Quantitative ADF STEM: acquisition, analysis and interpretation

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Abstract. Quantitative annular dark-field in the scanning transmission electron microscope (ADF STEM), where image intensities are used to provide composition and thickness measurements, has enjoyed a renaissance during the last decade. Now in a post aberration-correction era many aspects of the technique are being revisited. Here the recent progress and emerging best-practice for such aberration corrected quantitative ADF STEM is discussed including issues relating to proper acquisition of experimental data and its calibration, approaches for data analysis, the utility of such data, its interpretation and limitations.

1. Introduction
Aberration correction in the STEM allows for the atomic resolution imaging of samples, while the incoherent nature of ADF allows for direct interpretation with a $Z^2$ contrast relationship [1]. More than only taking ‘pretty pictures’, since the 1970’s [2, 3] there have been efforts to quantify this image intensity. Generally, quantitative ADF is taken to mean intensity information and often it is atomic-resolution data that is studied. Spatial information such as peak-position shifts and strain mapping are closely related areas but are only discussed here in the context of error analysis. The mathematics of image normalisation is given in the highlighted literature and instead this review will concentrate on areas of best-practice, experiment design and error analysis in quantitative ADF.

2. The annular dark-field detector
The design of most ADF detectors is fairly similar. To facilitate retraction when not in use, these are usually mounted horizontally with a 45° inclined scintillator attached to a light guide, figure 1 [4]. A hole through the scintillator and light guide (often lined with a metal tube) allows the bright-field electrons to pass to another detector or spectrometer.

Scattered electrons hit the scintillator and are converted to optical photons; this light is guided to a photomultiplier tube (PMT) which amplifies the output signal. The output from the photomultiplier has some dark-level, set by the amplifier brightness (or offset) which is added to the experimental signal; this combined signal is then amplified further by an amount depending on the amplifier’s gain (or contrast) setting. Finally this is integrated over the dwell-time specified by the user and passed through a so-called analogue-to-digital converter (ADC) [5]. The output units are often displayed in arbitrary counts; importantly this should not be confused with electron-counts. Modern detector and amplifier systems are sufficiently sensitive to register single electron scattering impacts [6].
3. Nomenclature and choice of analysis strategy

Quantitative ADF is a rapidly evolving field being developed in several groups; so first a brief mention of some of the most common terms in use. The most basic unit is the ‘arbitrary-counts’ output direct from the ADC. If the detector linearity is acceptable (see later) and a suitable vacuum level is subtracted, then these units will be proportional to the scattered signal. With this arbitrary-counts data either ‘peak-intensities’ can be measured or, because single-pixel measurements are often corrupted by noise, ‘averaged intensities’ from within some small area around the peak can be taken. For isolated atoms mask choice is flexible [7, 8], but in periodic structures this becomes more difficult and may be circles [9], squares [7], or Voronoi cells [10-12]. This last approach of Voronoi cells has the advantage that all image scattering is associated to some atomic column.

Averaged intensities are more robust to noise, but the result depends on the size of the mask used for averaging. For peaked signals (resolved columns) a wider mask results in a lower average, alternatively if units of ‘integrated-intensity’ are used up to a certain point a wider mask gives an increased value beyond which it plateaus [7]; in some cases then choice of mask size may be an issue. To eliminate choosing any mask, fitted ‘Gaussian-volumes’ can be used where peaks in the intensity data are fitted with Gaussian peaks [13]. For thin samples which do not experience excessive beam-broadening, cells and fitted-Gaussians are equivalent [14]. While Voronoi cells are quick to calculate, in thicker samples or where large probe-tails exist fitted-Gaussians may become more accurate.

If contrast ratios [15, 16] or statistical treatments are used [13], no further pre-processing is required, however for comparison with simulation the data must be normalized by the detector sensitivity.

3.1. Comparison with reference image simulation

Perhaps the most direct way to interpret experimental data is through comparison with image simulation. First, experimental data will be normalized by the mean detector efficiency and then some metric such as ‘fractional-intensities’ [9] or ‘locally-averaged intensities’ [10] is measured. Reference data are simulated (carefully matching accelerating-voltage, convergence angle, and detector angles) for a range of sample conditions including thickness, composition, or both, before the same metric is extracted from the simulated images. Comparing experiment to the reference data then allows an assignment on a column by column basis, figure 2.

