

User Manual for eRDF Analyser v1.0 (2017)

eRDF Analyser is an interactive and integrated tool for electron reduced density function analysis. This tool allows users to input an electron diffraction pattern (obtained from a TEM) and guides them interactively through the process of fitting and extracting the reduced density function (RDF) for their material. It currently works for material compositions with up to 5 elements.

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This tool is available as open source code and in open executable form (both covered under the terms of the GNU General Public License version 3). We ask that you cite the following paper, “eRDF Analyser: An interactive GUI for electron reduced density function analysis” (in preparation) if you use output from this program in your own work.

1 Introduction to RDF analysis

In statistical mechanics, a pair correlation or distribution function (PDF) describes the probability of finding a neighbouring particle at a distance r from a reference particle. Radial distribution function is an example of such a function, which is experimentally accessible through diffraction experiments using X-rays, neutrons or electrons. This enables characterisation of structural order of material systems e.g. defects in crystals, nanocrystallinity or medium-range order in nanoparticles, and short-range order in amorphous materials or glasses.

While diffraction data from X-rays and neutrons has been widely used in PDF analysis with the exception of synchrotron techniques, their scattering cross-section is too small for the study of atomic short-range order within nanovolumes of materials. Electron diffraction is particularly useful in this regard. Radial distribution function and its associated reduced density function (RDF) analysis of electron diffraction intensities or electron energy loss spectra can provide information on average interatomic distances and average coordination.

The theoretical basis of RDF extraction from experimental electron diffraction data, as performed by the eRDF Analyser software, is presented in the manuscript (in preparation).

2 About eRDF Analyser

Although there are a few other available packages which can perform RDF analysis on electron diffraction patterns, their dependence on host software platforms may present compatibility issues; the use of automated procedures also lacks the ability to fine tune the application to specific needs. eRDF Analyser was developed in-house to allow high degree of flexibility and customisation of the analysis on an alternative platform. It also takes into account most recent developments in parametrisation of atomic scattering functions. It is now freely distributed as an integrated GUI written in MATLAB which allows users to start from an initial diffraction pattern and obtain the RDF without having to use other routines. The output from eRDF Analyser can be directly used as input into Reverse Monte Carlo (RMC) software for refinements of atomic models based on diffraction data. This version only produces the RDF $G(r)$ and not $J(r)$.

2.1 Features available in eRDF Analyser v1.0

- Accepts text input of entire electron diffraction pattern or azimuthally averaged intensity
- Allows free-hand customised masking of beam stop and any other anomalies in diffraction pattern
- Colour contour plotting of the diffraction pattern for easy definition of the circles with equal intensity and finding the centre of diffraction pattern
- Optional automated routine to optimise user-defined centre of diffraction pattern
- Azimuthally averages intensity to give experimental $I(q)$
- Also calculates azimuthal variance (to be further developed in future versions)
- Enables optimisation of data range (q -range) for fitting $I(q)$
- Allows choice of parameterisation using Kirkland's updated fitting coefficients¹ or those proposed by Lobato and van Dyck² for elastic electron scattering factors
- Provides an automated fitting of experimental $I(q)$ as a basis for further manual optimisation

2.2 Installation (for standalone packages)

The standalone package requires MATLAB Runtime version 9.0 (2015b) to run. This can be downloaded from <http://www.mathworks.com/products/compiler/mcr/index.html>. After a one-time installation, eRDF Analyser should be able to work similar to any other software program.

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1. Kirkland, E. J. in *Advanced Computing in Electron Microscopy* **40**, 243–260 (Springer US, 2010).
 2. Lobato, I. & Van Dyck, D. An accurate parameterization for scattering factors, electron densities and electrostatic potentials for neutral atoms that obey all physical constraints. *Acta Crystallogr. Sect. A Found. Adv.* **70**, 1–13 (2014).

3 Using eRDF Analyser

3.1 GUI

The software GUI has two panels, ‘Diffraction Data’ (for processing the diffraction pattern and choosing data range) and ‘RDF Plot’ (for fitting and obtaining RDF). At start up, the first panel ‘Diffraction Data’ is displayed by default. The process flow is documented in the following sections.

