Direct determination of trace rare earth elements in ancient porcelain samples with slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry

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Abstract

A method for the direct determination of trace rare earth elements in ancient porcelain samples by slurry sampling fluorinating electrothermal vaporization inductively coupled plasma mass spectrometry was developed with the use of polytetrafluoroethylene as fluorinating reagent. It was found that Si, as a main matrix element in ancient porcelain sample, could be mostly removed at the ashing temperature of 1200 °C without considerable losses of the analytes. However, the chemical composition of ancient porcelain sample is very complicated, which makes the influences resulting from other matrix elements not be ignored. Therefore, the matrix effect of ancient porcelain sample was also investigated, and it was found that the matrix effect is obvious when the matrix concentration was larger than 0.8 g l^{-1}. The study results of particle size effect indicated that when the sample particle size was less than 0.057 mm, the particle size effect is negligible. Under the optimized operation conditions, the detection limits for rare earth elements by fluorinating electrothermal vaporization inductively coupled plasma mass spectrometry were 0.7 ng g^{-1} (Eu)–33.3 ng g^{-1}(Nd) with the precisions of 4.1% (Yb)–10% (La) ($c = 1$ μg l^{-1}, $n = 9$). The proposed method was used to directly determine the trace rare earth elements in ancient porcelain samples produced in different dynasty (Sui, Ming and Qing), and the analytical results are satisfactory.
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1. Introduction

Porcelain was firstly invented in China. It was found that proto-porcelain was produced even in Shang and Zhou Dynasty 3000 years ago. Ancient porcelain studying is always an important field in archaeology, and the analysis of their chemical composition plays a vital role among these studies [1,2]. Usually, the ancient porcelain was produced using local materials, and the materials in different areas take on different geochemistry and minera-logical characteristics. The chemical composition of ancient porcelain would be affected by the manufacturing technique, which varied with the different historic periods. However, as a whole, trace elements in ancient porcelains,

whenever they were produced, could not be controlled by manpower, and is the reflection of the characteristics of materials in that area. Therefore, a unique "chemical fingerprint" would be left in the ancient porcelain by the material from local area and the producing technique, which could be used to judge where and when, even how the porcelain was produced [3].

Among trace elements in ancient porcelain, rare earth elements (REEs) were one of important "chemical fingerprint" elements, there were obvious concentration changes with the variations of materials and producing technique, therefore, the determination of REEs could provide much information for studying ancient porcelain [4].

At present, Neutron activation analysis (NAA) [5,6], X-ray fluorescence (XRF) [7,8] and Particle-Induced X-ray Emission (PIXE) [9,10] were widely used in studying

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ancient porcelain. However, NAA and PIXE require very expensive nuclear reactor or particle accelerator; XRF has a poor sensitivity and requires a time-consuming sample preparation. With the development of archaeological study of ancient porcelain, researchers paid more and more attention to ICP-MS due to its advantages such as high sensitivity, large dynamic linear range, multi-element capability and the possibility to perform isotopic measurements, and several reports on the application of ICP-MS in archaeological studies have been appeared [11–13].

However, conventional pneumatic nebulization ICP-MS requires to convert the solid samples into the sample solution prior to its analysis, it is laborious and time-consuming. Especially, for the refractory samples like ceramic, the sample pretreatment is much more difficult. Furthermore, conventional pneumatic nebulization is not suitable for samples with high viscosity and high concentration of salts, and its sampling efficiency is only 1–3%.

To circumvent above problems, different solid sampling techniques have been employed, such as direct sample insertion [14], slurry nebulization [15], laser ablation [16] and electrothermal vaporization (ETV) [17]. Of all these methods, ETV is accepted as a distinctive sampling method for ICP-OES/MS [18,19] due to its attractive features, including in situ separation of analyte from the matrix; high sampling efficiency; lower detection limit and fewer sample consumption. It is in particular suitable for the direct analysis of liquid sample with milliliter level or solid sample with milligram level.

Solid sampling can reduce sample preparation time and possibility of sample contamination, as well as the risk of analyte loss prior to analysis. Success has been achieved for direct solid analysis using ETV-ICP-OES/MS. Two approaches have been reported for ETV-ICP-OES/MS direct analysis of solid samples, one is direct solid sampling cup-in-tube technique [20] and the other is slurry sample introduction [21]. Slurry sampling combines the benefits of solid and liquid sampling, simplifying sample pretreatment and enabling the use of aqueous calibration solutions. In addition, the analytical performance of ETV-ICP-OES/MS could be improved by the utilization of a suitable chemical modifier. For determination of refractory elements or easily forming carbides elements, such as REEs, different chemical modifiers, such as HF, CF_2Cl_2, CH_3F [22–24], have been used. In our previous works [25–27], it has been proven that fluorinating electrothermal vaporization (FETV)-ICP-OES/MS with the use of polytetrafluoroethylene (PTFE) emulsion as fluorinating reagent is a very effective method for the determination of REEs and other refractory elements. This technique has been successfully applied to the analysis of biological [28] and environmental [29] samples.

In this work, a PTFE slurry was employed as a fluorinating reagent to convert the silica matrix and analytes (REEs) in ancient porcelain into their fluorides at high temperature. Based on the volatility difference between silicon fluoride and the fluorides of REEs, the high-volatility silicon fluoride was evaporated prior to the vaporization of REEs, and thus, an in-situ separation of Si from REEs could be realized in the ashing step. With calibration using aqueous standards, the proposed method was used to determine directly trace REEs in ancient porcelain sample powder without any chemical pretreatment.

2. Experimental

2.1. Instrumentation

An Agilent 7500a ICP-MS (Agilent Japan) equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) as electrothermal vaporizer is used. The transfer line consisted of a laboratory-built connecting interface and a Polyethylene tube (6 mm id) with total length of 70 cm (detailed in [26]). Pyrolytic graphite coated graphite tubes were used throughout the work. The operating conditions for ICP-MS and ETV are given in Table 1.

2.2. Standard solution and reagents

The stock standard solution (1 g l^{-1}) for rare earth elements were prepared from their specPure oxides using the conventional method. The mixed stock solution of 15 REEs was prepared as 50 mg l^{-1}. For calibration, the aqueous standard series and test solution containing 6% PTFE were prepared from the mixed stock standard solution by dilution step by step. And the standard solutions for matrix matching were prepared from corresponding metals or metal oxides using conventional method. All other chemicals were of superpure grade. Double-distilled water was used throughout the experiments. A 60% PTFE emulsion was purchased from Shanghai Institute of Organic Chemistry, Shanghai, China.

Table 1
Equipment and operating parameters

ICP-MS plasma	
RF power	1250 W
Outer gas flow rate	15 l min^{-1}
Intermediate gas flow rate	0.9 l min^{-1}
Nebulizer gas flow rate	0.6 l min^{-1}
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Data acquisition	
Sampling depth	6.0 mm
Scanning mode	Time resolved analysis
Integration time	20 ms
Sweeps per reading	1
ETV heating procedure	
Drying	100 °C, ramp 15 s, hold 15 s
Ashing	1200 °C, ramp 15 s, hold 40 s
Vaporization	2600 °C, hold 4 s
Sampling volume	10 μl