This direct method is intuitive but has one main drawback; systematic errors are difficult to detect. For example, some errors yield global scaling factors (see Section 9). This means that thickness or composition assignments made purely by comparison with simulated libraries can always find a match.
and the analysis reliability depends purely on the accuracy of the data normalisation. An additional complication is the wide range of simulation software packages to choose from [17-21] (and others) each of which give very similar but sometimes slightly differing results for identical conditions.

Finally, as image simulation may never capture all the subtleties of the experimental data, care must be taken in what metric to perform the matching on. Perhaps the ‘best-practice’ in quantitative ADF is the unit of the ‘scattering cross-section’ [2, 3, 7, 22]. This parameter is robust to magnification, defocus and convergence angle [7], source-size [7], astigmatism and other aberrations [23], scan-noise [24], and small sample mis-tilt [25]. These scattering cross-sections are then principally only dependent on accelerating voltage and detector inner- and outer-angle.

3.2. Statistical interpretation of intensities
Where a large number of nominally identical atomic-columns are within the field of view, it may be possible to statistically decompose the intensities into their underlying grouping (sorted by atomic thickness) using, for example the Integrated Classification Likelihood (ICL) [13]. Figure 3 shows the main stages in this process.

The applicability of this approach is limited by two considerations; the need for a large number of observations per unique thickness, and for the spread of intensities from equal thicknesses to be significantly less than the difference between those of differing thicknesses [27, 28]. However, when these conditions are met, this approach is robust against systematic errors.

4. Variations in detector response
In Section 2 the hardware of the ADF detector was introduced, here the response of the detector and amplifier combination to electron illumination is explored.

4.1. Asymmetry in detector efficiency
Ideally electron scattering to all angles (all points on the detector) should be recorded with equal sensitivity. Unfortunately this is not always the case; the central hole in the scintillator means that light from beyond this less efficiently reaches the PMT. This generally results in a reduced efficiency at low inner angles and can be accommodated via the comparison simulations [20], flux-weighting
Figure 3. Stages in a statistical analysis of ADF data; a) the raw image, b) the ICL analysis of the intensities, c) the intensity data re-plotted as a histogram with the appropriate number of Gaussian components fitted, d) the atom-count assignments based on b) and c), and e) the validation test comparing the experimental assigned counts with simulated intensity data. Figure modified from [26].

[29], or through use of a reduced effective outer-angle [30]. Figure 4 shows a comparison of six of the most common detectors currently used.

| Manufacturer | Company 1 | Company 2 | Company 3 | Company 4 |
|--------------|-----------|-----------|-----------|-----------|
| Detector Map | ![Detector Map](image) | ![Detector Map](image) | ![Detector Map](image) | ![Detector Map](image) |
| Angle Ratio  | 5.47 x    | 3.09 x    | 2.89 x    | 5.91 x    | 2.90 x    | 3.50 x    |
| ‘Flatness’   | 8.9 %     | 6.8 %     | 24.9 %    | 10.4 %    | 9.7 %     | 14.5 %    |
| ‘Roundness’  | 8.2 %     | 5.4 %     | 10.6 %    | 5.4 %     | 28.1 %    | 2.4 %     |
| ‘Smoothness’ | 30.0 % *  | 15.1 %    | 16.3 %    | 18.0 %    | 87.2 %    | 23.2 % *  |
| ‘Ellipticity’| 19.6 %    | 4.8 %     | 8.9 %     | **0.5 %** | 4.3 %     | 13.3 %    |
| Average      | 16.7 %    | **8.0 %** | 15.2 %    | 8.6 %     | 32.3 %    | 13.4 %    |

Figure 4. Comparison of the sensitivity response of six commercially available ADF detectors, evaluated for various performance metrics. Smoothness values marked with an asterisk indicate probable overestimation from sample occlusion or detector burn-in damage. See reference [31] for metric interpretation.
Of course the ideal solution is to improve the detector design and some progress has already been made towards this by physically separating the light-guide from the scintillator and through the introduction of two-material detectors [32].

