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MEASUREMENT UNCERTAINTIES OF ENERGY DISPERSIVE X-RAY SPECTROSCOPY IN THE SCANNING ELECTRON MICROSCOPE (SEM-EDX/EDS)

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Advanced Engineering Materials

ABSTRACT

Fully quantitative elemental composition measurements using energy dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDX) are only possible for elements with an atomic number of at least 11, in samples which meet stringent requirements, and where elemental standards of well-known composition and similar chemistry are available. In practice, is often not possible to meet these criteria and low atomic number samples are increasingly requiring analysis; in these cases, qualitative or semi-quantitative EDX results can still be useful. This report describes the detector and system checks and corresponding measurement uncertainties using both conventional standards and a low atomic number ionic liquid standard containing only light elements with well-known composition. Example use cases for quantitative, semi-quantitative and qualitative EDX measurements are described and lower bound uncertainties estimated. A decision tree is provided to guide good practice in experimental approach and data analysis.

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Approved on behalf of NPLML by
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Glossary/Abbreviations

SEM	Scanning Electron Microscope
EDS or EDX	Energy Dispersive X-Ray Spectroscopy
Z	Atomic number
k-ratio	Ratio between the intensity of a characteristic X-ray peak in the sample and the peak intensity of a similar pure element

1 INTRODUCTION

Energy dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDX or SEM-EDS – the terms are generally used interchangeably) can be used to characterise elemental compositions with a spatial resolution of around 1 – 5 µm.

EDX can be quantitative or qualitative. Qualitative EDX analysis is the most flexible and has fewest requirements. Fully quantitative EDX has stringent experimental constraints and requires elemental standards, but can measure elemental compositions with ± 5 % relative uncertainty. Standardless analysis methods are often described as 'semi-quantitative'; they are more flexible in terms of experimental requirements but the uncertainties are greater at up to ± 30 % relative uncertainty, and in the case of normalised standardless analysis, large errors may be hidden in a plausible output value [1], [2].

International Standards covering analysis and quantification by EDX include ISO 15632:2021 [3] which covers measurement of the EDX spectrometer efficiency and resolution, and ISO 22309:2011 [4] which describes how to perform quantitative EDX, specifically limited to elements with atomic numbers (Z) > 11 (Na and above).

Light element quantification by EDX has greater uncertainty and additional uncertainty sources, such as increased X-ray absorption within the sample, particularly if higher-Z elements are also present, and increased sensitivity to surface topography [5]. This is why the quantitative analysis procedure in ISO 22309:2011 is considered applicable only for elements with Z > 11. However, the commercial need for EDX measurements is increasing for low-Z materials such as battery electrodes (carbon), organic materials (carbon, nitrogen, oxygen), and semiconductor devices (silicon).

Therefore, this report looks specifically at quantitative EDX measurements and uncertainties of an ionic liquid, a low-Z standard material with known composition, to provide lower-bound uncertainty values for what to expect with quantitative EDX on low-Z materials. To put these values into context, the report also describes qualitative measurements on a low atomic number sample, and quantitative and semi-quantitative measurements on a Fe/Cr/Ni certified reference material i.e. a much higher atomic number based sample.

The remainder of this section briefly considers the background to the requirements for qualitative, semi-quantitative and quantitative analysis. Figure 2 then lays out, in a decision tree format, which EDX analysis methods are possible for different use cases. Section 2 describes the samples used in this report and gives examples of experimental acquisition of datasets using two different EDX systems, called in this report System A and System B. Section 3 then provides analysis of data sets and composition uncertainties for each analysis method. The results are shown without attribution to the different detector systems as samples were not necessarily analysed under identical conditions, or by both systems, so comparisons would not be appropriate. Appendix 1 lists the specifications of the NPL EDX systems used in this report.

1.1 QUALITATIVE EDX METHOD OVERVIEW

When electrons of sufficient energy hit a sample, they generate X-rays of specific energies characteristic of the elements present. The main challenge of qualitative analysis is to ensure that all X-ray peaks are detected and correctly labelled as a sample element or a detector artefact peak. The intensity of the X-ray peaks are not interpreted, although in complex or noisy spectra, low intensities may cause low concentration elements to be missed. Accurate qualitative EDX is a prerequisite of any quantitative EDX.

An example of a periodic table that lists the characteristic X-ray emission energies (Kα, Lα, and M peaks) for each element can be found at: https://www.edax.com/resources/interactive-periodic-table. X-ray techniques with higher energy resolution, such as X-ray photoelectron spectroscopy (XPS) or SEM wavelength dispersive X-ray spectroscopy (SEM-WDS) can split these into multiple lines (e.g. $K\alpha_1$, $K\alpha_2$, $K\beta_1$, etc.), but since the energy resolution of EDX detectors are usually ≥ 100 eV, only a single broader peak is measured.

Elemental assignment of X-ray peaks might be ambiguous if the peaks from multiple elements have similar energies (within 30 eV of each other). ISO 22309:2011 Annex B lists groups of elements with ambiguous X-ray peaks.

Electrons can only generate characteristic X-rays with considerably lower energy than the primary electron energy. The ratio between the incident electron energy and the characteristic X-ray energy is called the electron overvoltage. An electron overvoltage of at least 1.8 is specified for quantitative analysis in ISO 22309:2011. It is not absolutely required but still recommended for qualitative analysis, as X-ray peaks close to the primary electron energy may be hidden or very weak. It is impossible to generate X-rays that have a higher energy than the primary electron energy.

Artefact peaks are not characteristic X-ray peaks of the sample. They need to be identified and corrected. EDX analysis software packages generally have features built in to do this, but it is still the operator’s responsibility to check that this has been done correctly and no peaks have been mislabelled.
Sum peaks (also known as **pile-up peaks**) happen when two X-ray photons hit the detector at the same time, and are mistakenly detected as a single X-ray whose energy is the sum of the two original photons. These appear as small peaks at higher energies that are the sum of multiple X-ray emission peak energies, e.g. at double the energy of the highest intensity peak.
Escape peaks are caused by X-ray fluorescence of the detector material, usually made of silicon, so that the detected X-ray energy is the X-ray emission peak. Escape peaks appear as small peaks at higher energies, e.g. at double the energy of the highest intensity peak.
The **noise peak** at near-zero energy is when electronic noise in the detector is mistaken for near-zero energy photons.

