

博士論文(要約)

Quantitative elemental analysis of water-submerged solids: Temperature segmented multivariate regression of laser-induced plasma emissions

(レーザー誘起プラズマ発光を用いた温度セグメント化
回帰モデルによる水中固体中元素定量分析手法)

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The contents of this thesis are currently not available on the Internet because these are going to be submitted and published in the following journals:

- Chapter 1, 2: Deep-sea Research Part I: Oceanographic Research Papers
- Chapter 3, 4, 5, 6: Spectrochimica Acta Part B: Atomic Spectroscopy
(including a part of discussions written in Chapter 7 and 8)

Therefore, the summary of each chapter is described here. These chapters will be available in 5 years since the degree day (23 March, 2017).

Aim and highlights of this study

The aim of this study is investigation of quantitative elemental analysis of water-submerged solids for the application to in-situ measurements of deep-sea rocks. The highlights are the following:

- Partial least squares regression analysis (PLS) was applied to quantitative analysis of signals taken using Laser-Induced Breakdown Spectroscopy (LIBS).
- Signal processing, especially normalization of spectra, contributed to reduce the effect of shot-to-shot fluctuations of signals on PLS calculations.
- For further enhancement of the accuracy in PLS calculations, appropriate temperature segmentation was effective.
- The database should be constructed by the large number of samples with the similar matrix of a sample.

Summary

In this work, the compositions of Cu and Zn of water-submerged solids were quantitatively analyzed, with the aim of application to deep-sea mineral surveys.

In Chapter 1, the motivation of this study was described. While deep-sea mineral resources are focus of much attention for geological interests and industrial use, estimation of distribution of mineral resources is a challenging task since conventional chemical analysis of rocks is mainly performed on land. In-situ chemical sensors have a great potential to contribute to chemical surveys with high temporal and spatial resolutions compared to conventional sampling, and they have been already applied to in-situ chemical surveys of seawater and dissolved gas. LIBS is applicable to the measurement of rocks on-site in deep-sea environments and has the advantage of real-time non-contact sensing in environments that are hard to access.

In Chapter 2, the challenges of applying LIBS to deep-sea environments were reported. While a double-pulse technique increases the signal quality significantly at shallow water depths, it is not applicable to studies at oceanic pressures. The long-pulse technique is known to be effective at obtaining well-resolved spectra up to 30MPa. This technique has been applied to deep-sea LIBS instrument, Chemicam. In sea trials, major elements of rocks and sediments were successfully detected at depths of 1000 m.

In Chapter 3, methods for quantitative analysis of the compositions of solids measured using LIBS were summarized. Due to matrix effects, the application of calibration curves is limited. While CF-LIBS has been applied to a number of research, requirements need to be satisfied for the calculation of chemical composition. Also, peaks of all elements contained in a target need to be detected, which can be the bottleneck for in-situ analysis. Multivariate regression analytical techniques are also applied to LIBS analysis. Among them, PCR and PLS are the most widely established methods and have been applied to various fields including in-situ applications, in air

and also for planetary explorations of Mars by NASA. ANNs have also been investigated as quantitative methods but are less widely adopted.

In Chapter 4 and Chapter 5, a novel approach for temperature segmentation was proposed for quantitative analysis of water-submerged samples, and the accuracy obtained from conventional signal processing steps (normalization, smoothing, and background subtraction) and the proposed method were compared. In Chapter 4, the relation with shot-to-shot fluctuations of signals and temperature was analyzed using brass samples. Cu and Zn compositions of brass and rock samples were quantified by PLS in Chapter 4 and Chapter 5, respectively. From the study of brass samples, normalization was found to be the most effective traditional method of pre-processing to increase the accuracy among three different established signal processing methods. It can be said that the effect of both peak and background fluctuations seen in the signals is reduced by normalization of spectra. It was found that temperature segmentation of database in an appropriate range for sample sets can further improve the accuracy of PLS calculations. The appropriate temperature was the highest range, from 8250 to 8750 K, for brass samples and the slightly lower range, from 7750 to 8250K for rock samples. The temperature range should be high enough for strong peak detection and multi-peak excitation, but at the same time it should be low enough to obtain spectra without significant peak broadening. In addition, it was found from the study of rocks, that the database should be constructed by a large number of samples, which have the similar matrix to a sample for validation. This finding is in agreement of the study of Martian rocks in low-atmosphere environments, and appears to be a consistent trend for field application of quantitative LIBS.

Overall discussions were given in Chapter 6.

Chapter 7 gave conclusions and future studies.