SOURCE IDENTIFICATION OF ELEPHANT IVORY AND RICE BASED ON MULTI-ELEMENT FINGERPRINTING AND SELENOPROTEOMIC ANALYSIS OF RICE USING MASS SPECTROMETRY BASED APPROACHES

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Ph.D. (ANALYTICAL CHEMISTRY)

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ABSTRACT

The present PhD research is focused on analytical chemistry challenges based on mass spectrometry based approaches concerning source identification of elephant ivory and rice based on multi-element fingerprinting and selenoproteomic analysis of rice.

In the first part, the so-called micro-analytical technique, named laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was developed for source identification of Asian and African elephant ivories. Thirty-seven ivory samples with known and unknown sources were directly analyzed after surface cleaning. Pre-ablation was used to avoid possible contribution from surface contaminants. Elemental compositions in each ivory sample were evaluated in term of intensity ratios. Calcium, which is a major matrix element in ivory, was used as an internal element to normalize elemental intensity and to correct for variations in ablation efficiency and plasma variation. Discriminant analysis (DA) with the use of 11 key variables (intensity ratios of Mg, P, Sc, Cr, Fe, Co, Zn, Ga, Rb, Sr and Ba with Ca) was employed to classify ivory samples. This study indicated that multi-element fingerprinting could be beneficial in determining the source of elephant ivory.

In the second part, the methods based on the multi-element fingerprinting by inductively coupled plasma mass spectrometry (ICP-MS) in combination with multivariate statistical techniques were developed and validated as tools for authentication of rice. A total of 31 Thai jasmine rice and 5 foreign (France, India, Italy, Japan and Pakistan) rice samples were analyzed after acid digestion. Twenty-one key variables (B, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, and Pb) were assessed by a radar plot technique and multivariate data analysis, including principal component analysis (PCA) and discriminant analysis (DA) enabling classification according to geographical origin. Thai jasmine rice could be clearly differentiated from foreign rice samples. In addition, the DA could be used to classify Thai jasmine rice obtained from different regions in Thailand including the northern, northeastern and central regions. The use of quantitative high-resolution and quadrupole semi-quant ICP-MS approaches was critically compared.

In the third part, an analytical ICP-MS-assisted proteomic method was developed for the identification of Se-containing proteins in rice grown naturally on seleniferous soils. Rice proteins were separated by two-dimensional (2D) gel electrophoresis. The position of Se-containing protein was tentatively identified by the correlation between one-dimensional isoelectric focusing electrophoresis (1D IEF) and sodium dodecyl sulfate polyacrylamide gel electrophoresis (1D SDS-PAGE) of a sample aliquot and then confirmed by ^{78}Se imaging in the 2D gels by laser ablation ICP-MS. Upon tryptic digestion, the proteins were identified by capillary HPLC with the dual ICP-MS and electrospray Orbitrap MS detection. Selenium was found to be present as both selenomethionine (SeMet) and selenocysteine (SeCys) in a dozen of rice proteins including a 19kDa globulin, granule-bound starch synthase, and the family of glutelin-type seed storage proteins. The Se/S substitution ratio was found to be two times higher for SeMet than that for SeCys.

KEY WORDS: MASS SPECTROMETRY / RICE / ELEPHANT IVORY / SOURCE IDENTIFICATION / GEOGRAPHICAL ORIGIN / MULTI-ELEMENT FINGERPRINTING / SELENIUM / SELENOPROTEOMIC ANALYSIS

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