1.2 QUANTITATIVE EDX METHOD OVERVIEW

EDX quantification is based on the principle that X-ray peak intensities for an element increase with concentration of that element in a sample. However, there are two problems:

(1) X-ray detector efficiency is not constant, so identical X-ray intensities hitting the EDX detector at, for example, 1 keV and 8 keV will not lead to identical peak areas at 1 keV and 8 keV; and
(2) the generated characteristic X-ray intensities are not linear with concentration, so doubling the atomic concentration of an element does not necessarily double the intensity of characteristic X-rays hitting the EDX detector.

All quantitative analysis considers the characteristic X-ray peaks only, which means it is necessary to remove the intensity contribution of background X-rays generated by Brehmsstralung radiation. Background correction is important in quantification, but different EDX analysis software packages use different methods and this usually cannot be tuned by the user. However, a poor background fit (Figure 1b), which leads to inadequate peak area determination, is still a useful warning sign to the operator that that the quantitative results have high uncertainty.

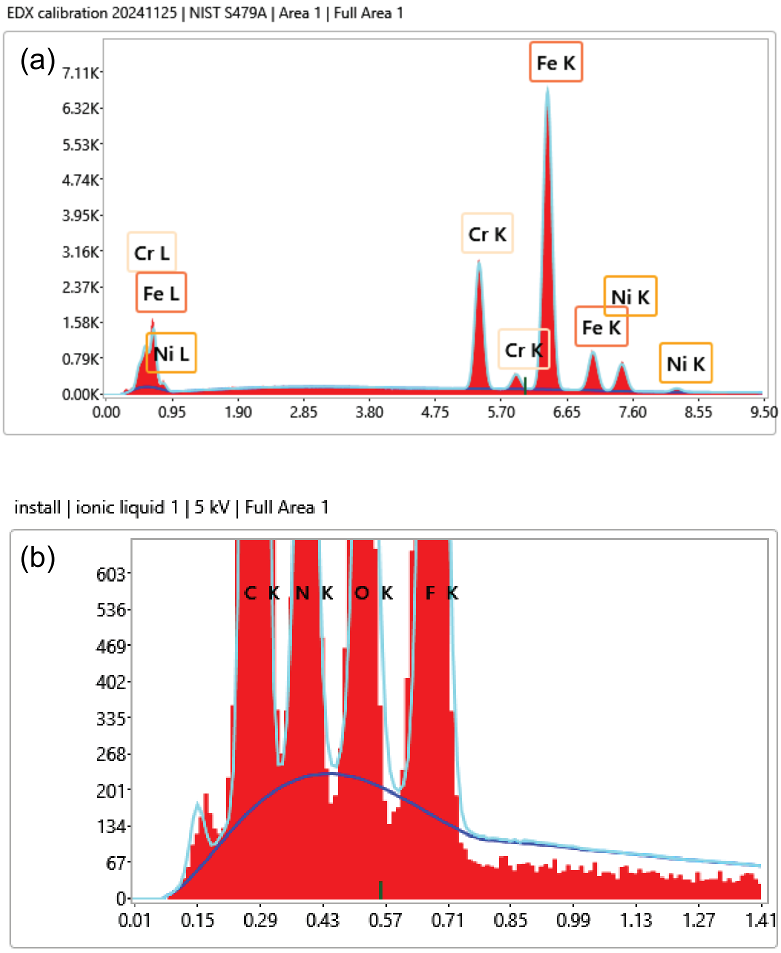

Figure 1: Example spectra with (a) good and (b) bad background fit.

Problem (1) explains why elemental standards are needed for full quantitative analysis, so that differences in detector efficiency can be cancelled out. The detector window material affects detector efficiency, especially in the low X-ray energy range (see Figure 9 in [5]). Beryllium windows absorb the majority of X-rays below 1 keV and therefore are not suitable for use with low-Z elements below Na (Na K = 1.04 keV). Si_3N_4 or polymer thin windows perform better, but the efficiency drops off significantly and is discontinuous in this energy range. Windowless detectors would be preferable but are not currently available at NPL in 2024. Contamination buildup in the SEM can also affect efficiency for all detector configurations.

Problem (2) is why background subtraction and matrix corrections are needed (also known as ZAF corrections: Z = atomic number, A = X-ray absorption, F = X-ray fluorescence). These account for the effects of:

- Electron backscattering (which increases with atomic number **Z**), where incoming electrons are either scattered back out of the sample without generating an X-ray, and electron stopping power, which describes how electrons lose energy (and the corresponding ability to excite atoms and generate X-rays) as they penetrate the sample.
- X-ray **A**bsorption, which means that X-rays generated by the sample are absorbed before they leave the sample and never make it to the detector.
- Secondary X-ray **F**luorescence, which means that high-energy X-rays generated in the sample generate lower-energy X-rays. As a result, the high-energy X-ray is not detected, but extra low-energy X-rays are detected by EDX.

The theory relating to ZAF matrix corrections are more naturally described by weight fractions instead of atomic fractions. This is why EDX compositions are calculated as weight % even though the k-ratios are more naturally expressed in atom %.

Not every X-ray line is in the standards database, so for example the Fe-L peaks (0.705 keV) may not be used for quantification if only the Fe-K peaks (6.403 keV) are included in the database. This must then be taken into account when selecting SEM accelerating voltage – for example, the Fe-K peak requires at least 12 kV electron energy to be adequately excited for quantitative analysis.

