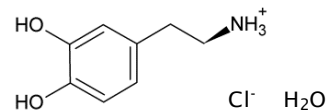
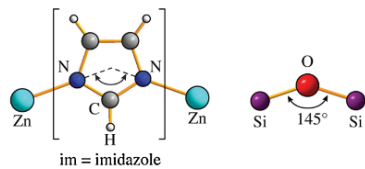
# Diffractometer selection

- 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

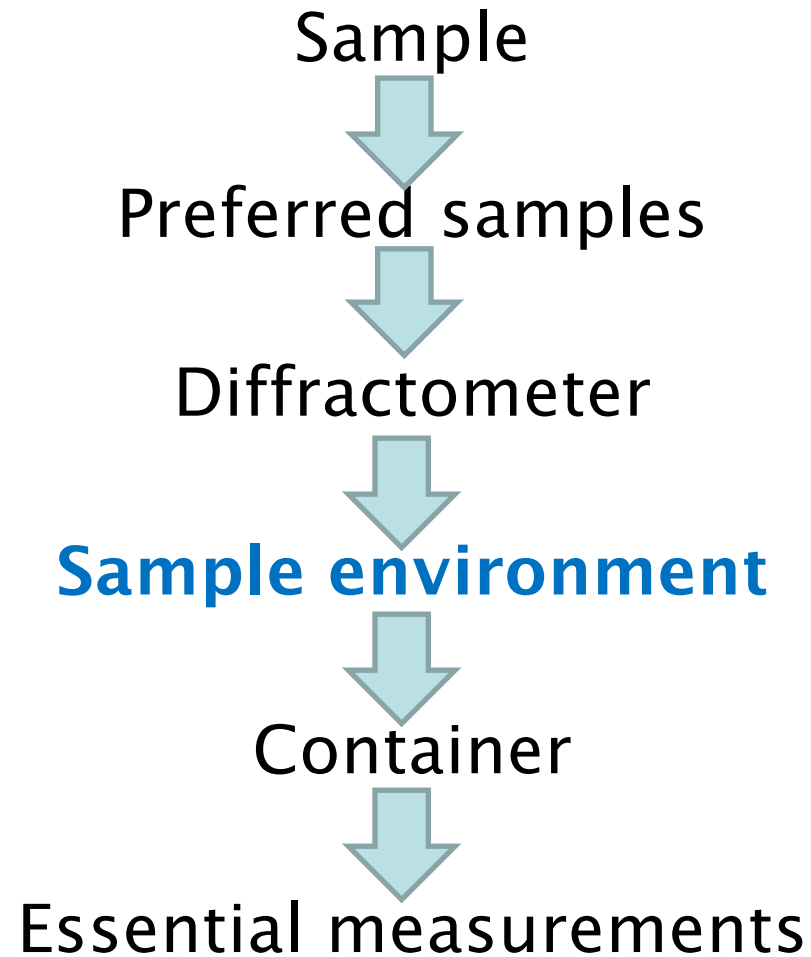


# X-ray diffraction

- 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.

