

ADVANCES IN QUANTITATIVE ELECTRON PROBE MICROANALYSIS OF LITHIUM IN DIFFERENT MATERIALS

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Electron probe microanalysis (EPMA) is a reliable and widely used technique to do non-destructive, accurate material characterisation for scientific and industrial applications. Nevertheless, despite of the great interest in lithium (Li) and the urgent need to do accurate non-destructive analysis at a micron scale, quantification of Li using EPMA has not been performed successfully yet. Recently developed periodic multilayers allow spectroscopy in the energy range around the characteristic Li K emission ~50 eV [1] but the detection and quantification of Li by a microprobe equipped with a bent crystal spectrometer and standard commercialised multilayers without diffraction gratings still is challenging.

The difficulties of Li detection are caused by different factors: the fluorescence yield of Li is extremely low, few characteristic photons are produced by the decays of the Li 1s core hole, favoring the emission of Auger electrons. Because of their low energy, the photons are strongly absorbed before even leaving the sample and its eventual coating. The signal therefore is principally coming from a thin surface layer that can be subject to contamination and that may be sensitive to electron bombardment. Further photon absorption by the microprobe components, especially by separation windows, will additionally decrease the measured intensity. As the Li K emission (2p – 1s transition) involves valence electrons, the shape of the Li emission band is highly dependent on the density of states (DOS) in the valence band and so highly dependent on the chemical state of the lithium atoms. Chemical shifts of some eV and strong peak shape alterations can occur and should be expected for EPMA of light elements [2,3], complicating quantitative analysis.

This work shows some promising results of quantitative EPMA of Li in different materials including battery compounds and metal alloys with Li concentrations down to 2 %. This was made possible after the integration of a new detection system as well as work on the quantification procedure using real standards and correction programs suited for low voltage EPMA.

Even if additional investigation is needed, the advances are of great interest to researchers working on lithium characterisation. We show that EPMA is a powerful tool to do quantitative analysis of Li even if it is contained in heavy matrices with elements showing characteristic emission bands in the same spectral range as Li. This novel Li quantification method is more accessible than other techniques using synchrotron radiation and less expensive than detection using a SEM or an electron microprobe equipped with multilayer gratings.

[1] Polkonikov, V., Chkhalo, N., Pleshkov, R., Giglia, A., Rividi, N., Brackx, E., Le Guen, K., Ismail, I., Jonnard, P., *Appl. Sci.* 2021, *11*, 6385.

[2] Schweizer, P., Brackx, E., Jonnard, P., *X-Ray Spectrom.* 2022, *51* (4), 403.

[3] Hassebi, K., Le Guen, K., Rividi, N., Verlaquet, A., Jonnard, P., X-ray spectrom. (<http://doi.org/10.1002/xrs.3329>) in press.

Reflection Zone Plate Spectrometer For Li K Emission Detection In Lithium Compounds

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Soft X-ray emission spectroscopy (XES) is a technique employed to investigate the electronic structure of materials by analyzing the energy spectrum of x-rays emitted from a sample. The technique involves exposing the sample to ionizing particles, such as electrons, and then measuring the energy distribution of the emitted x-rays. By detecting these characteristic x-rays, we can determine the presence of specific elements and be used for quantitative analysis.

One type of optical dispersive element that can be used in XES is a reflection zone plate (RZP) [1], which is composed of concentric zones of varying thicknesses. RZPs act as diffraction gratings when x-rays are incident upon them, resulting in diffraction and interference of the x-rays, while simultaneously focusing them. Compared to other optical elements like periodic multilayers, RZPs offer higher spectral resolution and can cover wider energy ranges, and can achieve energy resolutions as low as 0.49 eV at the Al L_{2,3} line (around 72 eV) [2].

In this study, we employed a Fresnel RZP in an electron microprobe to detect Li K emission in different lithium compounds. Li K emission is a characteristic emission produced when Li 1s levels are ionized in the material. However, detecting this emission can be challenging due to its low fluorescence yield, re-absorption effects, and interference from other spectral lines in the same energy range. We reported the measurement of the Li K emission bands in several lithium compounds using an RZP spectrometer, demonstrating the potential of this approach for various applications in x-ray spectroscopy.

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References

[1] A. Erko *et al.*, *Opt. Express*, vol. 22, no. 14, p. 16897, Jul. 2014, doi: 10.1364/OE.22.016897.

[2] A. Hafner *et al.*, *Opt. Express*, vol. 23, no. 23, p. 29476, Nov. 2015, doi: 10.1364/OE.23.029476.