4.2. Detector response linearity

The term ‘detector linearity’ is a somewhat ambiguous term used to describe several slightly different things. Fundamentally we need to evaluate the ‘detector-plus-amplifier’ combination as a whole, and this depends greatly on the amplifier settings. Ideally the output should respond linearly with respect to brightness [33], but also with respect to gain [6]; lastly, and most importantly, it must be linear with respect to beam-current [34-35]; these three individual linearities are illustrated by figure 5. Also remember, that as scattered electrons falling on the detector are Poisson distributed, not only does the mean-intensity of thick regions need to be below the amplifier’s saturation limit but also the high-count tail of this distribution [5].

![Figure 5. Evaluation of amplifier output linearity with brightness setting (left [33]), with gain setting (middle [6]), and with the current at the detector itself at various gain settings (right [34]).](image)

Once the bounds of linearity are known, and working within these, the operator can set brightness towards the low end and contrast slightly higher (say 35% and 60% respectively for the above plots). This maximises the available dynamic range without risking saturation in thick sample areas.

5. Asymmetry in post-specimen flux-distributions

Having discussed the asymmetry in ADF detectors above, next we must consider the electron distribution which falls on them. Most STEMs are equipped with a CCD in the detection plane and with the ADF retracted these can be used to observe the flux which falls in this plane.

Figure 6 shows examples of these patterns for the most commonly used instrument types. Some show convergent-beam electron-diffraction or Kikuchi like patterns or no texture and this is only a result of the specimen thickness used to generate the high-angle scattering. In all cases the logarithm of the intensity is shown to improve the visibility of the dynamic range which spans around three orders of magnitude. The red circles indicate typical convergence angles of around 10 mrad for uncorrected, and 20 mrad for corrected systems. In all cases an “outer cut-off” can be seen and depending on the instrument is between 130 - 200 mrad [29, 34]. This means that below a certain camera-length ADF outer-illumination-angle will not increase any further [36]. In some cases the edge is bounded with a slightly enhanced intensity; this is thought to arise from the ‘folding-back in’ of even higher angle scattering by the uncorrected residual aberrations in the post-specimen optics.
Figure 6. Various experimental STEM flux maps. Red circles indicate the BF disk (≈ 10 mrad for uncorrected, 20 mrad otherwise).

For uncorrected and probe-corrected instruments this outer cut-off is round; TEM-corrected instruments yield more complicated patterns owing to the additional non-round post specimen lenses in the image corrector [34]. Here the 6-fold hexapoles yield a 3-fold parasitic aberration resulting in a triangular flux pattern in the detection plane; with the addition of an in column energy-filter this is further distorted in one direction (figure 6). For this reason, and because no image simulation packages include the effects of non-round post-specimen lenses, probe-corrected-only instruments are expected to give the best quantitative ADF accuracy.

6. Strategies for recording detector scans
When recording detector efficiency scans two choices need to be made; what current/gain regime to use, and whether to map in real-space or angle-space. In all cases, to avoid any possible effects of variable integration time [6], the same dwell-time should be used for the detector scan and experiment.

6.1. Dropped gain versus dropped current
When imaging total high-angle scattering may be around 10% of the primary beam and is spread across the whole ADF detector. However, ADF normalisation requires a detector sensitivity scan equivalent to 100 % of beam-current. This leaves the operator with a dilemma and a choice, should the detector scan be recorded in so-called ‘dropped gain’ or ‘dropped current’ methods.

In the dropped gain method, the full primary beam is focussed onto the ADF detector [33], where to avoid massive amplifier saturation the gain settings are set very low. To prevent errors arising from gain-non-linearity, this same low gain must then be used for the imaging experiment which may
reduce sensitivity. There is also uncertainty about the behaviour of the scintillator crystal (afterglow, depletion, saturation) with such differing illumination conditions between the imaging and mapping.

