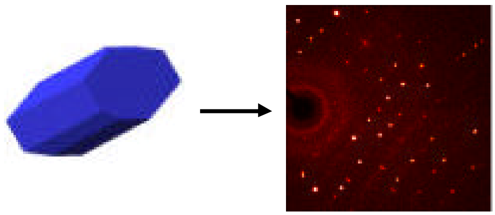
Data collection



Area detector diffractometers

- 1970s–1990s: serial diffractometers
- then image plate (IP) systems
- mid-1990s➔:charge-coupled detectors

  CCDs now standard instrument

  affordable

  displaced serial diffractometers

Area detectors: some advantages

- simultaneous recording of many reflections
- much faster data collection possible
- collection time independent of structure size
- high data redundancy possible
- rapid screening of samples
- matrix not required before data collection

Area detectors: some more advantages

- complete diffraction pattern measured
- reduced probability of obtaining wrong cell
- poorer crystal quality can often be tolerated
- less crystal movement necessary
- easier to use with accessories
- easier to visualise the diffraction pattern
- handle twinned or incommensurate crystals

Disadvantages?

- possibly higher capital and maintenance costs
- higher computing requirements
- need corrections for detector non-uniformities, etc
- problems with harmonics (e.g., ?/2)
- restricted detector sizes may lead to problems

  e.g., with large unitcells and with Cu *K*α X-rays
- may not be so easy to change radiation

Area detectors

The most obvious and major advantage of an area detector is its ability to record diffraction data over a substantial solid angle:

can simultaneously measure many reflections

number depends on

(a) size of unit cell

(b) dimensions of the detector

Area detectors

AD records all the intercepted diffraction

- all reciprocal space is observed
- not just around predicted reflection positions
- useful for diagnosing problems
- can identify twinning
- can study incommensurate structures

Matrix not required before data collection

- can be extracted from stored images later
- but useful here for cell checks

Types of area detectors - MWPC

1. Multi-wire proportional chamber (MWPC)

- pressurised chamber filled with gas
- two orthogonal grids of high-potential wires
- X-ray photons ionise detector gas
- this induces current in one or more wires
- readings from each set of wires for each photon
- get arrival time and position for each photon

Types of area detectors - MWPC

Advantages of MWPC's

- instantaneous output (ideal time resolution)
- no inherent noise in the detector
- high counting efficiency

Disadvantages of MWPC's

- parallax reduces spatial precision (esp. short l)
- overall count rate limited by dead time
- dead time is for *whole detector* for *every photon*
- high pressure chamber + thin window for X-ray
- not routinely used in chemical crystallography

Types of area detectors - TV

2. Phosphor coupled to a TV camera

- phosphor converts X-rays to visible light
- light via fibre optics to low-light-level TV camera
- gives an instantaneous readout

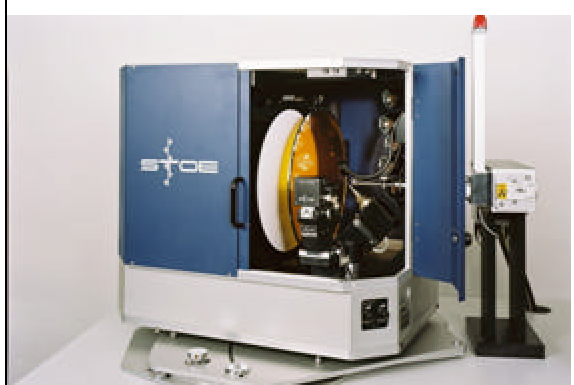
but ...

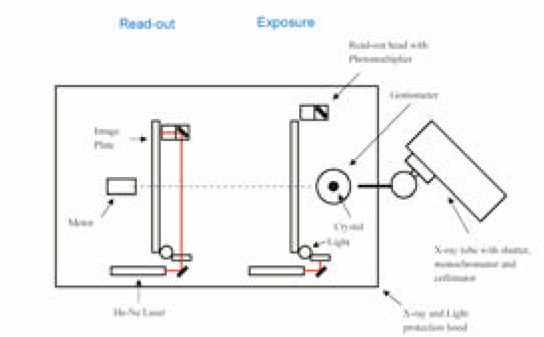
- the active area is relatively small
- the dynamic range is limited
- the signal-to-noise ratio is relatively poor
- technology no longer commercially available

Types of area detectors - IP

3. Image plate (IP)

- phosphor does not convert X-rays to light
- IP intercepts diffracted X-ray photons
- stores image as trapped electron colour-centres
- read out by irradiation by visible laser
- characteristic light detected by a photomultiplier)
- plate erased by strong visible light, then re-used