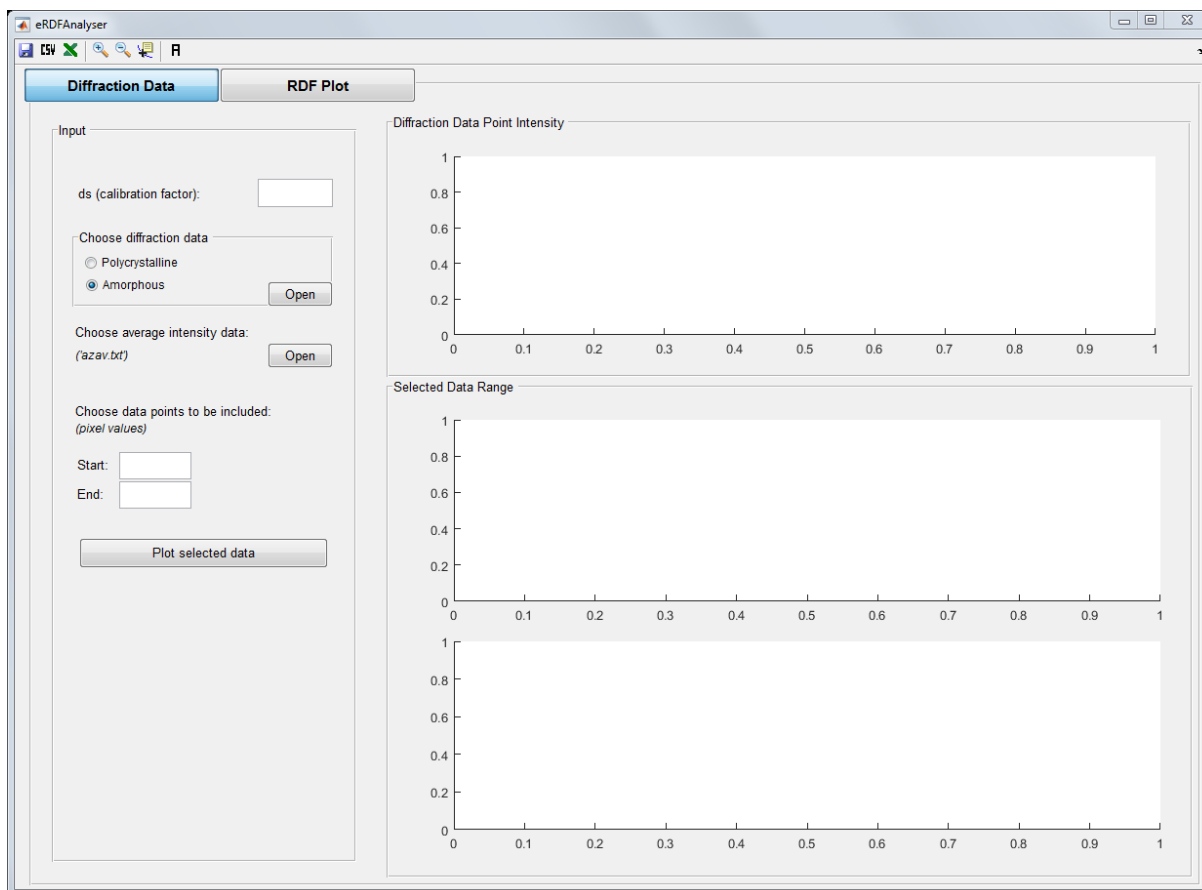


Figure 1: eRDF Analyser GUI Panel 'Diffraction Data'

3.2 Calibration

As mentioned earlier, calibration of the scattering vector is crucial for accuracy of the r values in the RDF $G(r)$. If using a crystalline standard, input the pixel size in terms of reciprocal space (in \AA^{-1}) as the calibration factor. If using a polycrystalline standard, this software allows a workaround (see note in section 3.4) for more accurate determination of the calibration factor. If calibration factor is not available at this point, just input 1 and follow the steps below.