In the dropped current method, the amplifier is first optimized for the imaging experiment; then, by either choosing a smaller objective aperture or reducing the strength of the extraction anode, the beam-current is reduced by a factor of around 10. The detector is then mapped with this weaker-beam, and the ratio of beam currents (as measured by either the CCD, or better, a Faraday cup / EELS drift-tube) incorporated in the normalisation analysis [35].

Both are thought to yield roughly similar accuracies; with the dominant error in the dropped gain method being the reliance on the linearity of output across such a wide range of electron dose, and in the dropped current method the precision with which the current ratio can be measured.

6.2. Confocal or swung-beam detector scanning

There are also two choices of geometry for recording detector efficiency scans, the ‘confocal’ or ‘swung-beam’ methods; both are recorded without a sample present.

In the confocal method the post specimen optics are set to refocus the probe in the detector plane (FEI ‘image mode’ or JEOL ‘STEM-align mode”), the scan-deflectors then scan the probe both in the sample plane and the detector plane [33]. Because of post-specimen magnification, confocal detector scans have dimensions of real-space millimetres. Whilst easier to record, scanning in this way passes only a narrow beam through the objective lens (OL) and does not faithfully replicate genuine scattering to the ADF.

Alternatively, the condenser-lens system can be adjusted to produce a cross-over in the back focal-plane of the objective lens and a pencil-beam at the specimen plane; the scan-coils now swing this pencil beam in angle-space through the OL. The scanning angle is calibrated by comparing the scanned-square as seen on the CCD (with ADF detector retracted) against a known diffraction pattern.

Conventional confocal method examples are shown in figure 4; while examples of swung maps for various camera-lengths are shown in figure 7.

In the swung-beam method maps are returned with units of mrad and the effect of the OL bore constriction is directly observed (compare with figure 6). This effect becomes apparent in figure 7 for camera-lengths ≤ 10 cm where the outer-angle is now imposed by the OL-bore rather than the detector hardware [29, 34, 36]. To verify the origin of this ‘cut-off’ effect we can also observe the behaviour of these swung-beam type detector maps while changing various deflectors in the microscope. The bottom row of figure 7 shows composite figure showing the effect of varying image-shift (CLA) and projection-shift (PLA), these were made my recording separate scans at different deflector settings and adding the scans together. Varying CLA (at 8 cm camera-length) the detector and cut-off ring move together, while varying PLA (at 40 cm camera-length) only the detector moves but this is always bounded by the same cut-off. This, taken with the cut-off’s invariance with camera-length, confirms that the origin of the cut-off lies after the CLA deflectors but before intermediate-lenses and PLA, that is, it is caused by the objective lens.

7. Inner and outer angle optimisation

To compare ADF data against simulations, inner and outer detector angles must be precisely measured [29, 33] for each of the required camera-lengths [36]. However, image simulations can also guide experiment design to maximise the precision of the recorded data, figure 8.

For compositional selectivity at fixed thickness the Z” relationship of ADF scattering [1] improves with higher inner angles [37, 38]. However, for light elements scattering to high angles is so weak the finite SNR becomes the dominant source of error so for thickness measurements at fixed composition lower inner angles are preferable [14, 39, 40].
Figure 7. Effect of camera-length (top) and beam-deflectors (bottom) on the swung-beam detector scans. For camera-lengths ≤ 10 cm the outer-angle is truncated and this must be reflected in any reference simulations. Changing image-shift (CLA) translates the apparent position of the whole OL and detector set, while changing projection-shift (PLA) changes only the apparent position of the detector. Green circle is constant in all figures and represents the observed shadow of the inside of the objective-lens bore.

8. Choice of normalisation approach
The significant asymmetry in the performance of ADF detectors cannot be ignored when comparing experiment with simulations; most importantly the effect of the reduced efficiency at the centre where the majority of scattering falls. This introduces a choice for the experimentalist as to whether this hardware defect should be accounted for in the reference simulations or in the experimental data normalisation.

