Emission spectroscopy
"Laboratory" exercise 3, class demo, no report, TFY4255 Materials Physics 2022
Lecturer: Antonius T. J. van Helvoort
Lab assistant: Syam Sadan.
The code has be made by Brynjar Mæhlum and Sivert Dagenborg helped with formatting to Juypterlabs. The data has been collected within TFY4255-H17.

Aim: Learn principles and practical aspects of (emission) spectroscopy data processing

The composition of a material can be deduced by analyzing the emission spectrum in the X-ray regime when the material is exposed to gamma-, X-ray radiation or a beam of electrons. Very practical handheld devices can be made based on the principles of characteristics X-ray spectroscopy [1] and characteristic X-ray detectors can be found on the smallest scanning electron microscopes (SEM), the most advanced transmission electron microscopes, homelab X-ray set-ups as well as synchrotron beam lines and Mars [2]. Although a fast and common analytical technique, it could be asked how trustworthy qualitative spectrum analysis is as the method is prone to artifacts. For quantitative composition analysis what would be the accuracy of the final result, the precision and the minimal detectable quantity, certainly when the data processing is hidden in blackbox software.

In this exercise an unknown material is characterized based on characteristic X-ray spectra taken in different setups (SEM, TEM and a X-ray set-up) and given as text files. To calibrate the set-ups, spectra of known materials are given. See Table 1 for details. The data analysis is using a python script given [3]. Line energies can be found in literature, for example ref [4].
After the lab, the "unknown" should be determined, the principles of qualitative and to some degree quantitative analysis, artefacts and the effects of different probes and probe-sample-detector geometries should be clear.

Table 1: Available data sets*

Name	Details
SEM_known_Cu.msa	Bulk Cu, collected on Hitatchi TM4000 at 15 kV
SEM_unknown.msa	0.3 mm thick unknown, Hitatchi TM4000 at 15 kV
TEM_known_NiO_on_Mo.emsa	NiO calibration specimen [6], collected at Jeol 2100 at 200 kV using a Oxford Instrument 80mm2 SDD
TEM_unknown.msa	Unknown material crushed and deposited on a 300 mesh Cu TEM grid with a holey 20 nm C-support. Data collected at Jeol 2100 at 200 kV using a Oxford Instrument 80mm2 SDD
XRF_known_Cu.msa	Bulk Cu, Mo_K X-ray source, AmpTek® energy dispersive detector.
XRF_unknown.msa	0.3 mm thick unknown Mo_K X-ray source, AmpTek® energy dispersive detector.

(*: The folder Lab3_data contains additional data sets)

Task 1: SEM-EDS

Load the SEM_Cu data. Calibrate (channel width and offset) the spectrum assuming the peaks in the spectrum are Cu_L and Cu_K. Their line energies can be elsewhere [4, Table 1.2 in [5]]. Use additional peaks to verify your calibration is correct. Plot and identify the peaks present in the data set SEM_unknown using [4]. What could be the unknown sample? Save the calibrated spectra and obtained numbers for the different peaks.

Questions/notes:
- Note the distance and ratios between alpha and beta peaks for the K and L families.
- Compare the peak widths and note down the ratio between Cu_K and _L peaks.
- In the spectra of the unknown note stray (spurious) peaks and other artifacts. What could be the origin for the spurious peaks?
- What would be the smallest detectable distance between two adjacent lines be in present set-up, the so-called "energy resolution"?
- Label all peaks with a peak-to-background ratio > 3. What is the noise level?
- Sketch the spectrum if instead of 15 kV, 5 or 30 kV electron beam was used.

Task 2: TEM-EDS

Load and plot the data (counts vs channels) for TEM_NiO on Mo. To calibrate the channels assume the two highest peaks are Ni_L and Ni_K. Details on this sample can be found in [6]. Use a third peak to verify your calibration is correct. Plot and identify the peaks present in the data set TEM_unknown using [4]. Based on the TEM-EDS, what could the unknown be? Save the calibrated spectra and obtained numbers for the different peaks.

Questions/notes:
- Note the distance and ratios between alpha and beta peaks for the K and L families.
- Compare the peak widths and note down the ratio between Ni_K and _L peaks.
- In the spectra of the unknown note stray (spurious) peaks and other artifacts. What could be the origin for the spurious peaks?
- What would be the smallest detectable distance between two adjacent lines be in present set-up, the so-called "energy resolution"?
- Compare the calibrated spectra of the unknown recorded in SEM and TEM. What are the causes for the differences such as background, peak ratios (K/L, alpha/beta) and missing/additional peaks?

Task 3: XRF

Load and calibrate the XRF_Cu reference data set formed by illuminating the sample with Mo_K_alpha radiation. Check if the found dispersion and offset are correct using additional peak(s). Plot and identify the peaks present in the data set XRF_unknown using [4]. Based on the XRF, what could the unknown be? Save the calibrated spectra and obtained numbers for the different peaks.

Questions/notes:
- Note the distance and ratios between alpha and beta peaks for the K and L families in the available energy range.
- Compare the peak widths and note down the ratio between Cu_K peaks.
- In the spectra of the unknown note stray (spurious) peaks and other artifacts. What could be the origin for the spurious peaks?
- Compare the calibrated spectra of the unknown recorded by XRF to those from SEM and TEM. What are the causes for the differences such as background, peak ratios (K/L, alpha/beta) and missing/additional peaks?
- What are the advantages/disadvantages of the three used set-ups, for example regarding energy resolution and operation conditions?

Summary and further thoughts:

Through this exercise you should have seen principles from quantitative spectroscopy, from a data array collected by a detector, calibration, recognizing artefacts in the spectra, to deducing structural information. Specifically, characteristic X-ray emission spectroscopy is reviewed and the effects of type and energy of the probe and the specimen/set-up geometry. Spectra have theoretical aspects (models, for example line energies) and effects of experimental contributions. In (blackbox) commercial packages the calibration and labelling is done for the user.

To go beyond qualitative analysis is analyzing the spectra in a quantitative way based on the counts (ie. area under the peaks). One could for the three given spectra of the unknown material, after excluding strays, compare the intensity (area) of the main components (see section 5.7 in [5]). The set-up parameters (energy, type of probe, geometry and detecting characteristics) will affect the correlation factor between the intensity ratio deduced from the spectra and the true composition (in this example unknown material the composition ratio between two main is 1). Note there is a finite accuracy and precision, independent if analysis done by user or in blackbox software. The qualitative and quantitative analysis of spectra can be applied to collect data in a (n x m) array to obtain qualitative or quantitative maps for the scanned area. Open-data as for example available for [2] should in principle be verifiable.

References
[1] https://www.youtube.com/watch?v=dZFl7TwmAwE (verified 221008)
[2] K. A. Farley et al., *Science* 377, eabo2196 (2022) DOI: 10.1126/science.abo2196
[3] https://github.com/brynjarmorka/spectroscopy-channel-calibration (verified 221008)
[4] A. C. Thompson, et.al., X-Ray Data Booklet (Lawrence Berkeley National Laboratory University of California 2001). http://web.mit.edu/8.13/www/JLExperiments/31/XBLx-raydatabook.pdf (verified 221008).
[5] B. Fultz and J. Howe, Transmission electron microscopy and diffractor of materials, 4th edition, Springer, 2013.
[6] https://www.tedpella.com/calibration_html/tem7.aspx (verified 221008)