3.3 Input diffraction pattern

Choose the type of diffraction pattern (polycrystalline or amorphous) and open the desired corresponding text file. The software will display the image and ask the user to carry out a sequence of guided actions as below:

1. Optionally apply a median filter to remove salt-and-pepper noise.
2. Draw a freehand ROI to mask beam stop – additional freehand definitions can be used to mask any other distorted areas in the image that could affect the azimuthal averaging. Click and drag continuously to mark the region. If masking is not required, just click anywhere on the image.

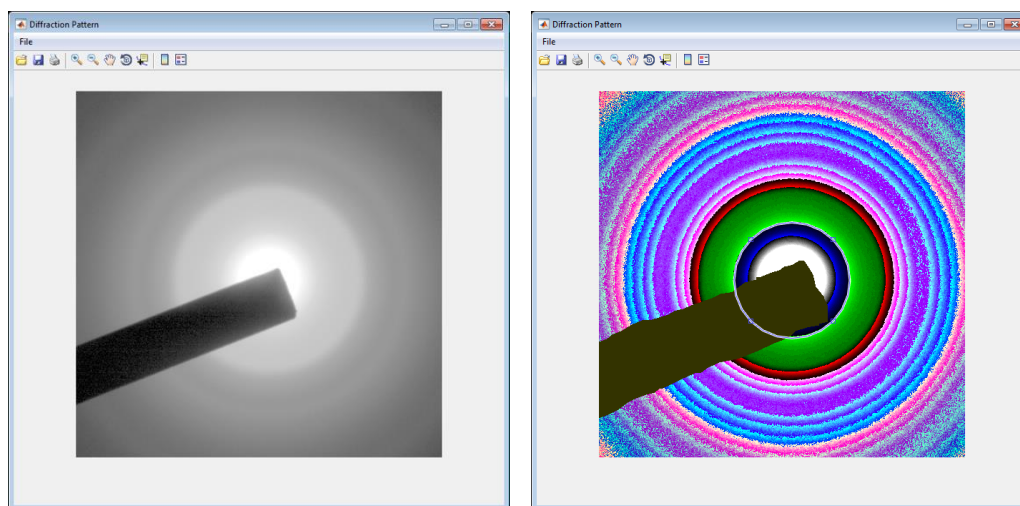


Figure 2: Images of diffraction patterns of amorphous SiO₂ before masking (left); and after masking the beam stop (right) in colour contour mode, with adjustable marker resized and positioned to fit a contour

3. Adjust and resize the circular marker to fit the rings (which will define the centre of the diffraction pattern). The image is displayed in colour contour mode for easier positioning of the marker. Double-click inside the marker once done.
4. Optional optimisation of the centre of the diffraction pattern. For centred polycrystalline patterns, the user is asked to input a value for number of radial projections, distance of contour from edge and size of grid scan (in terms of pixels), or can continue with the default value displayed. The software then generates a concentric circle larger than the initial user-defined circle, such that it does not exceed the field of the diffraction pattern array. A functional that compares line scans of the two opposite sites of radial lines within the two concentric circles is then calculated. For amorphous diffraction patterns (recorded with centred and off-centred beams), the software generates a pair of concentric circles encompassing the initial guess circle and calculates a functional that minimises the sum of azimuthal variance within the limits defined by the circles. In both cases, optimisation of the functional (and the position of the centre) is performed by a grid scan.

If users are reasonably confident of their initial centre definition, decreasing the value of the size of grid scan can result in noticeably faster completion of the optimisation routine. It is our experience that due to colour contour plotting of the diffraction pattern the initial guess in centre definition is fairly accurate and optimisation rarely results in deviation from the initial guess position by more than 5 pixels.

5. The user is then prompted to select a folder to save the subsequent output. Azimuthally averaged intensity and variance plots are displayed – the raw data and plots are saved as text and .png files respectively.

3.4 Input azimuthally average intensity profile of diffraction pattern

Users have the option to directly input the averaged intensity (text file) if they already have the information without averaging the diffraction pattern (DP). If continuing from the previous step, choose the relevant 'azav.txt' file as prompted by the software.

NOTE: If the intensity profile is that of the polycrystalline calibration standard, use the **Data Cursor** tool at the top menu to get the pixel values (x-axis) of the first few peak positions (Figure 3). By dividing the known reciprocal lattice spacings by the respective pixel values, and averaging the results, an average ds value is obtained. The user can now go back and input the sample diffraction pattern as in section 3.3 and continue with the sample analysis.