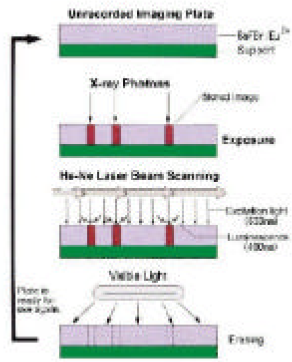
Stoe IPDS Image Plate Diffractometer

Steps in obtaining an IP image

Exposure

Readout

Erasure



Types of area detectors - IP

Advantages and disadvantages of IPs

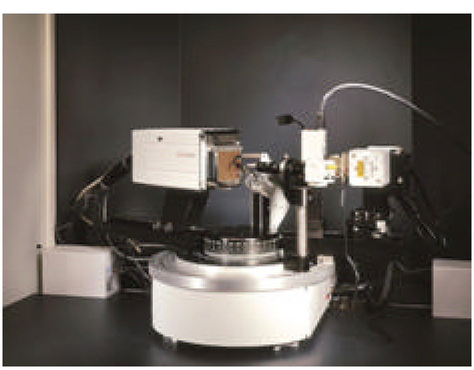
- large sizes available
- different shapes can be fabricated
- relatively inexpensive
- high recording efficiency
- good spatial resolution but ...
- read-out is a separate process (minutes)
- new, faster image plates may help
- can use two or more plates but this adds to cost

Types of area detectors - CCD

4. Charge-coupled device (CCD)

- diffracted X-rays are intercepted by a phosphor
- phosphor emits light
- light is conveyed through fibre-optic coupling

- CCD detector is a cooled semiconductor chip
- incident radiation produces electron-hole pairs
- the electrons are trapped in potential wells
- then they are read out as currents



Types of area detectors - CCD

Advantages

- efficient recording
- high dynamic range
- low inherent noise level
- short read-out time
- good potential for development

Disadvantages

- need high quality CCD chips
- chip size limits detector size

Features of [CCD] area detectors

A single-crystal X-ray AD diffractometer requires

- a source of X-rays
- a goniometer for orienting the crystal
- a detector and its ancillary equipment
- control and computing systems
- preferably a cryostat to cool the crystal

Features of area detectors

Diffractometer configuration

- AD records many reflections simultaneously
- still need to rotate the crystal in the X-ray beam
- typically offset detector to one side of beam

  get higher $?_{max}$ for a single detector setting
- $?_{max}$ of 25 – 30°, enough with Mo-$K\alpha$ radiation
- 2D detector means less crystal movement

Features of area detectors

Can have various goniometer geometries

- one circle – can only rotate f (fixed w and c)
- two circles – can rotate ϕ and ω (fixed χ)
- three circles – can rotate ϕ, ω and χ

- but one circle + low symmetry + one orientation —//→ all unique reflections

- no general agreement beyond that: flexibility vs. accessibility

Correction factors for raw CCD images

(a) Spatial distortion

- due to imperfect demagnification of the diffraction image by any fibre-optic taper
- need to map CCD pixels to face-plate positions
- then apply a correction to every image
- valid until you change phosphor/taper/CCD

Correction factors for raw CCD images

(b) Non-uniform intensity response

- between the detector face and the CCD chip
- can arise from various components of the system
- calibration uses a uniform intensity 'flood field' and measures the resulting CCD image

Correction factors for raw CCD images

(c) Bad pixels

- arise from fabrication faults in the CCD
- can affect individual pixels or rows of them
- these fail to respond correctly to incident light
- multiple faults mean the chip should be rejected
- but a few bad pixels can simply be flagged as such

Correction factors for raw CCD images

(d) Dark current

- due to thermal excitation generating electrons
- then these are trapped in CCD pixel wells
- background signal even with no X-rays on
- slowly builds up detector background
- this will be superimposed on the true image

Correction factors for raw CCD images

(d) Dark current

- reduced by half for every 7C° drop in temperature
- minimise by cooling the CCD (-45 to -80 C°) then
- correct by recording a dark-current image:
  → no X-rays on → match exposure time
  → match temperature → average readings
- then subtract this from each measured frame

Corrections for raw CCD images

(e) Zingers – random detector events

- due to radioactive decay or cosmic rays
- more likely on longer exposures
- very sharp – typically occur on only one frame
- detect by recording the same exposure twice
- significant event on only one exposure is suspicious
- use the lower reading for the affected pixels

Correction factors for raw CCD images

Summary

- most systems have corrections integrated
- but you still need to know about them

especially the dark current corrections

a wrong dark time can ruin your dataset

Experimental conditions

(a) Radiation

Cu radiation diffracted much more efficiently, but
- resolution is more limited
- absorption and extinction effects are worse
- may be essential for absolute configuration

Mo radiation not diffracted so efficiently, but
- resolution is better
- absorption and extinction effects are less
- crystal movement is less
- fewer problems with attachments

Experimental conditions

(a) Radiation

- Changing radiation on an AD may not be simple:

  may need a different phosphor (expensive)
  extensive re-calibration (time-consuming)