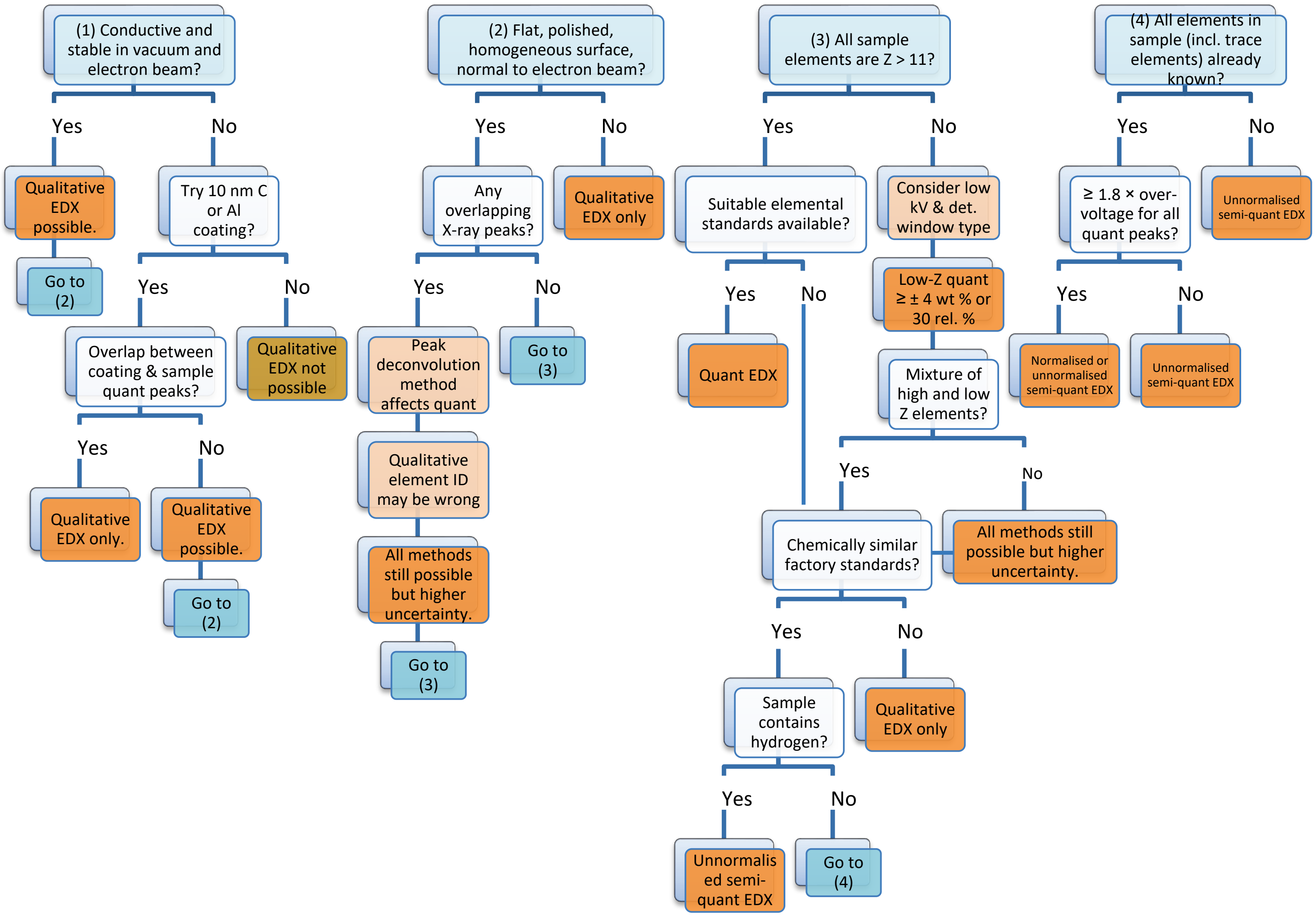

Figure 2: Is quantitative EDX possible on my sample? Decision tree for available methods using SEM-EDX.

2 SAMPLES AND EDX SPECTRA

2.1 IONIC LIQUID PMIM NTF2

Ionic liquid 1-Propyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, or PMIM NTf2 for short has chemical formula $C_9H_{13}F_6N_3O_4S_2$. This was developed by BAM (Bundesanstalt für Materialforschung und -prüfung) for a quick check of EDX detector efficiency and energy scale calibration in the low-energy range [6]. Since the sample is a liquid, it has a constantly renewed and flat sample surface.

The NPL Surface Technology group have also worked with BAM to use X-ray photoelectron spectroscopy (XPS) to measure the composition of this material [7]. XPS measures directly the atomic fractions excluding hydrogen, whereas EDX measures weight fractions so that 100 weight % includes hydrogen, but the hydrogen fraction cannot be measured. XPS and EDX measure different quantities in different units even though both spectra are related to electron orbital transition energies per atom, because the ZAF correction factors required for EDX, described in Section 1.2, are based on weight fractions, not atomic fractions.

The nominal composition determined by stoichiometry is shown in Table 1. Hydrogen contributes to the weight fraction but does not scatter X-rays, therefore is not measurable by EDX.

Table 1: Stoichoimetric elemental composition of ionic liquid PMIM NTf2, and atomic fractions measured on the same material using XPS [7].

Element	Atomic Mass	Num. atoms	Weight %	Atom %	Atom % excl. H	Atom % from XPS
C	12	9	26.7	24.3	37.5	37.98
N	14	3	10.4	8.1	12.5	11.68
O	16	4	15.8	10.8	16.7	15.37
F	19	6	28.1	16.2	25.0	25.36
S	32.1	2	15.8	5.4	8.3	9.61
H	1	13	3.2 (0 in EDX)	35.1	-	
Total	405.2	37	100	100	100	
Total (EDX)	-	-	96.8	-		

Figure 3 shows four EDX spectra of the ionic liquid sample acquired using System A. All spectra were acquired using 5 kV electrons, a mid range pulse process/amp time (different systems have different names for this parameter) setting, and 120 s live time, but different EDX detector energy channel bin widths (5, 2.5, 2.5 and 10 eV for Spectrum 1, 2, 3 and 5 respectively). The peaks are broader and ~ 20% shorter for Spectrum 5 with 10 eV bins, but the other three spectra are very similar.

All X-ray peaks were observed at the expected characteristic energies for the C-K, N-K, O-K, F-K, S-K and S-L lines, which means the detector energy scale is well-calibrated for the range below 3 keV.

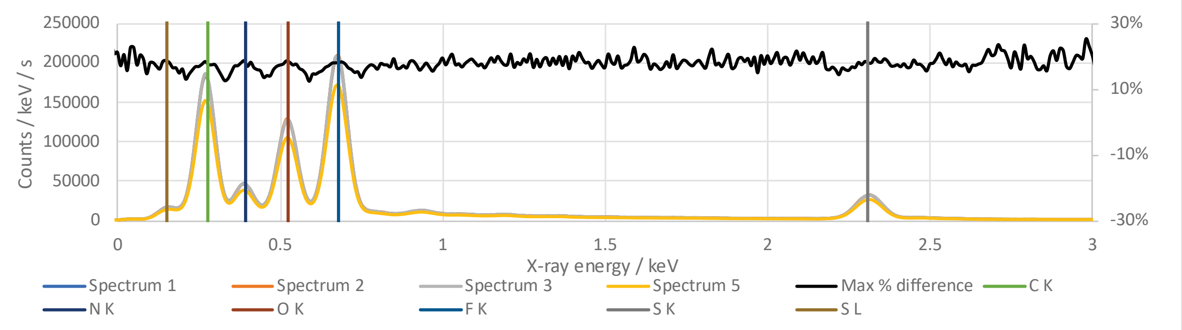

Figure 3: EDX spectra of the ionic liquid sample acquired with 5 kV electrons. These spectra were used for quantitative analysis in the examples in this report. The black line is plotted on the right hand side vertical axis and shows the maximum percentage deviations between the four spectra.