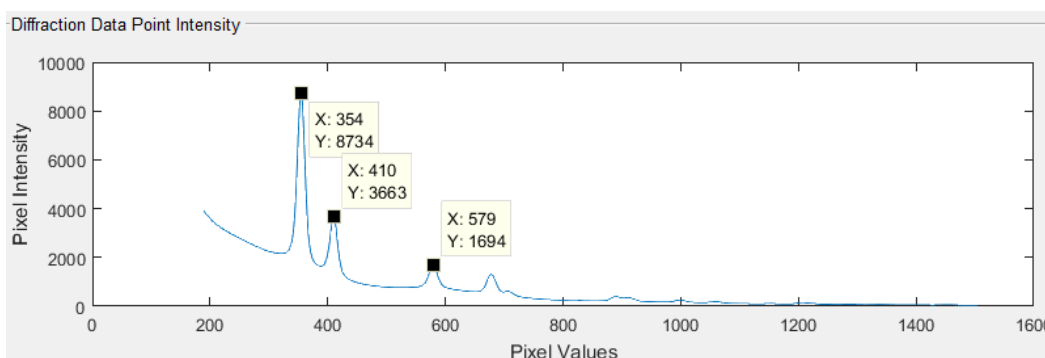


Figure 3: Intensity profile of polycrystalline evaporated aluminium calibration standard

- If using the intensity profile obtained from the previous section 3.3, enter a value of '0' for 'Centre of DP' – this is valid for all intensity profiles which start from the centre of the diffraction pattern. If the user inputs an intensity profile that is central symmetric, corresponding to a scan along a radial line from edge to edge, then enter the size of the diffraction pattern (if 2048 x 2048 pixels, enter 2048).
- The 1-D intensity profile is now displayed in the first plot of the GUI panel in terms of pixels. Using the **Data Cursor** tool at the top of the menu to look at the pixel values, the user is able to choose the pixel range to use in the subsequent steps for fitting, e.g. excluding noisy regions at the edges of the profile. Enter these values in the 'Start' and 'End' fields and click 'Plot selected data' – a magnified view of the beginning and end of the data range is presented in the bottom two plots for further modification. Update the data range by entering the preferred pixel values and clicking 'Plot selected data' again.