Some simulation packages can accommodate the detector sensitivity profile (DSP) in the creation of the library data [20]; this allows for a simple experimental normalisation to be used [33]. However, this precludes using other simulation codes that cannot introduce the DSP [17-19, 21]. In this case the asymmetry must be accounted for in the normalisation stage by either imposing some artificial effective-outer-angle [30], or more phenomenologically, by weighting the observed detector efficiency (figure 4) by the electron flux distribution (figure 6) [11, 29]. A more in depth discussion of this issue is given in Martinez et al. [29].
Figure 8. Experiment design optimisation study. Left: the probability of error in thickness measurement for a 75 cell slab of SrTiO$_3$ for a fixed electron dose. Right: plot for a fixed 100 mrad outer angle detector were only inner angle can be varied (compare with figure 7). Note the probability of error for fitted image-Gaussians, cross-sections and peak-intensities. Figures modified from reference [14].

9. Considerations on the accuracy of experimental intensities and peak-positions

9.1. Sample tilt
With the exception of small nano-clusters, to obtain atomic-resolution ADF STEM must be recorded close to low-order crystallographic axes. In the theory of electron channelling, where atoms in aligned crystals act as small lenses for the beam (focussing it for those that follow), we can understand this ‘wave-guiding’ effect as keeping intensity on an atomic-column as it propagates through samples far thicker than the probe’s depth of field [41, 42]. The counterpoint then, is that small mis-tilts away from this condition have marked detrimental effects on both image resolution and scattered ADF intensity, figure 9.

Figure 9. Left: simulated ADF images of silicon [110] with increasing tilts. All images expressed in fractional beam current (simulation details and image credit, reference [43]). Right: quantitative assessment of the loss of scattering for mis-tilted crystals of [110] oriented gold. Here a tilt of only 20 mrad yields a 40% drop in scattering (simulation details and image credit, reference [44]).
Experimentally, sample tilts of up to 15 mrad can still yield an atomic resolution image [25, 43] but can lead to a loss of ADF intensity of up to 25% or more [25, 44]. Fortunately it is possible to design the experimental conditions to also be robust to these intensity losses. If an integrated cross-section approach is followed [7], and if the ADF detector inner angles are chosen suitably [25] it is possible to create a ‘tilt plateau’ where the scattering cross-section remains almost invariant to sample tilts for miss-tilts of up to one probe convergence angle [25].

Sample mis-tilt not only affects image-intensity, but can also affect the apparent position of atomic-columns within an image. Often, this effect is neglected, however, where precise peak-position shifts are being measured (oxygen octahedral tilts, cation shifts, etc.) this becomes essential. Consider the data shown in figure 10 [45]. Here the apparent positions of Sr and Ti-O columns shift, but moreover they shift differently from each other. This is shown in the lower graphs for various sample thicknesses; if we consider the 11.3 mrad tilted sample (blue line) an apparent shift of 15 pm may be observed between the two different sub-lattices that is purely a tilt-artefact.

Further if we consider the constant composition with increasing thickness case, such as the Sr column data alone; here a tilt of only 8.5 mrad can yield an apparent shift of up to 20 pm that is approximately proportional to thickness up to around 8 nm. This is relevant for strain mapping of nanostructures, if a reference lattice is defined in a thick region from which lateral strains are measured at a thinner surface region [46].

From figure 10 we might consider a ‘rule of thumb’ that for column positions measurements better than 20 pm, sample tilt must be less than the convergence angle, and for accuracies better than 5 pm this should be less than one-half convergence angle [45].
9.2. Atomic-column ‘cross-talk’
For thicker specimens, beam-broadening within the sample can lead to scattering reaching the detector originating from several Ångstroms to the side of the probe position, figure 11 [7, 15]. It should be noted that while STEM images are recorded as a function of incident probe-position, signal(s) reaching their respective detectors are integrated over the volume of any electron interaction. Figure 11 also highlights the improved robustness to the integrated column (or cell) versus the peak intensity.

Figure 11. Left: Schematic of beam broadening and its effect on column and background intensity (figure credit: [15]). Middle: x-z intensity plot through [110] oriented GaAs sample with the probe positioned over a Ga column (black intensity plot) showing the intensity cross-talk to the nearest As column (dashed red line). Right: equivalent signal integrated laterally over an atomic-column (cell) for the nearest and neighbouring columns for different forms of probe coherence (figure modified from, and probe coherence details in, reference [12]).