Figure 4 shows seven EDX spectra of the ionic liquid sample acquired using System B, this time comparing 5, 10 and 20 kV electrons. All spectra were acquired using a mid-range pulse process/amp time, and a range of live times between 2.4 and 43.2 s. The X-ray peak intensities depend strongly on electron energy between 5 (purple), 10 (orange) and 20 kV (green), but the live times have only a minor effect on the spectrum count rates.

The energy scale is miscalibrated for < 1 keV X-rays, but correct for energies > 2 keV. This is shown in Figure 4 by a horizontal offset between the expected and measured C-K, N-K, O-K, F-K and S-L X-ray peak energies, but the S-K X-ray peak (2.307 keV) is at the correct position.

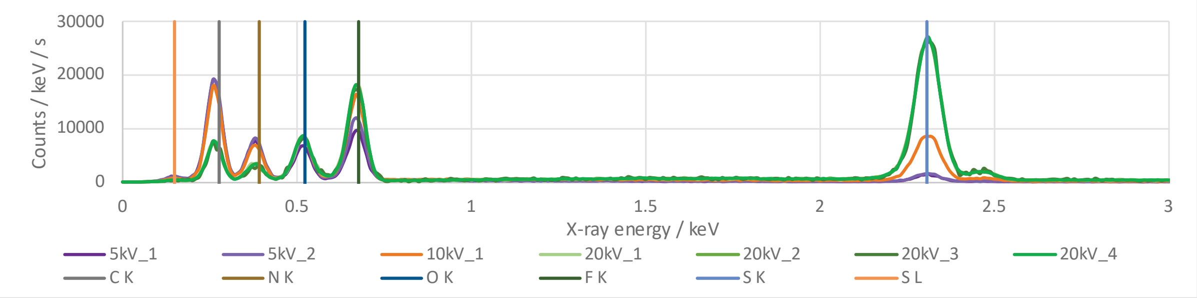

Figure 4: EDX spectra of the ionic liquid sample acquired using 5, 10 and 20 kV electrons (purple, orange and green sets of lines respectively).

2.2 NIST S479A

This certified reference material (CRM) is described in ISO 22309:2011 Annex E. Reference values for its elemental composition were determined by wet chemical analyses, and reproducibility studies were performed between laboratories and within NIST over 8 years. The NIST EDX composition, reported in Table 2 below, is consistent with the EDX compositions measured by EDX in an interlaboratory comparison. Details of both the NIST and interlaboratory comparison measurements are described in ISO 22309:2011 Annex E.

Systematic deviations from the certified composition values are attributed mainly to inadequate fluorescence correction in the ZAF matrix corrections, particularly for Cr, which fluoresces strongly. This error is a limitation of the EDX quantification method. Therefore, in this report, composition measurement uncertainty will be with respect to the NIST EDX composition, i.e. we only consider uncertainties within the EDX method.

Table 2: Composition of standard reference material NIST S479a.

Element	Certified composition wt % ± 1σ	NIST EDX wt % ± 1σ	Absolute Error wt %	Relative Error
Cr	18.1 ± 0.1	19.3 ± 0.27	-1.2	- 6.6 %
Fe	71.0 ± 0.1	70.3 ± 0.27	0.7	1.0 %
Ni	10.9 ± 0.1	10.5 ± 0.10	0.4	3.7 %

Figure 5: NIST S479a (round) and pure cobalt (rectangle) in a 30 mm diameter Bakelite mount.

The NIST S479a sample at NPL was mounted in bakelite along with a pure cobalt sample polished, and carbon coated. The carbon coating thickness is not known.

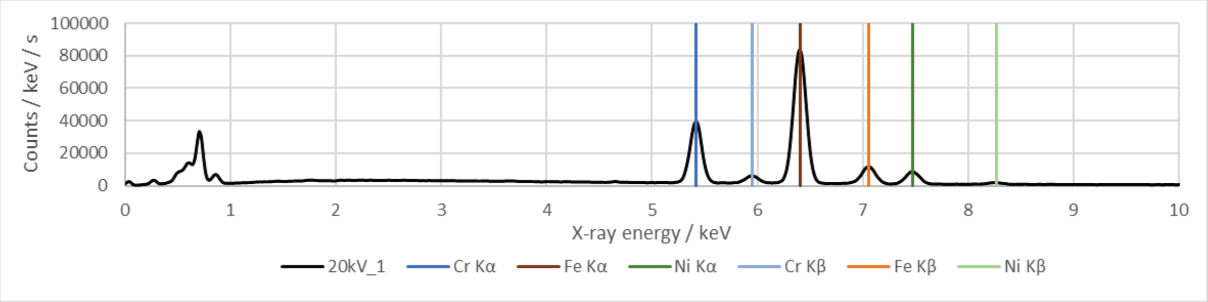

Figure 6: EDX spectrum of the NIST S479a sample acquired with System A using 20 kV electrons.

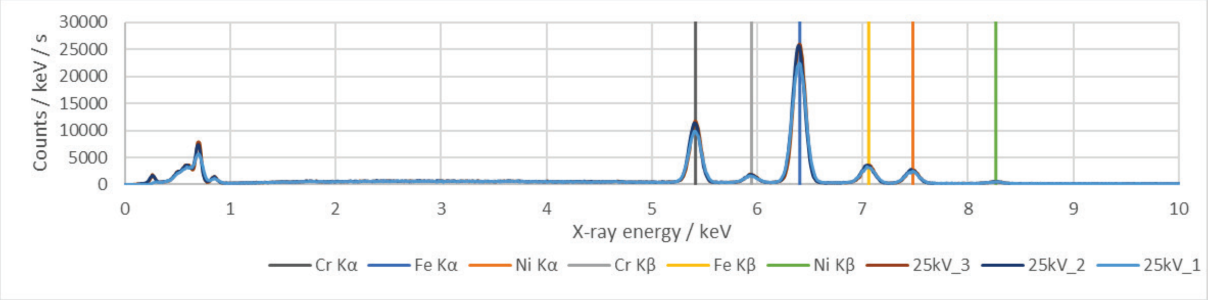

Figure 7: EDX spectra of the NIST S479a sample acquired with System B using 25 kV electrons. The spectra were acquired with different detector speeds amp/pulse process times but all total 30 seconds live time. Pulse process/amp times quadruple between each of 25kV_1, _2 and _3. The energy resolution is slightly worse at faster detector speeds/shorter process times but the effect of peak broadening on quantification is minimal in this case as there is no peak overlap.

3 EDX ANALYSIS METHODS

This section describes the application of the four analysis methods: qualitative, semi quantitative (normalised and un-normalised), and quantitative, in order of increasing experimental requirements, to low atomic number samples. It compares these results with equivalent high atomic number samples.