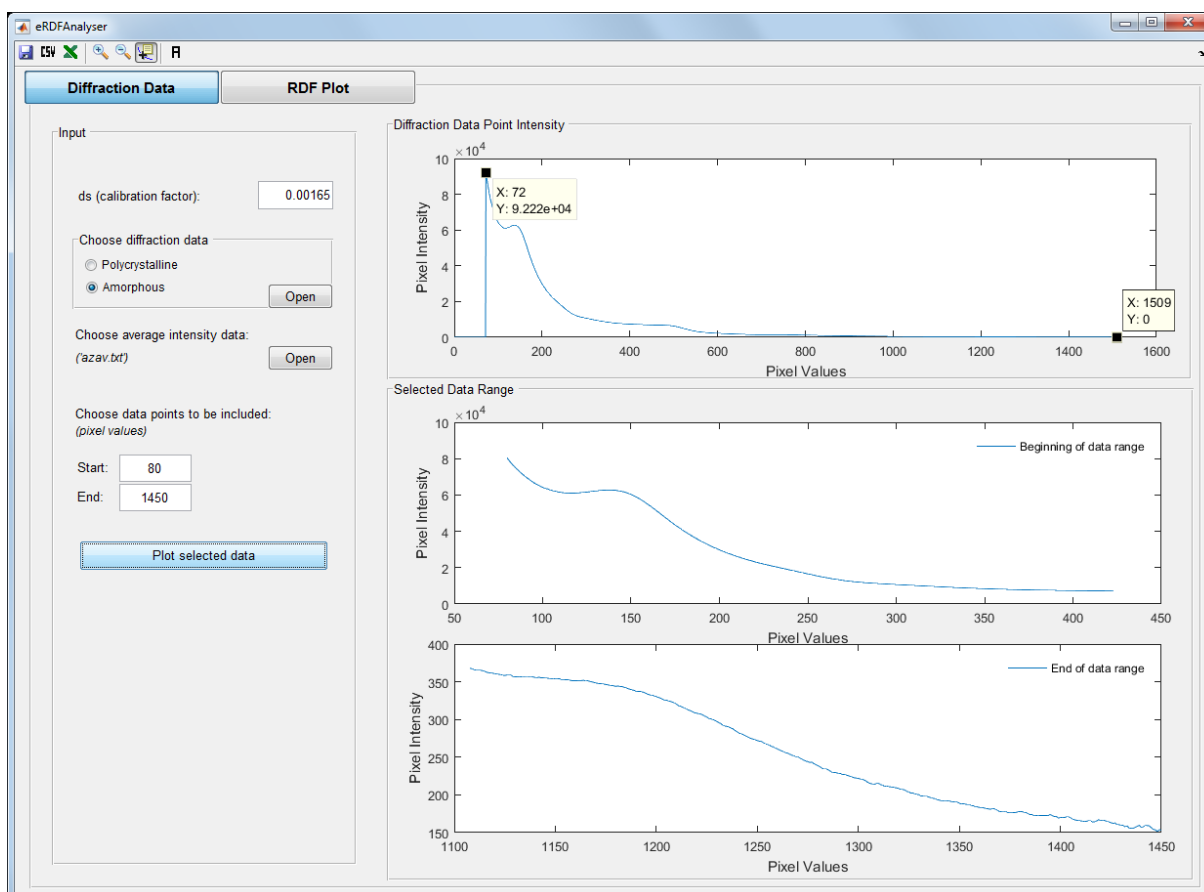


Figure 4: Selection of data points from intensity profile of amorphous SiO₂ diffraction pattern

3.5 Fitting of data

Switch to the 'RDF Plot' panel and click 'Plot selected & calibrated data range'. The calibrated intensity profile should be displayed in the first plot (Figure 5). The default fitting uses Kirkland coefficients but users have the option to use Lobato coefficients instead. Choose the relevant elements present in the sample, choosing 'None' for the rest of the unfilled elements. Input the material composition in terms of atomic ratios. Users can choose to have the software automatically fit an atomic scattering curve to the experimental scattering intensity $I(q)$, with further optional manual optimisation, or to perform manual fitting from scratch.