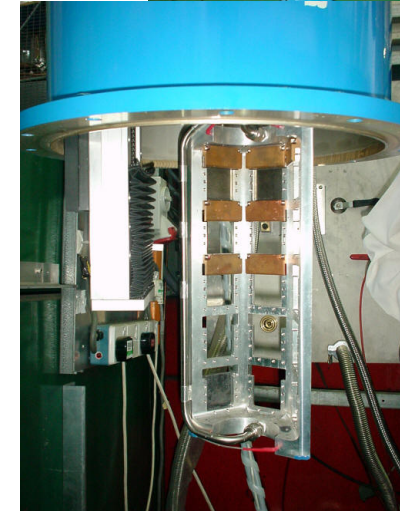


# Experiment Design



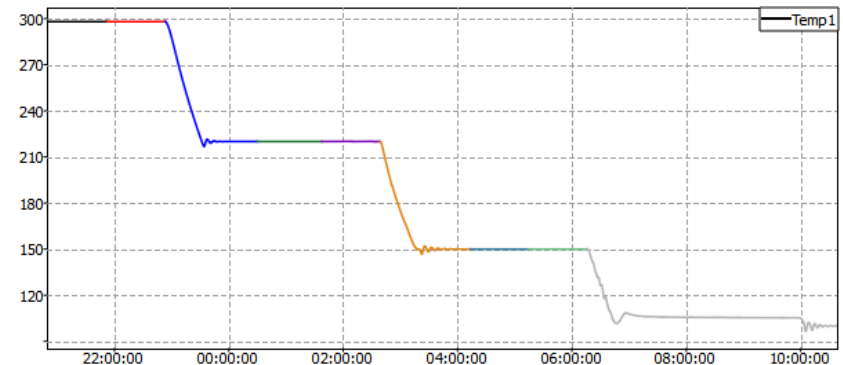
# Sample environment

- 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

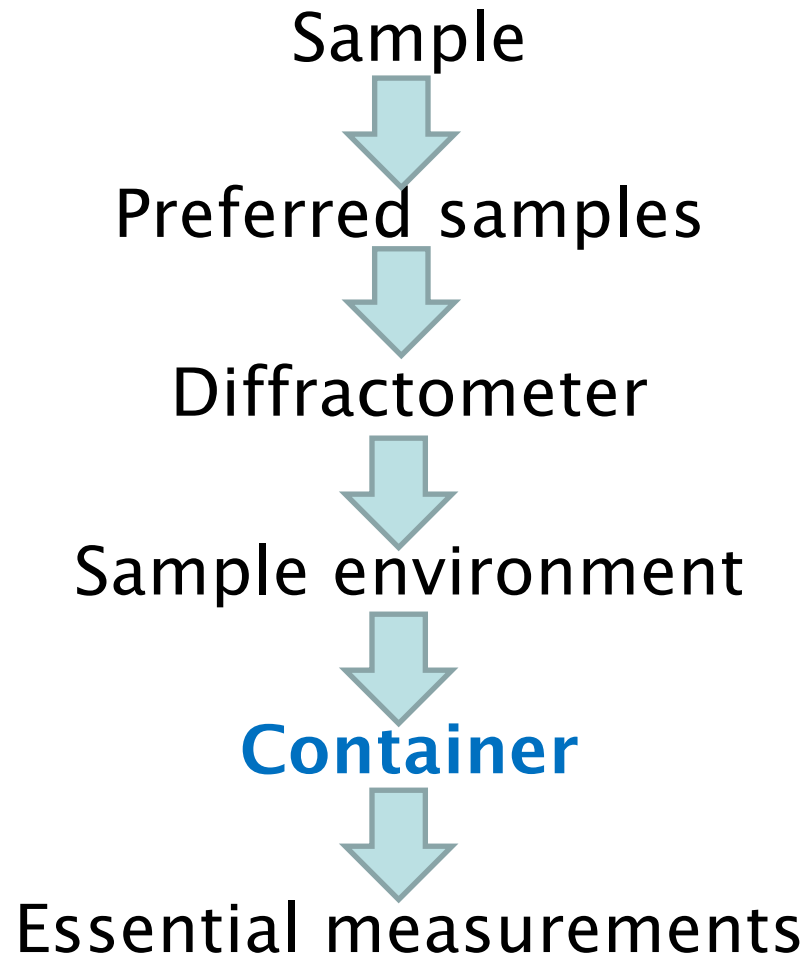


# Sample environment

- 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.

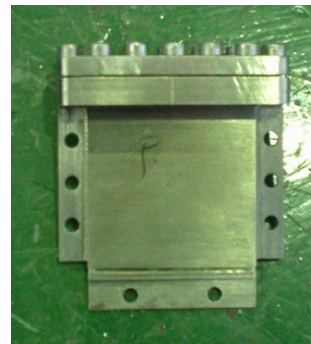
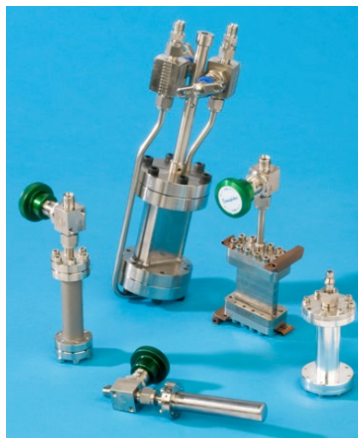
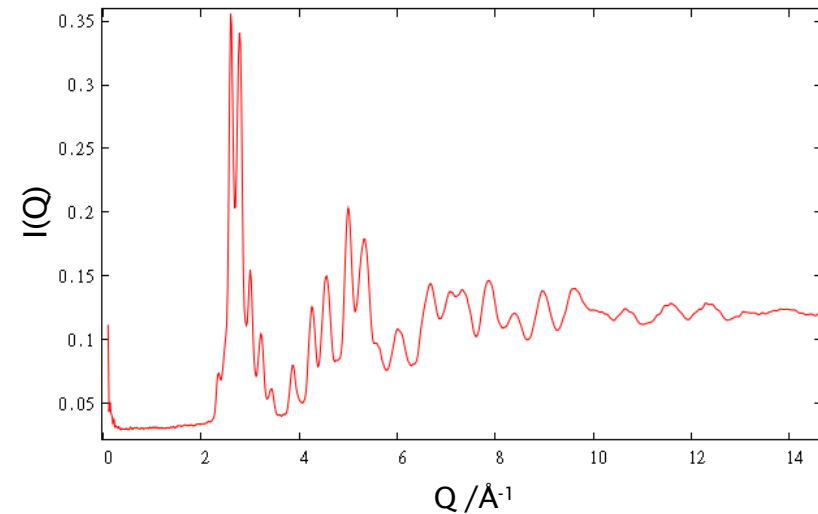