3.1 QUALITATIVE ANALYSIS

Often qualitative compositional information is sufficient, or the sample or experimental contraints means that quantitative analysis is not possible. Use-cases include: simultaneous electron backscatter diffraction (EBSD) and EDX mapping, analysis of particles deposited on a substrate, fracture surfaces and microstructural features smaller than the X-ray generation volume of 1 – 5 µm, such as secondary phase particles or thin epitaxial layered structures.

Table 3. Experimental requirements for qualitative EDX analysis.

	Sample / standards	**SEM-EDS system**
Required	Feature of interest is within 1 – 5 µm of the sample surface.	SEM accelerating voltage – electron energy is greater than the X-ray peak energy for all elements.
Recommended	All candidate elements are already known. Sample is stable under electron beam and vacuum.	SEM accelerating voltage – electron energy is at least 1.8 × X-ray peak energy for all elements. Windowless, polymer, or Si3N4 window EDX detector for light element detection ($Z \leq 11$) Energy-scale calibration according to ISO 22309:2011 and manufacturer instructions.
Not required	Flat, polished sample surface Homogeneous through interaction volume	Sample surface positioned normal to the electron beam and 35° to the EDX detector

3.1.1 Example: sea mussel fibres

Sea mussel fibres are organic materials (H, C, O, N) but potentially contain higher atomic number elements as minor or trace elements. The aim of EDX was to identify which, if any, of these elements were present, and whether they were localised to particular parts of the fibre structure (stems, filaments, plaques). Figure 8 shows an example SEM image of a few sea mussel fibre plaques. The samples were fixed to an aluminium pin stub with carbon tape and coated with 5 nm carbon. This sample is not suitable for quantitative analysis because of its severe topography and sample charging even after carbon coating.

Figure 8: Example SEM image of Seastex sea mussel fibre plaques mounted on carbon tape. The scale bar reads 500 µm.

Figure 9 compares two EDX spectra from the same spot on the sample at both 5 kV and 20 kV. The 5 kV spectrum is useful for confirming the organic primary constituents. However, EDX at a higher electron energy of 20 kV is required to detect higher-Z elements. At 5 kV, only C, O, N, and Si can be identified. At 20 kV, additional X-ray peaks at higher energies corresponding to Br, P, S, Ca and possibly Cl can be identified. (The Cl K peak @ 2.622 keV is ambiguous because it could also be a pile-up peak from S K @ 2.307 + C K @ 0.277 = 2.584 keV).

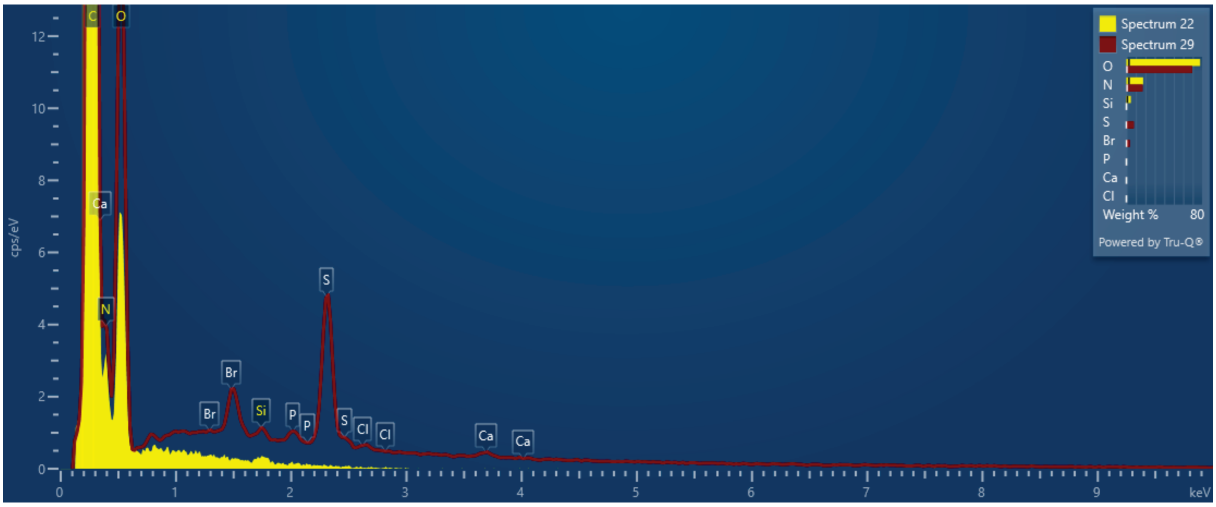

Figure 9: Two EDX spectra from the same region of the Seastex plaque, collected using 5 kV (yellow area) and 20 kV (red line) electrons.

Figure 10 compares the raw, pile-up corrected, fitted (i.e. simulated background plus characteristic peak areas), and theoretical (i.e. simulated from the calculated quantitative composition) spectra. The large deviations between the pile-up corrected (grey), fitted (pink) and theoretical (cyan) spectra confirm that this spectrum is unsuitable for quantitative analysis. Comparison of the raw (green) and pile-up corrected (grey) spectra shows that the small grey peak at 0.8 keV is an artefact from insufficient pile-up correction (C_K @ 0.277 + O_K @ 0.523 = 0.800 keV) and should not be assigned to an element.

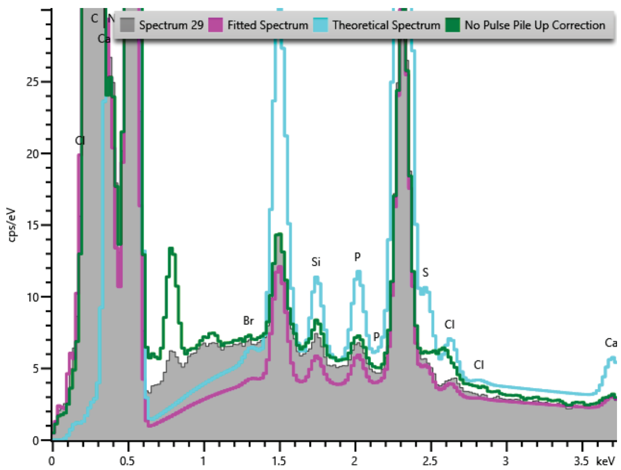

Figure 8: Low-energy part of the 20 kV EDX spectrum of Seastex plaque: before and after pile-up correction (green line and grey area respectively), after peak area fitting (pink line), and theoretical spectrum expected from the calculated composition (cyan line).

