A micro-fluidic sub-microliter sample introduction system for direct analysis of Chinese rice wine by inductively coupled plasma mass spectrometry using external aqueous calibration

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ABSTRACT

A microfluidic sub-microliter sample introducing system was developed for direct analysis of Chinese rice wine by inductively coupled plasma mass spectrometry (ICP-MS). It consisted of a microfluidic chip integrating variable-volume sampling channels (0.1–0.8 μL), an eight-way multi-functional valve used in flow injection analysis (FIA), a syringe pump and a peristaltic pump of the Ar ICP-MS instrument. Three solutions, i.e., 15, 40 and 100 g L^{-1} glucose in 20% ethanol were used to simulate Chinese rice wine of the dry type, the semidry type and the semisweet type, each. The effects of their volume introduced into ICP-MS on the plasma stability and ICP-MS intensities were studied. The experimental results showed that neither alteration of plasma stability nor carbon deposition was observed when the sampling volume of 20% ethanol containing 100 g L^{-1} glucose was downscaled to 0.8 μL. Further reducing the sampling volume to 0.4 μL, no significant difference between the intensities of multi-element standard prepared in three simulated Chinese rice wine matrices and those in aqueous solution was observed. It indicated no negative effect of Chinese rice wine matrix on the ICP-MS intensities. A sampling volume of 0.4 μL was considered to be a good compromise between sensitivity and matrix effect. The flow rate of the carrier was chosen as 20 μL min^{-1} for obtaining peaks with the highest peak height within the shortest time. Based on these observations, a microflow injection (μFI) method for the direct determination of cadmium and lead in Chinese rice wine by ICP-MS using an external aqueous calibration was developed. The sample throughput was 45 h^{-1} with the detection limit of 19.8 and 10.4 ng L^{-1} for Cd and Pb, respectively. The contents of Cd and Pb in 10 Chinese rice wine samples were measured. The results agreed well with those determined by ICP-MS with the conventional sampling system after microwave assisted digestion. The recoveries of three Chinese rice wine samples ranged between 95.5 and 102.8%. Furthermore, the determined contents of Cd and Pb in a certified reference material of red wine (GBW 10031) and a quality control test material of wine (FAPAS T07163QC) by the proposed method were in fairly good accordance with the certified/assigned values. All results verified the accuracy of our method.

1. Introduction

Chinese rice wine (8–16% v/v ethanol), also named yellow wine, is one of the three most ancient alcoholic beverages in the world. It is traditionally made from sticky rice, wheat and some medicinal plants or herbs. Chinese rice wine is widely consumed in south China and is also used as an ingredient in traditional Chinese medicine for the prevention of aging and cardiovascular diseases [1–4]. In the National Standard of China GB 13662-2008, Chinese rice wine can be classified into four categories according to the concentrations of the total sugars: dry type (total sugars ≤ 15 g L^{-1}), semidry type (15.1 g L^{-1} < total sugars ≤ 40 g L^{-1}), semisweet type (40.1 g L^{-1} < total sugars ≤ 100 g L^{-1}) and sweet type wines (total sugars > 100 g L^{-1}). Among the four types of Chinese rice wine, semidry type and semisweet type are dominant and the sweet type is produced in the smallest amounts.

Chinese rice wine may contain low levels of Cd and Pb. The amounts of Cd and Pb depend on the raw materials, soils, material used in building the fermentation or aging processes by which it is made [5]. Cadmium and lead in Chinese rice wine may be accumulated in consumers' body such as liver, kidney, brain, etc., becoming potential contaminants. These elements produce harmful effects on the human health, affecting to several organ systems, such as nervous, gastrointestinal, reproductive and skeletal, and biochemical activities

[6,7]. Additionally, trace metals in Chinese rice wine are considered as good indicators of wine geographical origin and can be used as criteria for guaranteeing authenticity [8,9]. However, information on metal levels in Chinese rice wine is scarce, even though such analysis has been extensively used in characterization of red wine and white wine [5,8].

Inductively coupled plasma mass spectrometry (ICP-MS) is a most powerful technique allowing the ultratrace analysis of a wide variety of samples, because of its exceptional detection power, multi-elemental and isotopic capabilities and wide dynamic range [10]. Therefore, it is an excellent tool for detailed characterization of the elemental composition of wines. Similar to red wine, Chinese rice wine contains high contents of ethanol and sugars. Normally, sample preparation should be carried out before the analysis. For example, wet digestion on a hot plate or in a microwave oven is performed to decompose Chinese rice wine [9,11,12]. To remove ethanol and sugars, Chinese rice wine samples are evaporated to dryness, and then the residues are ashed in a muffle furnace. Finally the ashes are dissolved in acid solutions [13,14]. However, the two methods are complicated and time-consuming in pretreatment process, with high risk of contamination and/or loss of analyte [12]. Besides, considerably dilution of Chinese rice wine is also employed [11,15]. Although it is a simple and time-saving way, spectral and non-spectral interferences caused by the organic matrix, especially by high contents of ethanol and sugars, are significant [16]. Thus, matrix matched calibration technique or the standard-addition method is recommended to minimize physical and chemical interferences [15,16]. However, employing matrix-matched standards is difficult, since Chinese rice wine samples contain unspecified or variable amounts of ethanol and sugars, and the standard-addition strategy is time-consuming and tedious.

