Reviewer's Dissertation Thesis Report

Masaryk University **Faculty of Science**	
Doctoral Study Field	Chemistry/Analytical Chemistry
Student	***Mgr. Veronika Faltusová***
Disertation Thesis Title	*Chemometry in plasma spectrometry*
Reviewer	Dr. Michael SPERLING
Reviewer's Workplace	University of Münster Institute of Inorganic and Analytical Chemistry, Münster, Germany

Text of the report (its extent is on reviewer's consideration) ...

In her thesis Mgr. Veronika Faltusova has commented her 8 peer-reviewed papers that are related to different chemometric aspects used for bulk analysis as well as imaging. Analytical methods were based on state-of-the-art plasma spectrometric techniques including laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), or laser induced breakdown spectrometry (LIBS). The developed chemometric tools span a broad variety of topics related to basic data processing, exploratory data analysis or classification, digital image processing and computer vision. Also the analytical application fields span a broad variety including geological samples (uranium ore, apatite, mafic rocks), metals (nickel-based structural materials for nuclear reactors), archaeological samples (glass artifacts) and foodstuffs. Even further, totally different analytical approaches related to such variety of topics and application fields is remarkable and Veronika Faltusova has demonstrated with her contributions her creative abilities to find solutions answering the questions given to the analyst.

The introduction is well written and is giving reference to the historical development of chemometrics. This is followed by 3 parts discussing the main chemometric tools developed. The first tool for data reduction of LA-ICP-MS data has been realizced in the form of a standalone software package called Ilaps. The second part is describing data classification and the third part concerns imaging and methods for data transformation. All three parts are written in a style giving easy access of the reader to follow the description of complex statistical procedures.

In part 1 Veronika Falusova is describing the necessity for dedicated data processing for LA-ICP-MS related to the type of analysis envisaged, such as bulk analysis, depth profiling or spatial mapping.

Since ICP-MS is a technique for the analysis of many elements, signal processing has to include the treatment of many channels (analytes). At the beginning of chapter 3.2 it is stated, that "LA-ICP-MS produces time-dependent signals for multiple elements at the same time". Here the parameter "time" is handled a bit inprecise, since only multicollector ICP-MS instruments are really able to measure different channels simultaneously.

Giving the example of calcite veins in garnet she is explaining the importance of selecting "regions of interest" (ROIs) with the help of a reproducible workflow including background regions for accurate baseline correction. However, it is not stated how the background regions are selected and if this selection is programmed within the software or done by visual inspection of the maps by the user of the software. Anyhow, this information is available from the attached publication related to Ilaps.

In chapter 3.4 the data handling for the purpose of quantification is discussed. Apart from background-correction, signal rejection during warm-up also cleaning of signal spikes is mentioned. The mentioned reason for such spikes (electronic noise) is not vary probably for modern instrumentation. A more probable reason is given by the cited reference [17]. The statement that "In LA, an external calibration is used for the quantification" is only mostly true, since also internal standardization and isotope dilution approaches have been reported. Also the statement, that "ablation rate must be reproduced flawlessly" is only true for samples that are not ablated quantitatively such as geological materials.

In chapter 3.5 the correction of matrix effects is discussed. The only matrix effect mentioned is the influence of the matrix on the ablation rate. Effects on aerosol generation, aerosol transport or plasma effects are not discussed.

In 3.5.1. Internal standardization is discussed. However, the most often applied normalization of signals by referencing to an internal standard (e.g. C13) is not mentioned at all. The discussed case of internal calibration with the help of an CRM, requiring secondary determination by another method (EPMA, XRF) is actually vary seldom applied.

In chapter 3.6 the correction of sensitivity drift is discussed. Sensitivity drift is a major problem in ICP-MS work, especially when analysis is time consuming. The statement, that "it is often linked to the stability of the electronic circuits" is very unlikely, since ICP-MS is sharing electronics with other techniques, that are not prone to drift the same extent (ICP-OES, ESI-MS). Sensitivity drift in ICP-MS is a specialty of ICP-MS.

It is mentioned here that a method developed by Cheatham for conventional SN-ICP-MS is commonly used for LA-ICP-MS. In this method a "drift correction standard" is

measured after every four or five samples. It is not clear how this approach can be done commonly for LA-ICP-MS including imaging of inhomogeneous materials.

In chapter 4 the computational method called "machine learning" is discussed. Different tools like PCA, classification are briefly introduced in a way, that can be followed easily by the reader. Unfortunately, the relation of this tools with the experimental work of this thesis is less clear within this chapter.

Chapter 5 is describing the experimental part of the thesis work. It starts with an explanation of the motivation for this work.

Data handling for imaging is discussed in chapter 5.1.3. and following. A typical problem of multimodal imaging, namely the combination of data obtained from different techniques is mentioned. Unfortunately, the major problem of such merging, namely the different spatial resolutions of the techniques and the lack of precision of the stages when approaching the µm level is not mentioned at all. Merging two images by manually adjusting their pixel size might work for resolutions in the range of 50-100 µm for both techniques but will not easily work for higher resolutions or more different resolutions such as when trying to merge images from SIMS, SEM etc. with those of LA-ICP-MS. Also two destructive techniques such as LIBS and LA-ICP-MS cannot be used sequentially on the same sample surface, since both techniques ablate the analyzed surface. Such problems are neither discussed here nor in the published material. Therefore, the described approach will only give an estimation of element distributions for samples not changing much in depth.

Again in chapter 5.1.5. correction of sensitivity drift by sequentially measuring the sample and a drift correction standard is mentioned. It is not really clear what is meant by measuring the standard "after every 5-10 samples". Is the image surface divided into different samples (e.g. rows) ? What is meant by "sample" here ?

Approaches for classification are discussed in chapter 5.2 with the first example of archaeological glass samples. Experimental parameters used for the LA-ICP-MS analysis given here (chapter 5.2.2.) are different from those given in the published paper (see page 542 in Venclová et al. 2028). It is mentioned that concentrations were measured at 5 spots on each sample. Unfortunately, neither here nor in the published paper is any information given on the selection of spots, there size, the number of pixels per spot etc.

In chapter 5.3. chemometric approaches for imaging are discussed. Methods for image segmentation, image comparison and multimode imaging are nicely discussed.

Within the conclusion, Mrs. Faltusova is summarizing her work, covering a very broad set of topics, materials and analytical techniques. The bibliography gives access to relevant literature.

Mrs. Faltusova has demonstrated her capacity to find appropriate solutions for analytical questions. The broad set of topics discussed in her thesis is outstanding. At very few places in the thesis, I missed some more details or more explicit clarity in the explanation. Representative for these I would like to ask the following questions:

a) What are the differences of the different ICP-MS detection techniques (ICP-QMS, ICP-SFMS, ICP-TOFMS, ICP-MC-MS) with respect to the statement that "LA-ICP-MS produces time-dependent signals for multiple elements at the same time" ?

b) Under what conditions can the requirement of "flawlessly reproduced ablation rate" be handled less strictly and still allow for quantification ?

c) What is the requirement for an internal standard to be able to correct for multiplicative sources of bias, such as matrix effect, sensitivity drift and the difference in ablation yield between samples ?

d) What are the main sources of drift in ICP-MS ?

Conclusion

In the dissertation thesis, the student has demonstrated his/her creative abilities in the relevant research area:

YES ☒ NO ☐

I am recommending the dissertation thesis for defence:

YES ☒ NO ☐

Date 19.09.2022

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Signature