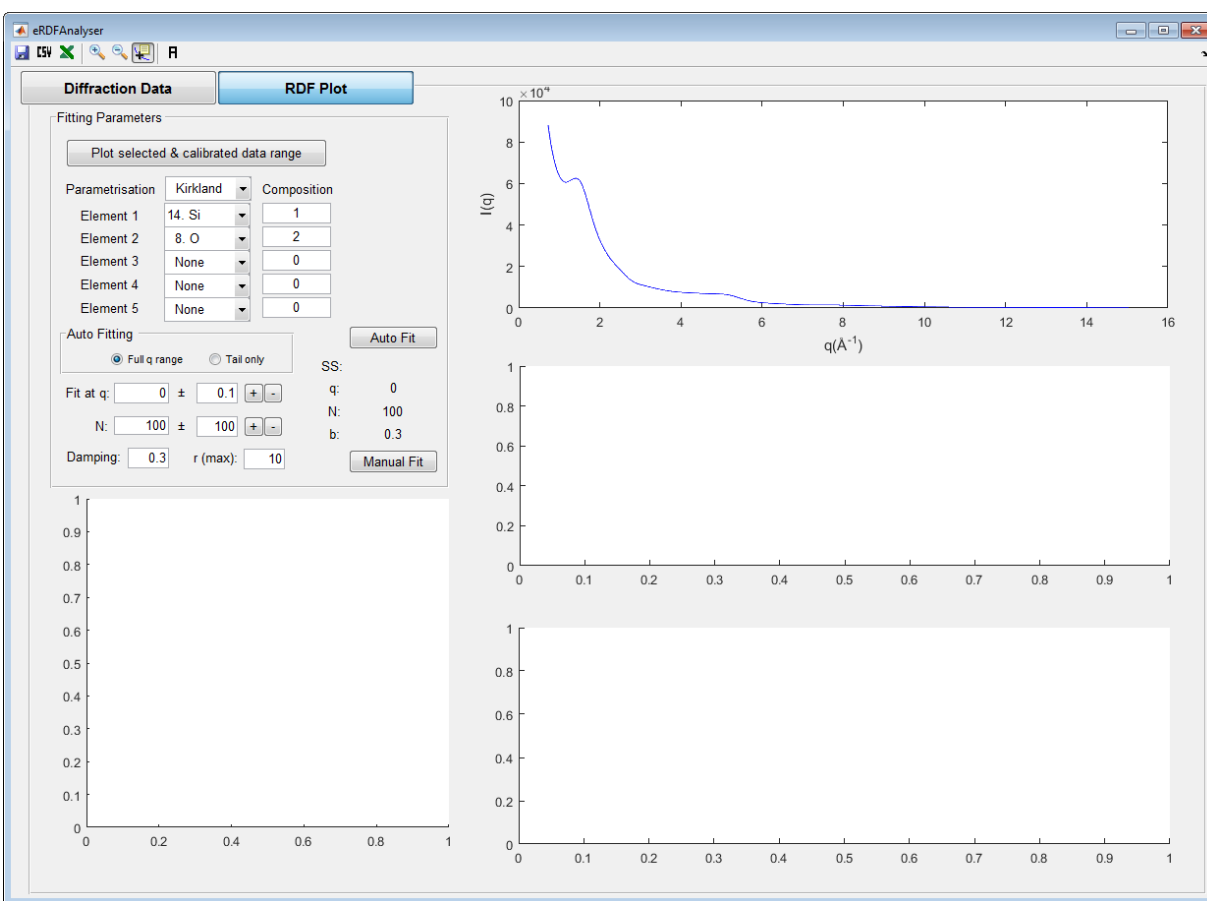


Figure 5: eRDF Analyser 'RDF Plot' Panel

3.5.1 Auto fitting

For automated fitting, click 'Auto Fit'. The default fitting is performed over the entire q range (Figure 6); however, users can choose to only use the tail end (approximately last third of the q range) for this fitting. The latter approach has been found to give better fits (Figure 7) for diffraction data in some cases e.g. those obtained from thicker samples or with extended q -range that will benefit from heavier weights at the tail end.

The resulting fit as well as reduced scattering intensity $\phi(q)$ and RDF $G(r)$ are plotted in the GUI. The maximum q value, value of coefficient N and a default damping factor of $b = 0.3$ are shown in the readout displays. The sum of squared deviations (SS) between experimental $I(q)$ and $I(q)_{fitted}$ is also displayed for reference.

While results of the automated fitting have been found to produce reasonable fits for experimental data of good quality, some optimisation may still be required. The damping factor for $\phi(q)$ can be adjusted within the automated routine, but manual fitting allows users to make further adjustments to certain parameters used in the fitting.