- Keep one instrument on each radiation?
- Buy a dual-source, dual-calibration instrument?
- Depends on the needs in each laboratory

Experimental conditions

(b) Temperature

sensitive crystals need cooling to LT

LT advantageous where not essential

decay is uncommon with AD/LT combination

(c) Other conditions

avoiding problems is better than correcting later
- crystal size
- crystal centering
- crystal orientation

Experimental procedures in outline

crystal screening

unit cell/Bravais lattice determination

data collection

↓

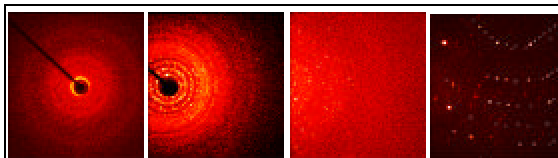
processing of the frames

data reduction

Crystal screening

- short initial exposures
- at different ϕ angles to monitor quality
- in random orientations
- stationary or small-angle oscillation

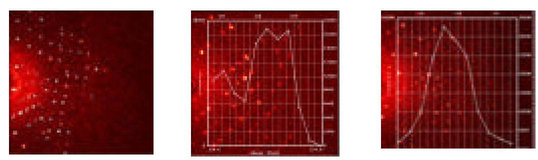
➔ crystal quality and diffraction intensity:
- poor, poly- or no crystallinity?
- splitting of reflections?
- overall weak diffraction?



Amorphous | Polycrystalline | Weak, not single | Split crystal

Diffraction from a range of sub-optimal crystals

Limited resolution | Split peak | Broad peak



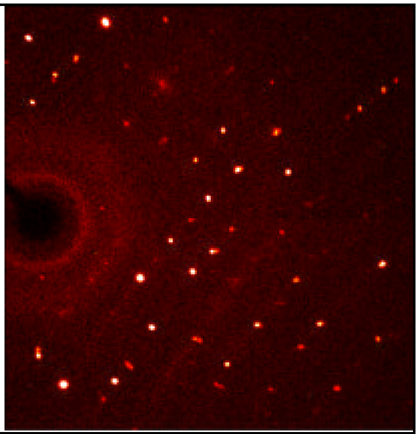
Crystal screening

- can quickly abandon truly hopeless crystals
- but remember CCDs handle quite poor crystals
- these frames are really only two-dimensional
- other problems may show up later
- how poor a crystal is worth trying?

Crystal screening

- depends on the quality of the structure needed
  - gross structure?
  - routine determination?
  - high precision study?
- also how much effort and skill will be needed
  - poor datasets tend to require more work
  - need to deal with disorder, twinning, etc
- is it worth the time and effort involved?

A good quality crystal. This single frame was collected by rotating the crystal through 0.3°.



Orientation matrix determination

Procedure

- collect frames over two or three small regions
- harvest reflections
- interpolate between frames to get setting angles
- convert to reciprocal space coordinates
- usually will have plenty of reflections
- may need to adjust inclusion criteria, especially ***I*** or ***I*/s** for weak diffractors, to get enough reflections

Orientation matrix determination

Procedure

- a provisional matrix and cell can be checked (and revised?) following the full data collection
- but with the correct cell you can check whether it corresponds to a known phase
- and it suggests you will be able to index and process the full dataset

Indexing parameters

(i) index limits

(ii) axial lengths

(iii) allowed index deviation from integral

(iv) minimum fraction which must be indexed

- defaults may work, if not these can be tweaked
- it may help to re-harvest the frames
- should also check the frames for bad reflections

Indexing parameters

Parameters (i) and (ii) exclude larger cells:
reduce them only if you really know the cell
start off with cell axes 3 Å ? 60 Å
indices 15 ? 20

Parameter (iii) excludes misfit reflections:
0.1 may be too low but 0.3 ? 0.4 is too high

Parameter (iv) may be useful with a minor twin component or other problems – but a rather blunt instrument.

If indexing fails

- first increase parameter (iii) - index deviation
- survey frames before increasing (i) or (ii) - limits
- is the default reflection list the best?
- harvest reflections using your own criteria
- modify limits on I or I/s
- change resolution limit
- other factors?

If still failing:

- examine frames and rocking curves
  look for splitting or other effects
- collect more frames – up to the full frameset?
- time to try another crystal?

Even if indexing seems to work ...