3.1.2 Example: Ti substrate coated with Pt particles

The aim of this EDX mapping was to distinguish Ti oxide from metallic Pt particles on a sintered Ti substrate with a discontinuous Pt coating, shown in Figure 11 Since Ti readily oxidises in air, any Ti is probably present as a Ti oxide.

This experimental setup was optimised for spatial resolution but not quantitative or even fully qualitative analysis. 5 kV SEM accelerating voltage was chosen here to minimise the X-ray information depth, since the Pt particles are nano-sized (Figure 11a). Figure 11e shows that the Ti-K peak (4.510 keV) is not excited, the Ti-L (0.452 keV) and O-K peak (0.523 keV) peaks are overlapped, and several minor peaks between 0.6 and 2 keV remain unidentified. However, these limitations are not important in this case because EDX maps of the raw spectrum heights at the Ti-L and Pt-M (2.048 keV) energies are adequate to distinguish the particle types.

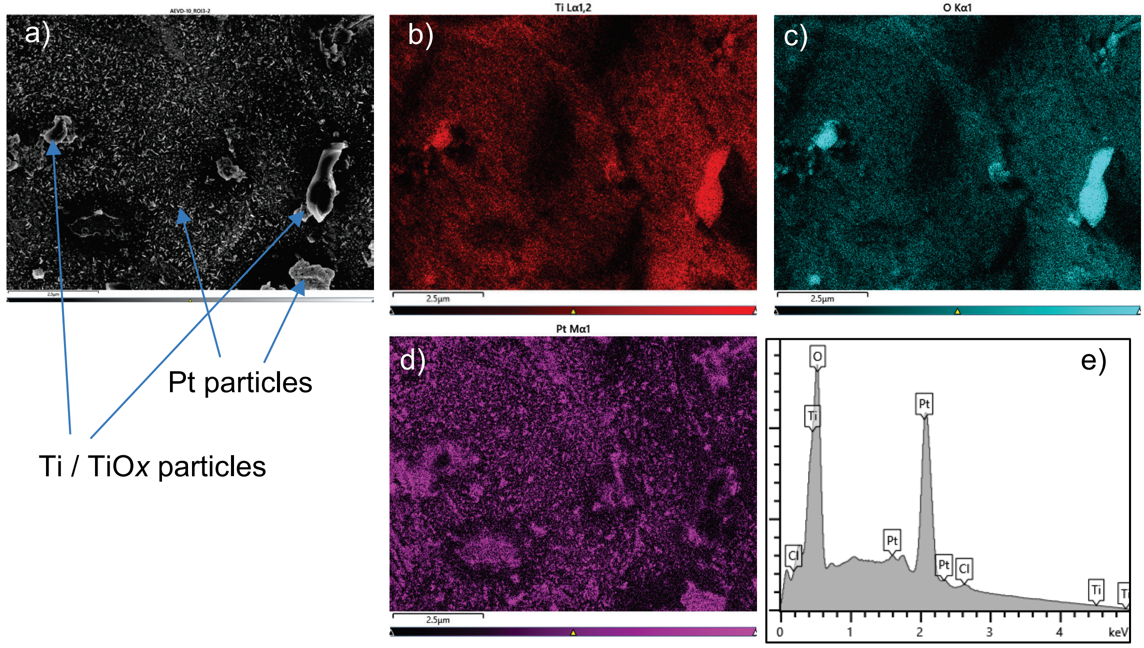

Figure 9: Qualitative EDX mapping of Pt particles on an oxidised Ti substrate. (a) Secondary electron image; (b) – (d) Qualitative color maps of EDX spectrum heights at the Ti-L, O-K and Pt-M X-ray energies respectively; (e) Sum spectrum from all pixels in the map.

3.2 SEMI-QUANTITATIVE – NORMALISED STANDARDLESS ANALYSIS

If suitable elemental standards are not available, databases of X-ray peak areas are available in most EDX software.

Normalised standardless analysis is inappropriate for hydrogen-containing materials, because hydrogen contributes to the mass of the sample but does not scatter X-rays, or where not all elements present have quantifiable X-ray peaks in the acquired spectrum. In these cases the expected total composition is less than 100 wt %.

Table 4. Experimental requirements for semi-quantitative, normalised, standardless EDX analysis, in addition to requirements for qualitative analysis in Table 3.

	Sample / standards	**SEM-EDS system**
Required	Flat, polished sample surface All candidate elements are already known – no hydrogen or unidentified elements Homogeneous through interaction volume	SEM accelerating voltage – electron energy is at least 1.8 × X-ray peak energy for all elements. Sample surface positioned normal to the electron beam and 35° to the EDX detector Energy-scale calibration according to ISO 22309:2011 and manufacturer instructions, e.g. using a Al and Cu standard sample. Factory-supplied k-ratio and matrix correction factor data from elemental standards with similar chemical properties to sample.
Recommended	.All elements for quantification have atomic number > 11	Stable electron beam current
Not required		

3.2.1 Example on NIST S479a

Compositions calculated by the standardless method with the two NPL systems are given in Tables 5 and 6. Since the detector hardware and analysis software methods are constrained to the equipment manufacturer, it is not possible to determine the reasons for the differences in calculated accuracies. The differences could be due to many factors such as differences in spectrum noise, SEM and detector geometry calibration, peak area fitting method, matrix corrections method, or the remote standards database used, but it is not possible to tell which one.

In one case the absolute errors less than or equal to 1 standard deviation of the NIST EDX measurements, and the relative errors less than 2 %. In the second case, calculated compositions have absolute errors of within 1 wt %, and relative errors ≤ 4 %.

Table 5: Measured composition using normalised standardless analysis of a single spectrum of NIST S479a, System A, 20 kV electrons

Element, Quant line	Energy / keV	Measured wt %	NIST EDX wt % ± 1σ	Absolute Error / wt %	Relative error	Factory standard
Cr K	5.414	19.5	19.3 ± 0.27	+ 0.3	+ 1.3 %	Cr
Fe K	6.403	70.0	70.3 ± 0.27	- 0.3	- 0.4 %	Fe
Ni K	7.477	10.4	10.5 ± 0.10	- 0.1	- 0.8 %	Ni
Total		100.00				

Table 6: Measured compositions using normalised standardless analysis, average of three spectra from NIST S479a, System B, 25 kV electrons

Element, Quant line	Energy / keV	Measured wt % ± 1σ	NIST EDX wt % () ± 1σ	Absolute Error / wt %	Relative error	Factory standard
Cr K	5.414	18.7 ± 0.17	19.3 ± 0.27	- 0.6	-3.1%	?
Fe K	6.403	71.2 ± 0.23	70.3 ± 0.27	+ 0.9	1.3%	?
Ni K	7.477	10.1 ± 0.06	10.5 ± 0.10	- 0.4	-4.1%	?
Total		100.00				

3.2.2 Ionic liquid sample and the difficulties of applying standardless calculations.

Normalised standardless analysis is inappropriate for the ionic liquid sample because it contains hydrogen, which means the expected total composition should be 96.8 % instead of 100 %. However, this error turns out to be quite small compared to the scatter between measurements and the absolute error with respect to the stoichiometric composition.

