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Analytical Note

Determination of heavy metals in leather and fur by microwave plasma-atomic emission spectrometry

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ABSTRACT

A sensitive method for the determination of heavy metals (Cd, Co, Cr, Cu, Hg, Ni and Pb) in leather and fur by microwave plasma-atomic emission spectrometry (MP-AES) based on microwave-assisted acid digestion and a multimode sample introduction system was developed. The leather was subjected to microwave-assisted digestion in a mixed solution of nitric acid and hydrogen peroxide before analysis by MP-AES. Results were compared with those from the standardized method instrument, inductively coupled plasma-atomic emission spectrometry (ICP-AES). Examination of a leather certified reference material (CRM, GSB 16-3087-2013) was used to validate the proposed method by statistical test, with good accuracy and precision shown for all heavy metals analyzed. Under optimum conditions, recoveries of 98.1%–102.6% and relative standard deviations (RSD) of 0.7%–3.0% were achieved, with limits of detection (LOD) ranging from 0.6 mg/kg (Cd) to 5.0 mg/kg (Pb). Furthermore, the MP-AES heavy metals analysis carried out on 23 test leather and fur samples showed an adequate concordance with results obtained from ICP-AES. The benefits of the MP-AES are related to low analysis cost and improved operational safety with nitrogen used for plasma generation. The MP-AES system investigated could offer comparable performance compare to ICP-AES and may be applied as an optional method for routine analysis in leather and fur testing institution.

1. Introduction

It is well known that the presence of heavy metals (for example, Cd, Co, Cr, Cu, Hg, Ni and Pb) is of considerable concern to human health, and agricultural, livestock and aquatic industries [1]. Heavy metals are usually found in leather and other textile products due to the use of tanning agents, dyes and additives containing metal salts in conditional tanning processes [2]. Therefore, the concentration of heavy metals in leather and leather products is regulated in several countries and it is clear that monitoring of heavy metals in leather is extremely important.

A variety of analytical methods for the determination of heavy metals have been developed and reported, including atomic absorption spectrometry (AAS) [3,4], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [5,6], inductively coupled plasma-mass spectrometry (ICP-MS) [7–10], and others [11–13]. Among these techniques, ICP-AES is the most widely employed [14], while AAS provides the highest analytical sensitivity particularly when using an electrothermal atomizer for atoms generation, however, this requires elements to be analyzed one by one. Microwave plasma-atomic emission spectrometry (MP-AES) is an alternative spectroscopic analysis technology in which a stable nitrogen plasma is produced using microwave energy [15]. Although microwave plasmas have been in existence for a couple of decades, the main usage has been restricted to specific research groups with very few studies in commercially available analytical instruments.

Recently, the use of nitrogen as a plasma gas has also been studied. In addition, comparisons of microwave and inductively coupled plasma sources suggest that MP performance approaches that of ICP [16]. Therefore the MP-AES, which runs on nitrogen, is of interest for many fields of analytical chemistry, as operating costs are significantly lower than for argon or helium dependent instruments [17,18]. Studies have reported the successful use of an MP-AES instrument (Agilent Technologies, 4100 MP-AES) for element analysis on agricultural materials [19]. However, there is no study that outlines the performance of the nitrogen MP-AES technique for analysis of leather and fur materials, with even less scientific information available on heavy metals.

The aim of this work is to develop an inexpensive method for the determination of heavy metals in leather and fur. In this work, samples underwent microwave-assisted digestion and detection by MP-AES

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and ICP-AES. Verification of the proposed method, including accuracy, precision and limit of detection (LOD) data, are discussed in this paper. The method was applied for the analysis of Cd, Co, Cr, Cu, Hg, Ni and Pb in leather and fur samples by MP-AES, and results were compared with the those from ICP-AES.

2. Experimental

2.1. CRM, reagents and samples

The stock standard solution (1000 mg/L) of Cd, Co, Cr, Cu, Hg, Ni and Pb were certified reference materials (CRM), which were purchased from National Institute of Metrology (China). 65% (w/w) nitric acid (HNO_3), 30% (w/w) hydrogen peroxide solution (H_2O_2), sodium borohydride ($NaBH_4$), and sodium hydroxide (NaOH) solutions were obtained from Beijing Chemical Works, all of guaranteed reagent (GR) grade. A reductant solution of 2% (w/v) $NaBH_4$ stabilized with 1% (w/v) NaOH solution was introduced during determination by MP-AES. The CRM for Cd, Co, Cr, Cu, Hg, Ni and Pb in leather (GSB 16-3087-2013) was obtained from China Leather and Footwear Industry Research Institute. All solutions were freshly prepared in pure water (18.2 MΩ · cm) before use. The 23 test leather and fur samples of different origin were collected from several large leather factories in China (see Table S1 in the Appendix A. Supplementary data).