While larger objective apertures can improve the diffraction limited probe size, de-channelling begins sooner meaning that optimal experiment design for quantitative ADF requires a trade-off of these considerations [16, 42, 47]. In some cases balancing of the elastic and inelastic contributions to image-intensity can lead to a sample mis-tilt invariant ‘plateau’ in the scattered cross-sections for tilts less than or equal to the convergence-angle [25]. This gives the experimentalist a very useful operating range of acceptable mis-tilt and again should be considered in the experiment design.

9.3. Strain contrast
Many materials are interesting because of their imperfections such as interfaces, grain-boundaries [48] and dislocations [49], many of which are accompanied by appreciable strain. These strains distort crystal planes and affect the electron-channelling behaviour and hence image contrast; this often increases image intensity in low-angle ADF images at the expense intensity in the HAADF, figure 12.

The precise role of strain in ADF contrast is not yet fully understood, but it is important to be aware of because it is often a manifestation of some other underlying effect such as varying mis-tilt or composition at interfaces [50, 51], each of which would also need to be reflected in any reference simulations.
Figure 12. Effect of strain on HAADF (a) and LAADF (b & c) images of SrTiO$_3$. The HAADF image (inner-angle = 35 mrad) is very sensitive to mis-tilt across the interface but also shows darkness in the strained regions between dislocations, while the LAADF (inner angle = 17 mrad) shows brighter contrast in these places (figure credit: reference [48]). Probe convergence angles was 9 mrad in both cases.

9.4. Amorphous layers and carbon background
For free-standing samples amorphous layers can often persist with even the most careful sample preparation, whether they are from focussed ion beam damage or from carbon contamination from within the microscope itself. Equally for samples supported on thin carbon (or other) membranes, the effect of this ‘second sample’ cannot be ignored [28]. In either case, and depending on defocus, they may appear invisible (figure 13) but still contribute to the quantitative image intensity [47, 52].

In figure 13, though it appears that little resolution is lost by under-focussing through the amorphous layers (last row of panels), this amorphous material remains and will increase beam-broadening.

If nanostructures are supported on a thin membrane, it may be possible to improve the quantitative analysis by subtracting some image intensity contribution extrapolated from the region outside the particle [28]; however, in other situations amorphous carbon may lead to an unavoidable overestimate of the sample thickness [47] or a loss of statistical counting precision.

9.5. Electron dose and pixel size
Excessive electron dose will usually cause sample damage [53], however too little dose and the low signal-to-noise ratio caused by excessive shot-noise may make quantitative measurements less precise. Statistical studies are useful for predicting the expected error as a function of dose for different applications such as nanometrology [14, 26, 28], or light element imaging [39, 40]. Recall from figure 8 that for a given fixed dose, the expected probability of error is always bigger for peak-intensity measurements compared with integrated cross-sections. It is often perceived that finer pixel-sampling gives ‘better’ pictures, however these may contain no additional quantitative information content. So long as the sampling is sufficiently high to meet the instrument resolution (say equal or better than twice Nyquist) then additional pixels do not improve the reliability of measurements [7, 28]. Up to 4x Nyquist may be useful when onward reregistration or processing is planned but again, beyond that no additional benefit is conveyed.
Figure 13. Effect of 50% thickness amorphous surface-layers on the contrast recorded in ADF STEM for various sample thicknesses. Note that amorphous layers on the rear-face of the crystal are invisible at all thicknesses. For the amorphous-first case small under-focus again renders this layer near invisible. Full simulation conditions, and figure credit, reference [52].

9.6. Scan noise and scanning distortion
Environmental instability can affect the quality of scanned image data dramatically [24, 54]. The important consideration here is to understand the frequency domain over which any environmental disturbance operates (see [55] for a more detailed discussion of frequency ranges). For data recorded sufficiently above the Nyquist sampling limit, high frequency scan-noise in the kHz range may corrupt peak-positions and peak-intensities, however it does not affect the integrated-intensity over an atomic-column. The same cannot be said of low frequency distortions (≈ 0.5 - 3Hz range) and the effect of these on quantitative ADF image intensities remains an important area of research [55].