Large uncertainty contributors can be identified by a quick inspection of the EDX spectra, even before any quantitative analysis. These include miscalibration of the X-ray energy scale in the < 1 keV range (Figure 4), and inaccurate background fitting which affects the X-ray peak area measurements (Figure 1b).

Table 7 shows average compositions calculated from the ionic liquid spectra shown in Figure 4 using System B. These spectra were acquired at three different SEM accelerating voltages (5, 10 and 20 kV), which contributed to the large scatter between measurements.

Table 7: Measured compositions of the ionic liquid sample using normalised standardless analysis which misses out hydrogen. No information in the analysis software about what factory standards were used for the calculation.

Element, Quant line	Energy / keV	Measured wt % ± 1σ	Stoichiometric wt %	Error wt %	Relative error	Factory standard
C K	0.277	31.9 ± 4.9	26.7	-5.2	-19 %	?
N K	0.392	13.6 ± 3.3	10.4	-3.2	-31 %	?
O K	0.523	15.4 ± 2.7	15.8	0.4	2.8 %	?
F K	0.677	23.9 ± 5.0	28.1	4.2	15 %	?
S K	2.307	15.3 ± 0.6	15.8	0.5	3.4 %	?
H			(3.2)			-
Total		100	96.8			

3.3 SEMI-QUANTITATIVE – UNNORMALISED STANDARDLESS ANALYSIS

The experimental procedure is more complicated, but is more conservative since errors tend to appear as total concentrations that do not add up to 100 wt %. Therefore, it is required for samples that may contain unknown (trace) elements or hydrogen, where normalised analysis would hide these errors by forcing the total to 100 wt %. This is available only with one of the two systems.

An additional spectrum from a pure element standard such as Co is acquired at the same sample position and beam current as the sample X-ray spectra. The sample preparation requirements are identical to normalised standardless analysis. This is used to normalise the EDX detector geometry and electron beam current with respect to the factory-supplied X-ray peak intensities values. Therefore, the beam current must be stable over the duration of the experiment.

Figure 12 shows example beam current normalisation spectra. The two spectra are almost identical which shows that the beam current was stable (± 0.2 %). Beam current drift during the experiment would appear as a change in the peak intensities.

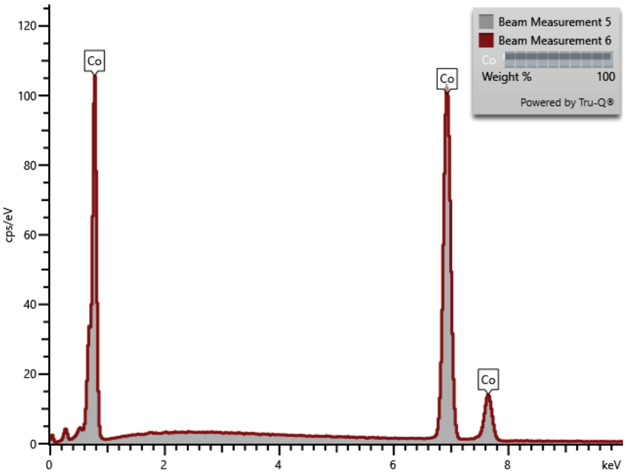

Figure 10: Beam current and detector geometry normalisation spectra from a pure Co sample. The change in beam current between the two spectra, acquired before and after the EDX experiment, was 0.2 %.

Table 8. Experimental requirements for semi-quantitative, unnormalised, standardless EDX analysis, in addition to requirements for qualitative analysis in Table 3.

	Sample / standards	SEM-EDS system
Required	Flat, polished sample surface. Homogeneous through interaction volume Single pure element standard (e.g. Co) for beam current and detector geometry calibration	SEM accelerating voltage – electron energy is at least 1.8 × X-ray peak energy for all elements Sample surface positioned normal to the electron beam and 35° to the EDX detector Energy-scale calibration according to ISO 22309:2011 and manufacturer instructions, e.g. using a Al and Cu standard sample Beam current and detector geometry calibration (‘Quant Optimisation’) in Aztec software Stable electron beam current Factory-supplied k-ratio and matrix correction factor data from elemental standards with similar chemical properties to sample
Recommended	All elements for quantification have atomic number > 11	
Not required	Elemental standards with similar chemical properties to sample	

3.3.1 Example on NIST S479a

Table 9 shows the composition of the NIST S479a sample calculated from a single spectrum (Figure 6) using the unnormalised standardless quantification method.

Table 9: Measured compositions from a single spectrum using unnormalised standardless analysis where all elements are known.

Element, Quant line	Energy / keV	Measured wt %	NIST EDX wt % () ± 1σ	Absolute Error / wt %	Relative error	Factory standard
Cr K	5.414	19.2	19.3 ± 0.27	- 0.13	- 0.7%	Cr
Fe K	6.403	68.7	70.3 ± 0.27	- 1.63	- 2.3%	Fe
Ni K	7.477	10.2	10.5 ± 0.10	- 0.28	- 2.7%	Ni
Total		98.1		- 1.9		

The absolute errors are all less than 2 wt %. The deviation from total 100 wt % (-1.9 wt %) is similar in magnitude to the absolute error. The relative errors are all < 3 %. The absolute errors appear larger here than the normalised analysis results calculated from the same X-ray spectrum (Table 5) because this is a more conservative analysis method that does not hide large uncertainties within the normalisation step.

3.3.2 Example on ionic liquid

Table 10 shows the composition of the ionic liquid calculated using the un-normalised standardless quantification method. All spectra (Figure 3) were acquired at 5 kV under similar SEM conditions but different EDX detector channel bin widths. Similar compositions were calculated from the four spectra. The peak broadening observed in Spectrum 5 with 10 eV bins (Figure 3) did not affect the calculated peak area, as expected for spectra with no overlapping peaks.

The absolute errors are much larger (between 1 and 4 wt % for the low-Z elements). These errors are reflected in the total wt %, which is 86 wt %, 10.7 % less than the 96.8 wt % total expected from stoichoimetry. (In this particular case, the absolute errors also sum to exactly 10.7 wt %, but this is only the case if all the absolute errors have the same sign.) The relative errors are ≤ 30 % for the light elements, and 0.9 % for S (Z = 16), which is consistent with the < 3 % relative error determined from unnormalised analysis on the FeCrNi alloy presented in Table 9.

