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Simultaneous on-line preconcentration and determination of trace metals in environmental samples by flow injection combined with inductively coupled plasma mass spectrometry using a nanometer-sized alumina packed micro-column

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Abstract

A flow injection (FI) on-line preconcentration procedure by using a nanometer-sized alumina packed micro-column coupled to inductively coupled plasma mass spectrometry (ICP-MS) was described for simultaneous determination of trace metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) in the environmental samples. The effects of pH value, sample flow rate, preconcentration time, and interfering ions on the preconcentration of analytes have been investigated. Under the optimized operating conditions, the adsorption capacity of the nanometer-sized alumina for V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb were found to be 11.7, 13.6, 15.7, 9.5, 12.2, 13.3, 17.1, 17.7 and 17.5 mg g^{-1}, respectively. With 60 s preconcentration time and 60 s elution time, an enrichment factor of 5 and the sampling frequency of 15 h^{-1} were obtained. The proposed method has been applied to the determination of trace metals in environmental certified reference materials and natural water samples with satisfactory results.

Keywords: Nanometer-sized alumina; Flow injection; On-line preconcentration; ICP-MS; Metal ions; Environmental samples

1. Introduction

Along with the development of science and technology, a lot of metals were used for different scientific and industrial purposes, and they are unevitably discharged into the environmental. To evaluate the effects of these metals on environmental, it is often required as a very sensitive and reliable method to determine very low content of metal in the environmental samples. The analytical techniques often used for this purpose include electrothermal atomic absorption spectrometry (ETAAS) [1–3], instrumental neutron activation analysis (INAA) [4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5–7], and inductively coupled plasma mass spectrometry (ICP-MS) [8–12]. ICP-MS is considered the most appropriate technique due to its super high sensitivity. However, the effects of complicated matrix, including spectral interferences and non-spectral interferences, constitutes a major limitation of this technique in carrying out accurate determination. And sometimes it is quite difficult or even impossible to determine the trace/ultratrace elements directly by ICP-MS. Therefore, in order to achieve accurate and reliable analytical results, an efficient separation and preconcentration of analytes is highly demanded prior to analysis.

The most widely used techniques for the separation and preconcentration of analytes include coprecipitation [12], liquid-phase extraction [13–15], solid-phase extraction [16–19], high-performance liquid chromatography [20–22]. Recently, solid-phase extraction (SPE) technique has increasingly become popular in comparison with the more traditional liquid–liquid extraction methods because of its several major advantages such as: (i) simple to operate; (ii) high preconcentration factor; (iii) rapid phase separation;

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and (iv) the ability of combination with different detection techniques.

The coupling of flow injection (FI) on-line micro-column separation and preconcentration techniques to ICP-OES/MS has been proved to be a good idea [23–25]. This combination not only provides an improvement in the detection limits, but also reduces the interference from matrix. On-line column preconcentration systems coupled with ICP-MS are based on the retention of the analytes in micro-column, packed usually with silica gel [26], chelating ion-exchangers [27,28], and metal-oxide [29]. Being one of the key factors of on-line micro-column separation and preconcentration method, sorbent material determines the sensitivity and the selectivity of the analytical method. Although activated alumina [30–33] was often used as a good sorbent material in this technique, to the best of our knowledge, few research works on the use of nanometer-sized Al_2O_3 as a sorbent material for adsorption of trace metals have been reported.

Nanometer-sized material [34,35] has many special properties and has gained more attention in recent years. One of its properties is that most of the atoms are on the surface of the nanoparticle, and so nanometer-sized material possessing a high chemical activity. In our previous research [36], a sol–gel method for the preparation of nanometer-sized alumina was reported, and its potentiality to be used as a sorbent for trace metals has been demonstrated. In this work, nanometer-sized alumina was trying to be used as the micro-column packing materials for flow injection on-line micro-column separation/preconcentration and ICP-MS determination of trace metals. The proposed method was applied to the simultaneous determination of trace metals in environmental samples with satisfactory results.

2. Experimental

2.1. Synthesis of nanometer-sized alumina

2.1.1. Apparatus and reagents

An ultrasonic oscillator (Shengyuan Instrument Factory, Shanghai, China) and a 7312-I electric agitator (Master Pattern Factory, Shanghai, China) were used in the synthesis procedure.

An X2-6-13 muffle (Yingshan Yahua Instrument Factory, Hubei, China) was used to achieve the high temperature needed.

All reagents, including $Al(NO_3)_3{\cdot}9H_2O$, $(NH_4)_2CO_3$, and *n*-butyl alcohol, were of analytical-reagent grade. Triton X-100 was used as a dispersant. Doubly de-ionized water was used throughout.

2.1.2. Synthesis procedure

Of various procedures for synthesis of nanometer-sized alumina, sol–gel method [32] was widely employed due to its good homogeneity, high purity and small particle size. After Triton X-100 was added into the solution of $Al(NO_3)_3$ as a dispersant, $(NH_4)_2CO_3$ was added slowly with vigorous stirring untill the solution turned thick. The solution was kept stirring for 1 h, then aged over 48 h. After the sol turned into gel, it was filtrated and then heated at 60 °C for 12 h.

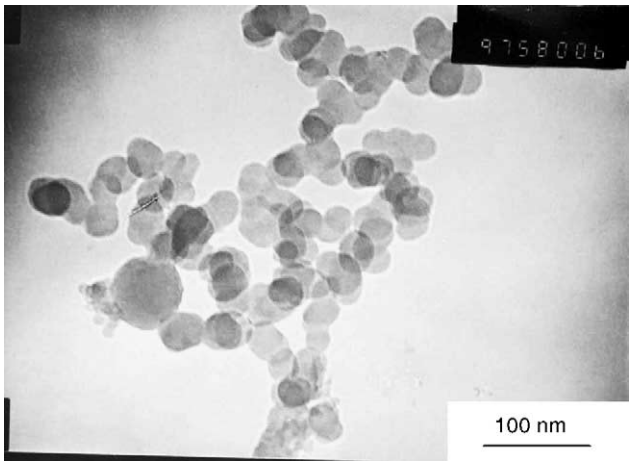

Fig. 1. TEM micrograph of Al_2O_3 powders.

The gel obtained was transferred into a three-neck flask, and *n*-butyl alcohol was added. After being oscillated with the ultrasonic oscillator, stirred vigorously for 45 min, and refluxed for 1 h. When dehydration process was completed, it was distilled to remove the *n*-butyl alcohol. After filtrating, the loose powder was calcined at 800 °C and nanometer-sized Al_2O_3 was obtained.

2.1.3. Characterization of nanometer-sized Al_2O_3

A transmission electron microscope (TEM) pattern of nanometer-sized Al_2O_3, which was shown in Fig. 1, was obtained using a JEM-100CX transmission electron microscope (accelerating voltage, 80 kV; electron beam, <10 μA). It can be seen that the particles are similar to sphere and are well distributed with the particle size of 40–80 nm.

The BET of nanometer-sized Al_2O_3 was examined by an ST-30N_2 adsorption surface instrument, and the results showed that the BET surface area of synthesized nanometer-sized Al_2O_3 was 287 $m^2\,g^{-1}$. An XRD pattern was obtained using a D/max-γA XRD (Rigaku, Cu Kα $\lambda = 15.418$ nm). It was found that the synthesized nanometer-sized Al_2O_3 is γ-Al_2O_3 by comparing with the standard XRD patterns.

2.2. Preconcentration and determination

2.2.1. Apparatus

An Agilent 7500a ICP-MS (Agilent, Japan) system was used for the determination. The optimum operation conditions were summarized in Table 1.

The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China) was used for sample