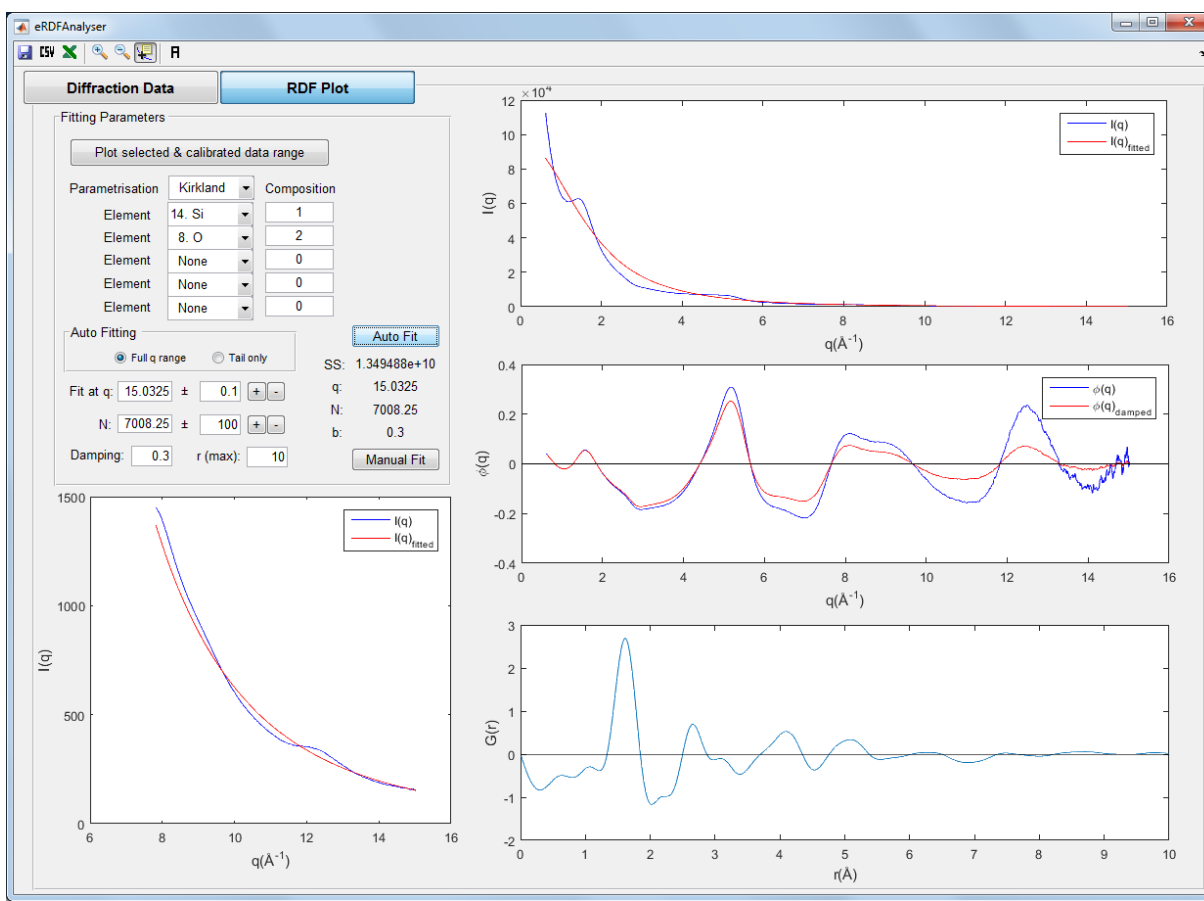


Figure 6: Results of automated fitting

3.5.2 Manual fitting

There are a few considerations when assessing goodness of fit. Adjustments can be made to both q and N until $\phi(q)$ oscillates about zero (q -axis) or close to it. Another way is to try and minimise the unphysical peaks (below 1\AA or the first inter-atomic distance) in $G(r)$. An additional measure is provided by the ‘SS’ readout which displays the sum of squared deviations between experimental $I(q)$ and $I(q)_{\text{fitted}}$. Sometimes, the user may need to revisit the data chosen in the first panel to select a range of better quality data.

To make $I(q)_{\text{fitted}}$ fit the experimental $I(q)$, adjust the values for q and N . Here, q is the point on the $I(q)$ curve where $I(q) = I(q)_{\text{fitted}}$, and N approximately relates to the number of material’s compositional units present in the scattering volume. Best practice would be to use the highest possible q value to extend the q -range – this is used as the default q value in the automated fitting procedure. The user can input any value in the ‘Fit at q ’ field and the software will find the closest q data point that is available. If optimising the automated fit, the values used will be updated in the GUI. Further adjustments to the q value at which to fit the curve can be made by fixed increments/decrements using the toggle buttons. Similarly adjusting the value of N , changes the gradient of $I(q)_{\text{fitted}}$. Click ‘Manual Fit’ after each adjustment of q or N to check the fit. A damping factor less than 0.5 has been found to be a reasonable value in reducing errors of truncation.