The factory standard database values, though optimised for EDX at 5 kV, are measured from compounds that are chemically quite different from the ionic liquid. This increases the uncertainty of applied k-ratios and ZAF matrix corrections, since the matrix correction factors depend not only on the element being considered for quantification, but also other elements in the sample and their local chemical bonding environment.

Another uncertainty source is a possible miscalibration of the EDX detector efficiency curve, particularly for X-rays < 1 keV. This seems consistent with the fact that compositions calculated from the lower energy X-ray peaks have higher errors than the sulphur (Z = 16, S K = 2.3 keV).

Table 10: Measured compositions of the ionic liquid sample using unnormalised standardless analysis. The standard deviations are averaged from 4 spectra.

Element, Quant line	**Energy / keV**	**Measured wt % ± 1σ**	**Stoich. wt %**	**Absolute Error wt %**	**Relative Error %**	**Factory standard (5 kV set)**
C K	0.277	25.6 ± 0.13	26.7	1.0	3.9	Pure C
N K	0.392	7.5 ± 0.19	10.4	2.8	27	BN
O K	0.523	13.1 ± 0.12	15.8	2.7	17	SiO2
F K	0.677	24.1 ± 0.16	28.1	4.0	14	CaF2
S K	2.307	15.7 ± 0.09	15.8	0.1	0.9	FeS2
H		-	(3.2)			-
Total		86.09 ± 0.69	96.8	10.7	11	

3.4 QUANTITATIVE – STANDARDS-BASED K-RATIO/ZAF PROTOCOL ANALYSIS

K-ratios can be calculated from X-ray peak intensities of an experimental standard measured under similar conditions within the same experimental session. This cancels out the dependence of k-ratios on beam current, SEM-EDX geometry, and SEM chamber contamination which affects EDX detector efficiency, i.e. it eliminates Problem (1) described in Section 1.2.

One standard is required for every element to be quantified, which should be chemically similar to the sample. This is readily available for NIST S479a as it is a metallic alloy with metallic pure element standards, but not for the ionic liquid sample. Using an elemental standard with significantly different chemistry from the sample introduces additional uncertainties into the matrix correction factors, such as for the ionic liquid sample, as previously discussed in Section 3.3.2 and Table 10.

Fully quantitative analysis with physical standards was only available for one of the systems.

Table 11 Experimental requirements for quantitative EDX analysis using elemental standards, in addition to requirements for unnormalised semi-quantitative analysis in Table 8.

	Sample / standards	**EDS system**
Required	Flat, polished sample surface. Homogeneous through interaction volume Single pure element standard (e.g. Co) for beam current and detector geometry calibration Elemental standards with similar chemical properties to sample	SEM accelerating voltage – electron energy is at least 1.8 × X-ray peak energy for all elements Sample surface positioned normal to the electron beam and 35° to the EDX detector Energy-scale calibration according to ISO 22309:2011 and manufacturer instructions, e.g. using a Al and Cu standard sample Beam current and detector geometry calibration ('Quant Optimisation') in Aztec software Stable electron beam current Factory-supplied matrix correction factor data from elemental standards with similar chemical properties to sample.
Recommended	All elements for quantification have atomic number > 11	Beam current and detector geometry calibration ('Quant Optimisation') in Aztec software
Not required		

3.4.1 Example on NIST S479a

The measured composition was calculated using k-ratios from experimental peak areas measured from pure element standards in a MAC 227 block (Micro-Analysis Consultants Ltd. standard block containing 40 standard pure elements or compounds in a brass mount). Table 12 shows that relative errors of < 1 % with respect to the NIST-measured EDX composition can be achieved using this method. (This excludes the 3 – 7 % relative uncertainty with respect to wet chemical analysis due to uncertainty in the ZAF matrix correction factors).

Beam current stability (0.2 % variation) was checked using spectra from a pure Co standard acquired before and after all other EDX measurements. All spectra were acquired within 20 minutes in the same experimental session.

Table 12: Measured compositions using quantitative analysis with pure element standards.

Element, Quant line	Energy / keV	Measured wt %	NIST EDX wt %	Absolute Error / wt %	Relative error %	Factory standard
Cr K	5.414	19.5	19.3	0.17	0.9%	Cr
Fe K	6.43	70.6	70.3	0.28	0.4%	Fe
Ni K	7.477	10.6	10.5	0.05	0.5%	Ni
Total		100.6				

4 SUMMARY OF EDX MEASUREMENT UNCERTAINTY

The numbers in Table 13 are the maximum relative uncertainties from the results presented in this report. Since only a small number of near-ideal samples and spectra have been analysed, we cannot claim statistical significance. The numbers are guidelines to provide a lower-bound EDX uncertainty for different material types and analysis methods.

Table 13: Guideline uncertainties for (semi-)quantitative composition measurement of low-Z and high-Z samples using the three quantification methods described in this report.

Relative uncertainty	Normalised standardless quantification	Unnormalised standardless quantification	Quantification with physical standards	+ Matrix correction factors uncertainty
Z < 11	30 %	30 %	N/A	?
Z ≥ 11	4 %	3 %	1 %	+ 3 – 7 %
	Uncertainty is not conservative – errors are cancelled out during normalisation.	Uncertainty can be estimated from the measured un-normalised total wt %.	Most accurate but suitable standards not always available.	Applies to all EDX quant methods.

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APPENDIX 1 - EDX SYSTEMS AT NPL

EDAX Octane Elect

- Mounted on ThermoFisher Apreo 2 S LoVac SEM
- Silicon nitride window
- Silicon drift detector with 10mm^2 detector area
- APEX 3.0 software (updated from APEX 2.0 in December 2024. The data in this report was acquired using APEX 2.0 and analysed using a mixture of versions 2.0 and 3.0.)
- k-ratio standards database optimised for 10 kV
- Qualitative analysis available
- Normalised standardless analysis available
- Unnormalised standardless analysis not available
- Analysis with physical elemental standards not available

Oxford Instruments XMAX80

- Mounted on Zeiss Auriga-60 SEM
- ‘Super atmospheric thin window’ (SATW)
- Silicon drift detector 80mm^2 detector area
- Aztec 6.1 software
- k-ratio standards database optimised for 5 kV and 20 kV
- Qualitative analysis available
- Normalised standardless analysis available
- Unnormalised standardless analysis available (single pure-element standard required for beam and detector calibration, usually Co)
- Analysis with physical elemental standards available