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Multi-element analysis of heavy metal content in soils using laser-induced breakdown spectroscopy: a case study in eastern China

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ABSTRACT: Laser induced breakdown spectroscopy is an emerging elemental analytical technique with the advantage of fast response, minimal sample preparation and multi-element analysis capacities. This work studied practical use of LIBS for rapid quantification of 4 (Cu, Ni, Cr, Pb) heavy metal elements in 169 agricultural soil samples. The objective is to conclude an appropriate method to reduce the interference of matrix effect in soils within the scope of data analysis, by comparing several univariate and multivariate methods of LIBS data interpretation (full spectrum and emission lines). The proposed multivariate methods, such as the least absolute shrinkage and selection operator and principal components regression were found to be effective in reducing the matrix interference and the predictive performance was stable in our experiment, approaching normalized root mean squared error of 6.84%, 8.87%, 9,71%, 10.76% for Cu, Ni, Cr and Pb, respectively. Meanwhile, the performance of univariate analysis suffered from such effect. The results showed the importance of utilizing proper multivariate chemometrics for LIBS data interpretation when quantifying the heavy metals in soils.

Keywords: Heavy metal; soil; matrix effect; Multi-element analysis; LIBS

1. Introduction

Heavy metal pollution is covert, persistent and irreversible [1]. This kind of pollution not only degrades the quality of the atmosphere, water bodies, and food crops, but also threatens the health and well-being of animals and human beings by entering food chain [2]. In China, agricultural soil has been widely contaminated as a result of uncontrolled discharge and emissions from rapidly expanding industrial areas, mining, the misuse of chemical fertilizers and land application of industrial effluents, and sewage waste [3]. In fact, intake of heavy metals via the soil-crop system has been considered as the predominant pathway of human exposure to environmental heavy metals in agricultural area [4].

Conventional methods of heavy metal analysis are relatively slow in terms of measurement/analysis and sample preparation time with the requirement of skilled manpower. In the laboratory, after general sample preparation procedures like air-drying and sieving, soil samples were usually digested with a typical concentrated acid mixture (e.g. HNO_3+H_2O_2, HF+HNO_3+$HClO_4$ or HF+HNO_3+ H_2SO_4+$HClO_4$). Then, the digested soil solutions were treated by analytical methods such as atomic fluorescence spectrophotometry and inductively coupled plasma atomic emission spectrometry [5–7]. However, these methods are limited by complex sample preparation (hours for a single sample) and may not meet the demand of real-time measurement in practice.

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that has been widely used for environmental analysis. The determination of elemental composition in a wide range of materials in the solid, liquid or gaseous phase can be achieved through this technique [8]. As for soil analysis, the practice of LIBS including the determination of nutrition such as total carbon content, nitrogen, phosphorus [9,10] to contaminants like pesticide residues [11] and heavy metals. LIBS relies only on the plasma, thus the technology has lots of well-known advantages [9], including (1) simplicity; (2)