2.2. Apparatus

The MDS-10 microwave digestion system from Sineo Co., Ltd was used for the microwave-assisted acid digestion of all leather samples. The Agilent 4100 MP-AES with Multimode Sample Introduction System (MSIS) (allowing simultaneous reductant solution introduction) was used for the analysis of heavy metals in leather and fur samples. An Agilent 710-ES ICP-AES was used as a reference for all determinations. As schematically shown in Fig. 1, the MSIS permitted the use of both vapor generation (for Hg) and routine pneumatic nebulization (for Cd, Co, Cr, Cu, Ni and Pb) sample introduction routes without having to change the sample introduction system.

The instrument operating conditions and settings to determine Cd, Co, Cr, Cu, Hg, Ni and Pb by MP-AES and ICP-AES are listed in Table 1. Viewing positions were not included as this parameter was optimized before running each experimental batch.

2.3. Microwave-assisted digestion

The leather and fur samples were cut into pieces of up to 0.5 cm edge length and 0.5 cm thickness. Approximately 0.2 g (weighed to 0.1 mg) of sample was transferred into the microwave digestion flask, which was made of polytetrafluoroethylene with maximum allowed pressure and temperature of 5 MPa and 260 °C respectively. 4 mL of 14.4 M nitric acid and 1 mL of 9.8 M hydrogen peroxide solution were added to each flask. The samples were processed by microwave-assisted digestion as follows: ramp temperature to 130 °C and hold for 5 min, ramp and hold at 180 °C for 10 min, finally ramp to 220 °C and hold for 20 min. The total ramp time from ambient to final temperature should take more than 20 min. After digesting, the microwave digestion flasks were allowed to cool to ambient temperature before handling. The digested samples were transferred and made up to 25 mL in a volumetric flask with an acidity of 0.7 mol/L, and then filtered for instrumental analysis. A blank containing identical reagent quantities, without the addition of sample, was also prepared. The leather certified reference material instead of samples with same weight (0.2 g) was digested in accordance with the above procedure to determine the heavy metal recovery.

2.4. Determination

After sample preparation, wavelength optimization was performed in order to select the optimal spectral wavelengths for measurement. Multi element standard solutions were analyzed by MP-AES and ICP-AES over the wavelength range of interest to monitor spectral interferences. The selected wavelengths are presented in Table 1. For calibration, mixed standard solutions were prepared from the stock standard solution of 1000 μg/mL by dilution with 5% (w/v) nitric acid.

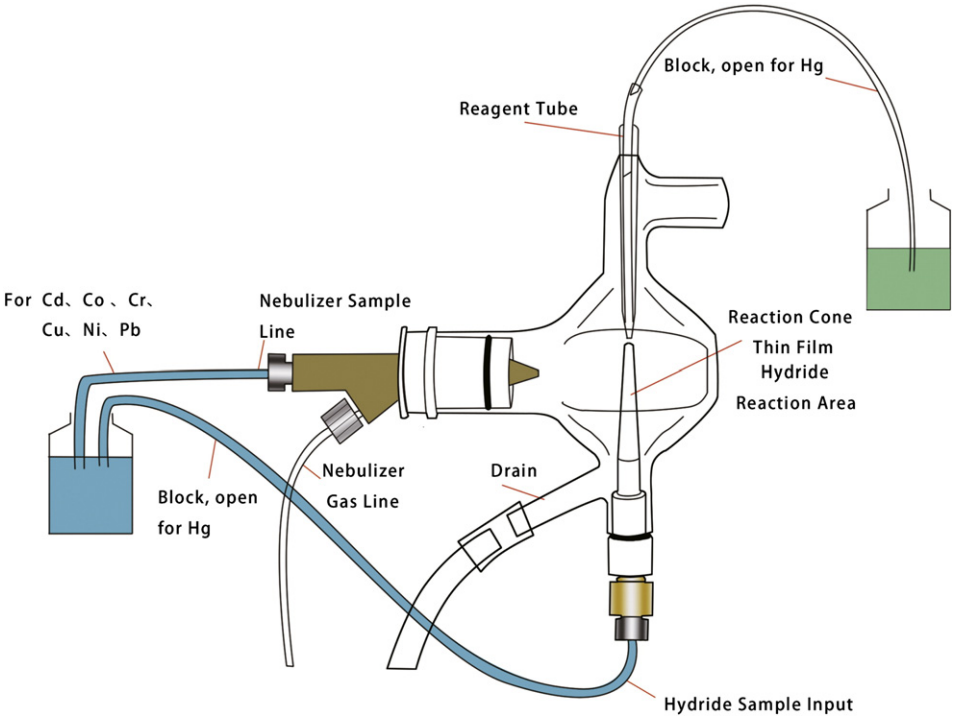

Fig. 1. Schematic diagram of the multimode sample introduction system for MP-AES.