One approach is to record multiple frames and realign these by cross-correlation [56-58], or to precess the slow-scan direction orientation and apply affine transformations to correct image drift [59]; in either case after averaging these data both improves the SNR and yields a column-position precision of several picometres or better [56, 60, 61]. However, rigid registration and averaging may not mitigate residual low-frequency time-varying environmental distortion, and artefacts often remain visible in strain maps [57, 60].

To correct scanning-distortions non-rigid registration must be used, where different regions may be moved by different registration vectors [46, 55, 62]. Approaches like these are able to locally compensate for distortions and to converge a frame-series of data to a ‘reduced-scan-distortion’ single frame. Using non-rigid techniques peak-position precision has improved to ≈ 1 pm levels [46].

9.7. Cold field-emission tip current fluctuation and emission decay
In general, emission fluctuations from cold field-emission type electron sources are monitored and compensated in real time. Where this fails fluctuations in image contrast may result and users should be aware of this when using such systems. Perhaps more important with these systems is to be aware of any emission current decay between the detector mapping and the experimental acquisition [11].
9.8. Summary of sources of error

Table 1 summarises the dominant sources of relative error in quantitative ADF. Not all will apply in all instances and magnitudes will vary with individual systems and experiments.

| Error Source                      | Severity                              | Cause                                      | Solution                                   | Comments                                                                 |
|-----------------------------------|---------------------------------------|---------------------------------------------|--------------------------------------------|--------------------------------------------------------------------------|
| Detector asymmetry                | Global error, up to 15% if ignored with worst case detector [29] | Detector geometry / design [31]            | Improve design / symmetry [32]             | Can be as low as 2% if corrected during normalisation or simulation [29], [30] |
| Sample tilt                       | Local error, up to 10% for peak-intensities, ≈2% for cross-sections, at 5 mrad mis-tilt [7], [44] | Loss of electron channelling condition     | Optimise convergence angle to be more robust to tilt [25], keep tilt ≤ 0.5α | Varies by column, depends on sample thickness                              |
| Detector angle mis-measurement    | Global error, ≈1% error per 1% error in inner-angle, ≈0.2% error per 1% error in outer angle | Errors lead to incorrect comparison simulations | Careful detector angle measurement, including outer-angle / flux cut-off evaluation [29], [33], [34] | Camera-length dependent. Statistical analysis approaches not affected [13] |
| Detector or flux ‘cut-off’ mis-alignment | Global error, up to 3% with shifts of around 10 mrad [30] | Incorrect projection lens settings or de-scan calibration; incorrect image-shift setting | Improve column alignment verify anode wobble centre in Ronchigram | May also cause appearance of astigmatism / peak-shifts [30]                |
| Magnification (pixel width)       | Global error, generally <2%; cross-section error scales with mag error squared [7] | Imperfect scan coil calibration             | Verify calibrations (in x and y) from bulk reference material | Statistical intensity analysis approaches not affected [13]               |
| Scan noise / distortion           | Local error, ≈0-5%, frequency and dwell-time dependant [24], [55] | Environmental instability [54]             | Room design [54], fast-scan and post-processing techniques [6], [55]–[57] | May also affect peak-positions and strain mapping [57], [60]               |
| Shot noise                        | Global error, generally <1% for cross-sections, worse for peak-intensities | Fundamental limit of Poisson distributed intensities [28] | Increase beam-current, dwell-time or number of frames [44] | Error scales with 1/√dose [44]                                           |
| Amplifier brightness / contrast problems | Local error depending on sample thickness, <1% if amplifier adjusted properly [5], [6] | Poisson distribution of counts can lead to ‘pre-clipping’ in thick sample regions [5] | Observe waveform during acquisition, increase brightness or reduce amplifier gain | Up to 10% if brightness too low or gain is too high [5]                    |
| Emission current fluctuation      | Local error, generally <1%, affects bands parallel to fast-scan | Power supply and tip stability             | Fast-scan averaging techniques [55]–[57]   | Cold-FEGs only. Error may become 5-10% if compensation fails               |

10. Example applications of quantitative ADF

Extracting reliable information from quantitative ADF relies on being able to fix as many experimental factors as possible, ideally to leave only one free parameter to explore.