Direct analysis of Chinese rice wine by inductively coupled plasma mass spectrometry is one of the hottest topics. As a complex matrix containing high alcohol and sugars contents, the introduction of Chinese rice wine into ICP-MS may result in problems such as plasma quenching or carbon deposition on the sampler and skimmer cones, or physical and chemical interferences [16,17]. Plasma quenching and carbon deposition have been routinely overcome by the reduction of the carbon load with many strategies. They include usage of ultrasonic or low-flow (<100 μL min^{-1}) nebulizers with the simultaneous addition of oxygen to the plasma, the water-in-oil emulsification, and discrete micro-sampling techniques such as electro-thermal vaporization or laser ablation sampling [16,17]. Nevertheless, polyatomic interferences due to the presence of carbon in the plasma can not be eliminated and usage of the standard-addition method is recommended [16], which is time-consuming. Although O_2 can be used as auxiliary gas to help the matrix decomposition, it may cause wear to nickel cones and refractory oxide polyatomic interferences [18]. Recently, a double-focusing sector field ICP-MS was optimized for the direct simultaneous multi-element analysis of crude oils and gas condensates after oxygen was added to the sample Ar flow [19]. To the best of our knowledge, direct determination of metals in Chinese rice wine by quadruple ICP-MS in the Ar environment has not been reported.

In this work, a microfluidic chip for introducing variable-volume sample at the sub-microliter level was fabricated. Combined with the 8-way multi-functional valve used in flow injection analysis (FIA), the introduction of sub-microliter sample in inductively coupled plasma mass spectrometry (ICP-MS) was achieved. Three solutions, namely, 15, 40 and 100 g L^{-1} glucose in 20% ethanol were used to simulate Chinese rice wine of the dry type, the semidry type and the semisweet type, each. The effects of the volume of three simulated Chinese rice wine matrices introduced into ICP-MS on the plasma stability and ICP-MS intensities were studied. The relationship between the sampling volume and sensitivity was evaluated and the carrier flow rate was optimized. To validate this method, spike recovery tests of three Chinese rice wine samples, and the analysis of a certified reference material of red wine (GBW 10031) and a quality control test material of wine (FAPAS T07163QC) were performed. Finally, the proposed method was applied in the direct determination of Cd and Pb in ten Chinese rice wine samples and the results were compared with those obtained by ICP-MS with the conventional sampling system after microwave assisted digestion.

2. Experimental

2.1. Chemicals and reagents

All the reagents and solvents were of analytical reagent or HPLC grade. Ultrapure water (Milli-Q Plus 185, Millipore Corporation) was used throughout. Before use, all the utensils were soaked in 10% HNO_3 for 24 h, rinsed thoroughly in ultrapure water, and all solutions were filtered through 0.45 μm membrane filters.

Approximately 10 μg L^{-1} Y in ultrapure water was used as the carrier solution, which was prepared by serial dilution of 1000 mg L^{-1} yttrium atomic absorption standard (Sigma-Aldrich, St. Louis, MO, USA) with ultrapure water. Approximately 10 μg L^{-1} yttrium was added in all standards and samples to serve as the internal standard. A series of 1, 4, 10, 20 and 50 μg L^{-1} multi-element standard work solutions was diluted from multi-element standard stock solution of 10 mg L^{-1} containing Cd and Pb (SPEX CertiPrep Inc., USA) in the carrier solution. Three solutions, *i.e.*, 15, 40 and 100 g L^{-1} glucose in 20% ethanol were used to simulate Chinese rice wine of the dry type, the semidry type and the semisweet type, each. High-purity nitric acid and 30% H_2O_2 (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used in the microwave assisted digestion process of Chinese rice wines for their measurements by ICP-MS with the conventional sampling system. A phloxine solution (0.01 mol L^{-1}) and 2% brilliant blue solution were used for obtaining the charge coupled device (CCD) images. A certified reference material of red wine (GBW 10031, National Standard Material Center, Beijing, China) and a quality control test material of wine (FAPAS T07163QC, The Food and Environment Research Agency, Sand Hutton, York, England) were analyzed to validate the accuracy of the proposed method.

2.2. Fabrication of microchip with variable-volume sampling channels

The channel design of the microfluidic device used in this work is shown in Fig. 1. Holes A and K were two inlets for the carrier solution and the hole B was the inlet for the sample. Holes C–J were the outlets of the sample waste of sampling channels P_1–P_2 (5 mm), P_1–P_3 (10 mm), P_1–P_4 (15 mm), P_1–P_5 (20 mm), P_1–P_6 (25 mm), P_1–P_7 (30 mm), P_1–P_8 (35 mm) and P_1–P_9 (40 mm), each. T was the outlet of the microfluidic chip. The channel between A and P_1 and the channel between K and P_{10} were two carrier channels. The channel between B and P_1 was the sample channel. The channels C–P_2, D–P_3, E–P_4, F–P_5, G–P_6, H–P_7, I–P_8 and J–P_9 were the sample waste channels of the sampling channels P_1–P_2, P_1–P_3, P_1–P_4, P_1–P_5, P_1–P_6, P_1–P_7, P_1–P_8 and P_1–P_9, each. All other channels in the microchip were auxiliary channels. The dimensions of all channels were 100 μm deep and 300 μm wide and the lengths of all channels were given in Fig. 1 in mm.

The microchip was fabricated on soda-lime glass using photolithographic and wet chemical etching procedures described elsewhere [20]. After the design on photomask was transferred onto the photoresist layer on the glass substrate, all channels on the glass substrate were etched with a mixture of 1 mol L^{-1} HF and 1 mol L^{-1} NH_4F for 100 min. After etching step, the chip was washed by high flow-rate running tap water to remove the remaining etchant in channels. Access holes were drilled into the etched plate with a 2.0 mm diameter diamond-tipped drill bit at the terminals of the channels. After permanent bonding by a thermal bonding procedure, the outlet of the microfluidic chip (T as shown in Fig. 1) on the edge of the glass chip was drilled 3 mm deep with a 0.35 mm diameter flat-tipped