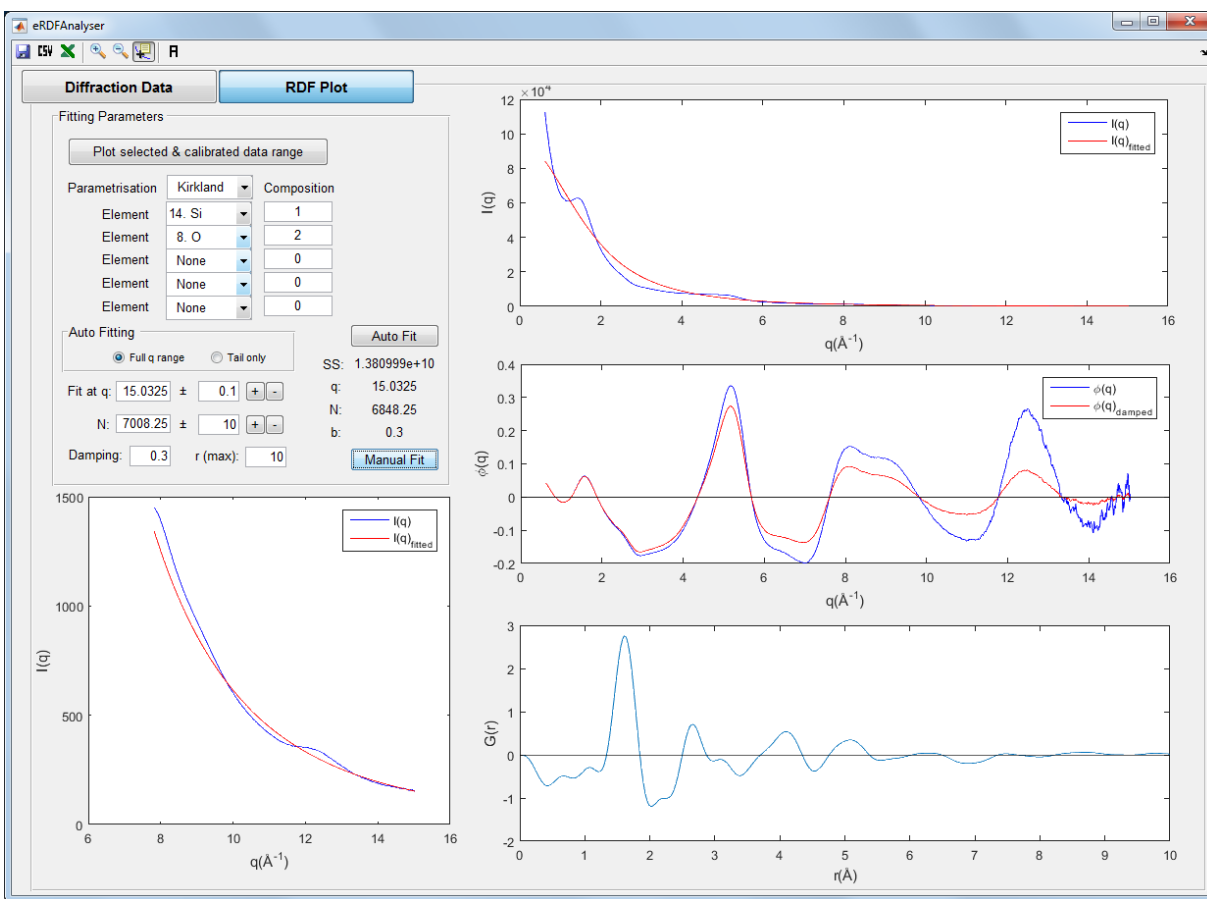


Figure 7: Optimised fit of $I(q)$ and final RDF $G(r)$ of amorphous SiO_2

3.6 Saving results

After optimising the fit and obtaining the RDF $G(r)$, the user may want to save some of the plots or results. There are three options available in the top menu. *Note: Since these files have generic names, generating and saving new results will overwrite existing files in the same folder.*

1. **Save Plots:** This saves the three plots of $I(q)$, $\phi(q)$ and $G(r)$ as separate .png files.
2. **Export Results as .csv:** This exports the raw data of all three plots and the parameters used for fitting to three CSV files. This method is recommended for users on Mac OS or those who do not have Excel installed on their systems.
3. **Export Results to Excel:** This exports the raw data of all three plots and the parameters used for fitting to a single Excel workbook.