Where thickness is constant (or presumed from extrapolation) quantitative ADF intensity can be used, with extensive simulation, to reveal local compositional variations [10]. It should be noted that in this case the limiting error will be some combination of the reliability of thickness extrapolation, the effects of de-channelling, effects from carbon contamination reducing the image contrast (up to 4% error), and from the simulated reference data (generally better than 1% error contribution). However, for the measurement shown in figure 14, the relatively good SNR of quantitative ADF still yields a lower error than that of atomic resolution spectroscopic chemical mapping approaches which may be as high as 10%.
Figure 14. Experimental ADF image (a) and the integration polygons (b) used to locally average the image intensity (c). Adjusting for thickness, and through comparison with extensive simulation, the resultant In-concentration map (d) at atomic resolution. Figure modified from reference [10].

For fixed composition it is possible to observe changes in thickness or structure, figure 15 [11, 63].

Figure 15. Pt nanoparticle (left) and the scattering cross-section analysis (middle). Atom counts were then used to rebuild a 3D atomic model of the sample (right). Adapted with permission from [11]. Copyright American Chemical Society (2014).

In rare cases, where both thickness and composition can be presumed to remain constant, the quantitative ADF signal can be used to infer the column-occupancy of heavy species [64]. Dynamic processes are special cases of quantitative ADF [11, 63, 64], but make use of the principle that individual images from a frames-series may be scrutinized separately to yield temporal resolution instead of tomography which sacrifices dynamic information to retrieve spatial resolution.

11. Future possibilities in quantitative ADF
The basic geometry of the ADF detector has changed little since its invention; however, several possibilities exist for the future of quantitative ADF with some new detector geometries recently being explored. Perhaps the most simple of these is the ‘quadrant-detector’ ADF, where the annulus has been divided into four quarters. These can be added together to give a classical ADF image or signals from opposite sides subtracted to give a differential phase-contrast signal [65]. Taking this concept
further, multiple annular rings (themselves each divided into quadrants) can be used, figure 16 [66]. Such a detector allows for a host of sum-, or difference-, images to be synthesized after the scattering data has been recorded, moving experiment design from a pre-imaging to a post-processing regime.

![Figure 16. Left: photograph of a fibre-optically coupled 16-segment detector. Right: example detector geometries available and their associated images of SrTiO₃. Far right: the simultaneously acquired conventional HAADF image. Figure modified from reference [66].](image)

This may allow light elements to be seen in the ABF images, or for strain and thickness / composition effects to be separated.

Taking this concept to its extreme is the use of pixelated detectors which can be used to record all the scattering in the detector plane (figure 17). This yields flux-patterns similar to figure 6, including Kikuchi patterns for thicker samples [67], but has the advantage of a homogenous detection efficiency through applying a conventional CCD gain-reference.

![Figure 17. Left: example pixelated detector readout. A beam-stopper was used to mask the BF-disk. Bright points indicate individual electron scattering events. Right: example images synthesized from the 4D dataset, the integrated ADF signal (arrows indicate the position of a twin-boundary) and synthetic LAADF and MAADF images where the edge region appears bright and dark respectively.](image)
With CCD technology dynamic range is an issue, making it difficult to record both the BF and DF regime; also frame-speed, as the whole detector-plane-image must be read-out at every real-space probe position. In figure 17 a beam-stopper was used to mask the BF disk, however this contains much useful sample information [68]. There also exist possibilities for detectors in other planes [69].

In the coming years the development of quantitative cross-sections for analytical signals such as EELS [22] and EDX [12, 70, 71] is expected, as well as hybrid solution engines that combine the complimentary robustnesses of simulation-comparison and statistical-interpretation based quantification techniques. These advances may allow for the combined measurement of both composition and thickness variation at atomic resolution. Further improvements may also be possible in the detector and objective lens hardware design. It is certainly expected that error-analysis driven experiment design will mature as a field to deliver the best possible results from the powerful aberration corrected STEM.

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