# Experiment Design



# 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.

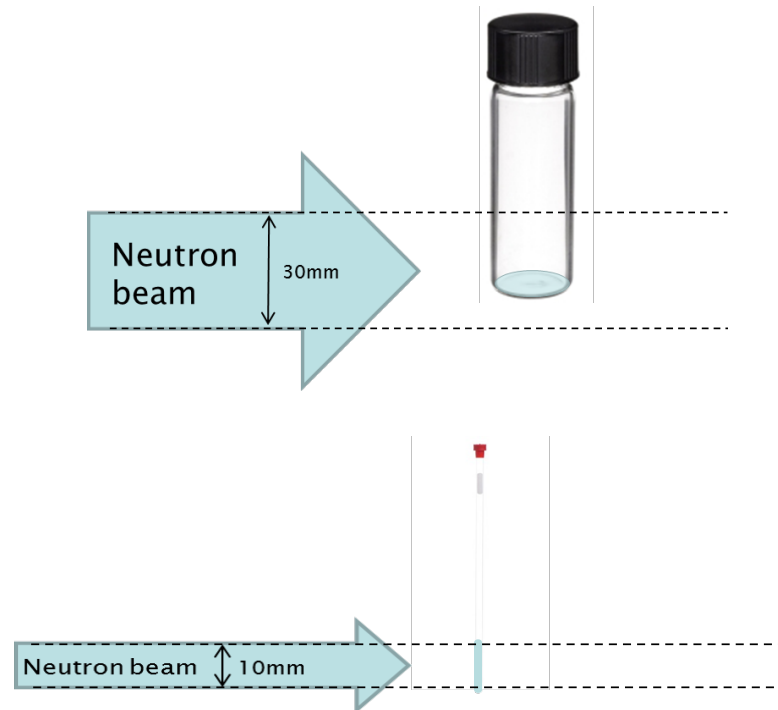


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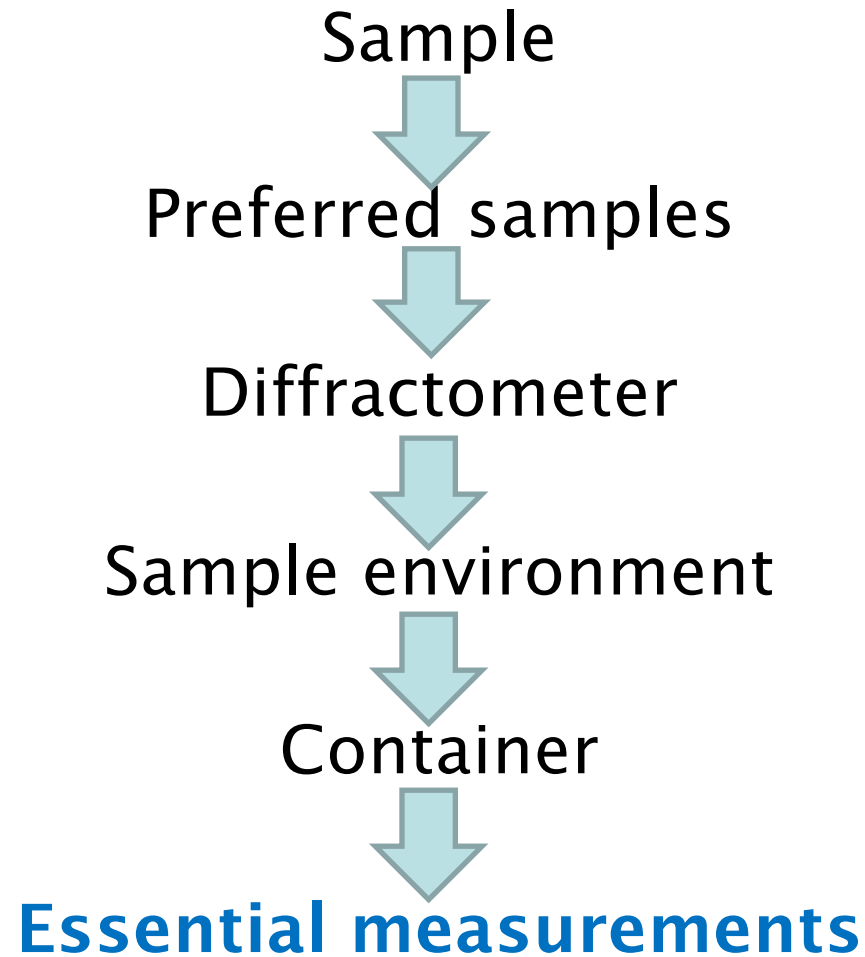
# Sample containment