- check the rocking curves
- peaks could be badly split or too broad
- indexing does not <u>guarantee</u> a useable crystal

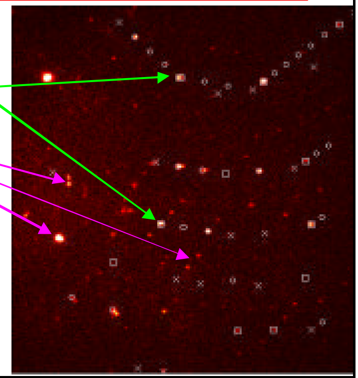
- check observed/predicted peak positions
- must correspond or indexing is dubious
- too many predicted spots = cell is too large, missed lattice centering, not single
- too few predicted spots = the cell may be too small

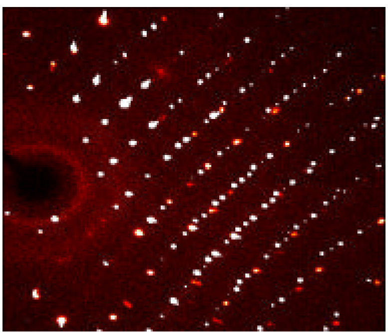
Even if indexing seems to work ...

frame overlaid □ with spot positions predicted from orientation matrix

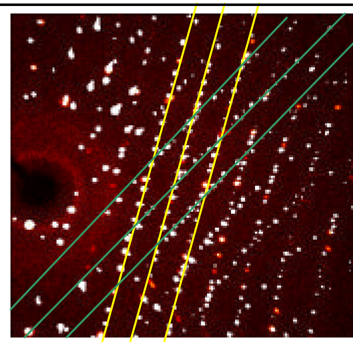
not all spots are accounted for

There are several possible causes for this, including broadened reflection profiles.





A pseudo-oscillation photograph made by superposition of 15 frames, to check indexing and crystal quality.



Not a good sign: the reflections here do not appear to belong to a single lattice – this crystal is probably twinned. The colours identify the two components.

Other things to check

- good matrix refinement?
  - reasonable s.u.'s on cell parameters
  - suitable values for various quality indicators
- mosaic spread – how big are the spots?
- overall intensity – governs rate of data collection
- symmetry – determines minimum fraction to collect
- is the unit cell known, in literature or locally?
- does the unit cell volume make sense?
- 18 Å^3 per non-H atom - for molecular compounds

discrepancy → wrong cell, wrong compound, solvent?

Data collection - important factors

1. Intensity ➔ frame measuring time

- must allow collection to adequate resolution
- peaks must go to ½-$^{2}/_{3}$+ of the required $2?_{max}$
- too long may result in detector overloads
- reducing it may mean losing higher angle data
- possible solution:
  - short time for low-angle data
  - longer time for the high-angle data
  - allow overlap for scaling
  - requires two detector settings
  - ∴ much longer to collect data

Data collection - important factors

2. Mosaic spread ➔ frame width

- from (x, y) reflection widths on individual frames
- plus z from widths of rocking curves
- match step size to reflection widths
- depends on program and strategy
  - narrow frames typical for Bruker SMART
  - wider frames typical on Nonius KappaCCD
- wider scan ➔ fewer frames ➔ quicker
- is the exposure time + scan width correct?

Narrow frames – all reflections are partial
➔ integration carried out as part of data reduction

Wider frames
➔ detector integrates most reflections on a frame

Data collection - important factors

3. Crystal symmetry ➔ minimum fraction

- Bravais lattice may not always be clear
  if in doubt assume the lower symmetry
- can pre-calculate calculate a set of frame runs
- for routine work probably simplest to collect
  - a whole sphere for triclinic crystals
  - at least a hemisphere for all others

Non-routine cases

- higher-symmetry crystals which diffract weakly
  ➔ averaging many equivalents may be helpful
- crystals prone to decay in the X-ray beam
  ➔ need a unique set as quickly as possible

Data collection - important factors

Inefficiency can lead to higher redundancy, but

- redundancy is a <u>good</u> thing
- involves equivalent and duplicate reflections
- used to correct data, for example for absorption
- merging can give a better unique dataset

In summary:
a poor choice of parameters may cause problems
but area detector systems are pretty tolerant

At last – the data collection itself

Completely automatic

- the crystal is moved through a small angle
- the accumulated diffracted intensity is recorded
- the angle is incremented to measure a new slice
- this is done to cover up to 180° per run
- usually several runs for a full frameset

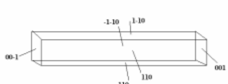
Monitoring crystal decay

Monitoring crystal decay

- at end of collection, re-record some initial frames
- compare the intensities, if necessary apply correction
- with LT and rapid collection, significant decay is rare

Record crystal properties (before collection?)

crystal colour
crystal shape
crystal dimensions



index faces for a numerical absorption correction?

A couple of references

- S. L. Barna, M. W. Tate, S. M. Gruner & E. F. Eikenberry, "Calibration procedures for charge-coupled device x-ray detectors", *Rev. Sci. Instrum.* 1999, **70**, 2927–2934.
- S. Ruhl & M. Bolte, "Strategies for data collection on a CCD-diffractometer", *Z. Krist.* 2000, **215**, 499–509.