Simultaneous determination of trace cadmium and lead in single human hair by tungsten electrothermal vaporization-flame atomic fluorescence spectrometry

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ABSTRACT

A new method was proposed for simultaneous determination of ultratrace cadmium and lead in a single string of human hair by coupling of a tungsten coil electrothermal vaporizer (W-coil ETV) and an argon–hydrogen flame for atomic fluorescence spectrometry (Ar–H_2 flame AFS). The sample digestion and experimental conditions for the determination of cadmium and lead in a single hair were investigated in detail. Under the optimal conditions, the limits of detection (LODs, 3σ) were 0.05 pg and 3 pg for Cd and Pb, respectively. The accuracy of the proposed method was demonstrated by analyzing a certified reference hair sample and several adult hair samples for trace Cd and Pb. By use of its high sensitivity and low sample consumption (typically 10 μL), it is potentially useful for determination of trace elements in a single string of hair from career and crime scenes for forensic purpose.

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1. Introduction

Hair is one of the most important biological samples that could be easily and noninvasively collected for forensic and clinical analysis. Besides, it is also rich in much information of the human body because the growth of hair needs the nutrients from follicles, including trace elements, carbohydrates, amino acids, etc. [1,2]. Therefore, determination of trace elements in the hair is an effective method in forensic analysis, because some favorable information stored in the hair could be obtained through construction of the fingerprint of trace elements, such as living location, working environment, and dietetic habit, which could provide useful evidence or shrink the scope of investigation [3]. Nevertheless, hair samples collected from criminal spots were usually tiny, even a single hair. Therefore, development of analytical methods for single hair analysis is important in forensic analysis.

Atomic spectrometry (AS) is the most common and dominant analytical method for trace elemental analysis of hairs, usually including atomic absorption spectrometry (AAS) [4–9], inductively coupled plasma-optical emission spectrometry (ICP-OES) [10,11], inductively coupled plasma-mass spectrometry (ICP-MS) [12–15]. However, in the common sample introduction methods such as pneumatic nebulization and hydride generation (HG), a large amount of sample is usually needed, and the determination of trace elements in a single hair is still challenging. Subject to the tiny amount of sample, improved conventional AS methods have been adopted to determine several elements in a single hair, such as electrothermal vaporization and gold amalgamation trapping with either AAS or atomic fluorescence spectrometry (AFS) for mercury detection [4], and laser ablation coupled to ICP-MS for determination of uranium [15]. A capillary electrophoresis with chemiluminescence (CE–CL) method has also been developed for sensitive detection of cobalt by our group [3]. However, these methods are limited to a couple of specified elements only. In addition, several nondestructive methods including instrumental neutron activation analysis (INAA), proton-induced X-ray emission (PIXE) [16], and X-ray fluorescence spectrometry (XRF) [17] have been used for determination of trace elements in a single hair. Nevertheless, irradiation contamination, high cost or low sensitivity greatly restricts their generalization. AFS is a widely used atomic spectrometric technique in trace element analysis for its high sensitivity and low cost, especially when coupled with HG. A series of biomedically and environmentally important elements could be accurately determined, such as mercury, cadmium, lead, arsenic, etc. However, the limited detectable element range and large sample consumption of traditional HG have hindered the further applications of AFS. To eliminate the limitation of HG and extend applications of AFS, electrothermal vaporization (ETV) was used to replace the HG system of traditional AFS instruments, and improved mass detection limit was obtained for the low sample consumption nature [18–21]. In our

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previous work, through interface-free hyphenation to further minimize analyte loss by inserting a W-coil ETV directly into the quartz tube of an Ar–H₂ flame, a new tandem atomizer was designed and coupled with AFS, with significantly improved performance obtained [22]. Considering the ultra sensitivity and very small sample consumption, it would be a suitable choice for determination of ultra elements in a single hair.

In recent years, the accumulation of heavy metals in the human body has become more and more serious especially in some developing countries, which come from occupational workplace, bioaccumulation, as well as environmental pollution, etc. Related analyses are mostly focused on the blood and urine. However, these samples usually cannot be easily collected in a special place like criminal spots, and do not record the information of long-term exposure to the specific living environment. Hair analysis has some unique advantages, such as relative simplicity of matrix, reasonably higher concentration of trace elements, easier sampling, transportation, and storage, compared to other biological samples. Furthermore, hair could reflect ever-increasing importance of specified substance during the growth for several months, and even process a potential chronological trace of elements according to farther periods corresponding to the hair segments more distant from the hair root [23,24]. In this work, using Cd and Pb as the model elements, analysis of a single hair by the W-coil ETV–Ar–H₂ flame AFS as well as the digestion method was investigated in detail.