- 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.

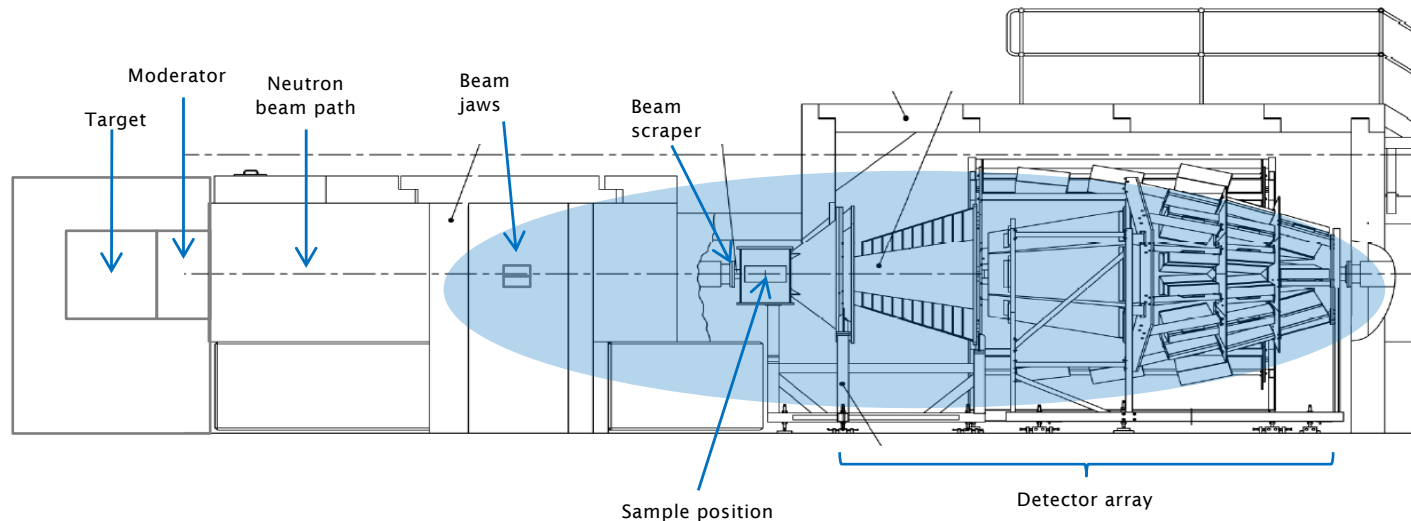




# Experiment Design



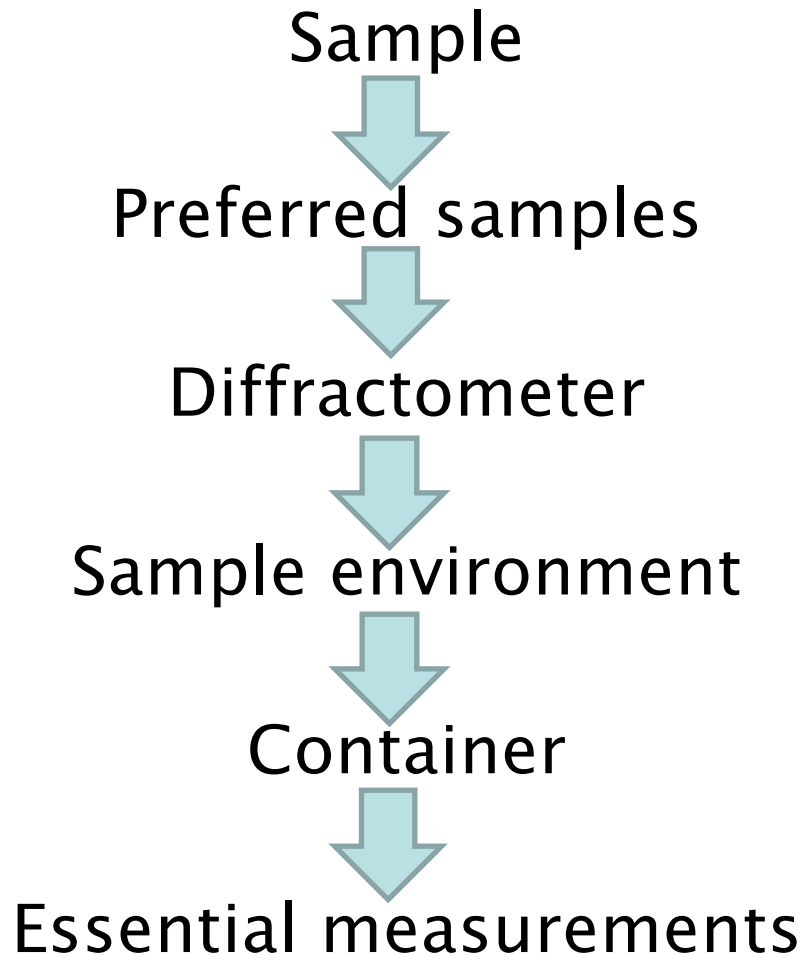
# Essential Measurements



- 