2. Experimental

2.1. Instrumentation

Fig. 1 shows the schematic diagram of the experiment as well as the tandem atomizer for the atomic fluorescence spectrometer. A commercial dual-channel AFS (Model AFS-2202E, Beijing Haiguang Instrument Co., Beijing, China) was used in this study. Two hollow cathode lamps (HCLs of Cd and Pb obtained from Research Institute of Non-Ferrous Metals, Beijing, China) were used as the excitation sources. The optimal instrumental conditions for the determination of Cd and Pb were as follows: current of HCLs, 70 mA for Cd and 80 mA for Pb; voltage for the photomultiplier tube (PMT), −300 V; height of atomizer, 12 mm; flow rate of carrier gas and shield gas, 700 and 700 mL min^{-1}, respectively; flow rate of hydrogen, 130 mL min^{-1}.

The tandem atomizer used to replace the hydride generator of AFS instrument, including the tungsten coil electrothermal atomizer/vaporizer and its connection to the Ar–H₂ flame, has been described previously [22]. The W-coil, powered by a laboratory-made current power source, was from a commercial slide projector bulb (HLX64633, 10A, 150 W, OSRAM, Munich, Germany), and assembled to the laboratory-constructed ETV quartz tube, on top of which was the Ar–H₂ flame just above the W-coil. A mixture of argon and hydrogen

was employed as carrier gas, and another flow of argon was served as shield gas. The gasses were controlled by three independent flowmeters.

2.2. Reagents and materials

All reagents used in this work were at least of analytical grade. 18.2 MΩ·cm^{-1} high purity deionized water (DIW) obtained from a water purification system (Chengdu Ultrapure Technology Co., Ltd, Chengdu, China) was used throughout this work. Stock solutions (1000 mg L^{-1}) of Cd(II) and Pb(II) were purchased from the National Research Center of China (NRCC, Beijing, China). High purity HNO₃, H₂O₂ and other reagents were obtained from Kelong Chemical Reagents Co. (Chengdu, China). Working solutions were prepared daily by serial dilution of the stock solutions and stabilized in 0.5% (v/v) HNO₃. High purity (99.99%) argon was obtained from Qiaoyuan Gas Co. (Chengdu, China). Hydrogen gas was generated by using a hydrogen generator (SPGH-300, Zhongya Gas & Intrument Research Institute, Beijing, China). A Certified Reference Material (CRM) GBW07601a (human hair) from NRCC was used to validate the accuracy of the proposed method.

2.3. Sample preparation and analytical procedure

To obtain reliable analytical results, sample preparation must be processed carefully to maximally eliminate any potential interfering substances absorbed on the hairs possibly from exposed volatile substance, shampooing, and cosmetic products, etc. In this work, hair samples were firstly collected from the nape of the neck by using a stainless steel scissor, and put into a beaker immersed completely with acetone (99.5%). The samples within the beaker were then put into an ultrasonic cleaner (KQ-300DE, Kunshan Ultrasonic Instruments Co., Ltd, China) for cleaning for about 10 min, and subsequently washed by DIW for three times. After that, the hair samples were cut into pieces at a length of 0.5–1 cm, and dried at 85 °C to a constant weight. Approximately 2 mg was weighed into a 2 mL centrifuge tube with 70 μL HNO₃ (65%) and 30 μL H₂O₂ (30%). The sealed samples were heated in a domestic microwave oven (Galanz, China) at 600 W for about 5 min. After cooling to room temperature, the residues were diluted to 2 mL with DIW and subjected to analysis.

For an integral measurement, 10 μL sample solution was firstly pipetted onto the W-coil and the mixed carrier gas was ignited with a burning torch to form an Ar–H₂ flame on top of the quartz atomizer. Then the heating program of the W-coil for analysis was processed as follows: 45 s drying procedure at 2.6 A for removing the solvent, 15 s pyrolysis step at 2.8 A for eliminating the sample matrix, 5 s cooling, 10 s atomization/vaporization at 4.5 A, and final 4 s at 9.0 A for cleaning out the W-coil for next measurement. During the atomization/vaporization step, the atomic fluorescence signal was acquired by the PMT detector simultaneously.
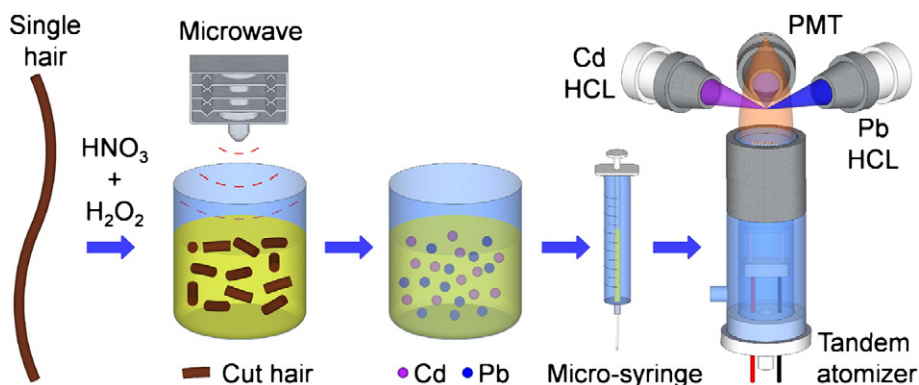

Fig. 1. The schematic diagram of the experiment. PMT: photomultiplier tube, and HCL: hollow cathode lamp.