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.

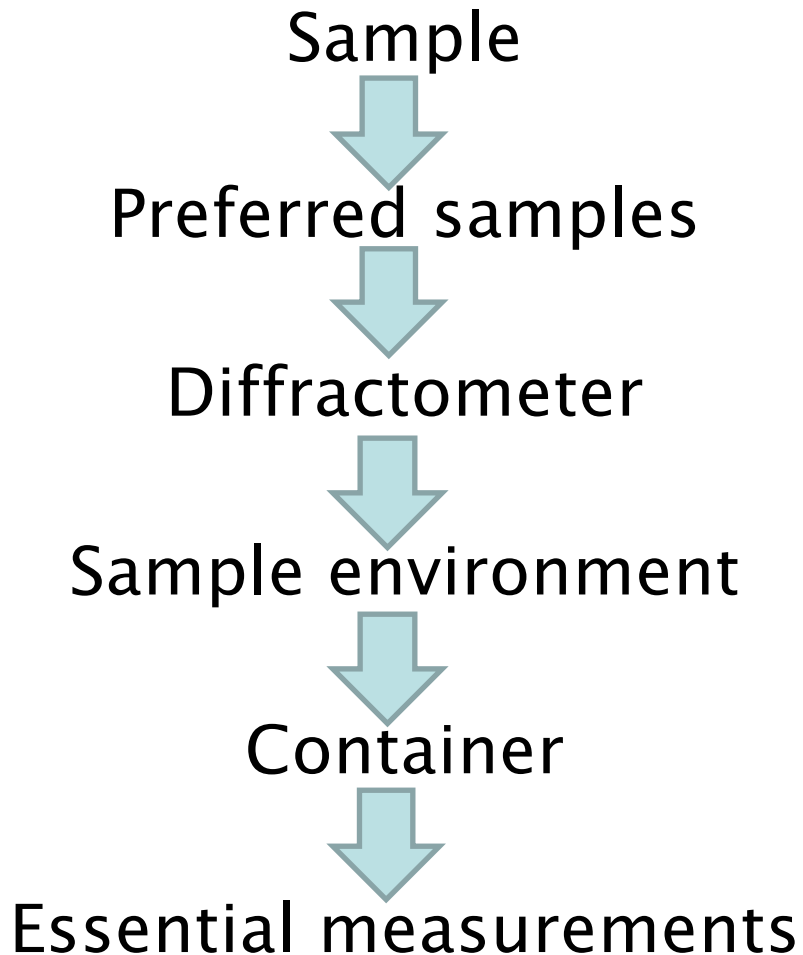
Consider using X-rays too.



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# 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.

