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**RESEARCH PAPER**

# Determination of Metallic Elements in Environmental Samples by Matrix-Assisted Microwave Induced Plasma Surface Sampling Atomic Emission Spectrometry

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**Abstract:** A novel method for the determination of metallic elements in environmental samples was developed based on matrix-assisted plasma surface sampling atomic emission spectrometry. A piece of filter paper was used as sample substrate. By direct interaction of the plasma tail plume with the filter paper surface, the filter paper absorbed energy from the plasma source and released combustion heating to the analytes originally present on its surface, thus to promote the atomization and excitation process. Surface sampling was performed in cases of both liquid and solid state analytes. Therefore, no flow injection system was required and the sample pretreatment process was simplified. The proposed method provided several advantages, including fast analysis speed (about 240 samples per hour), little sample consumption (μL or μg level), and simple instrument design and system operation. These advantages made it attractive as a potential miniaturized atomic emission spectrometry (AES) system for in situ and high-throughput elemental analysis. Quantitative analysis of metal ions was achieved in this study for elements Ag, Au, Ba, Cd, Cr, Cu, Eu, La, Mn, Ni, Pb, Sr and Y. Under the optimal conditions, the LOD values of the 13 elements ranged from 1.0 to 88 ng $mL^{-1}$. Repeatability, expressed as relative standard deviation (RSD) from 10 replicates, ranged from 2.3% to 6.8%. To validate the proposed method, the system was employed to determine metallic elements in standard reference materials of environmental samples. The content of each element detected by this system was well in agreement with the certified values.

**Key Words:** Atomicemission spectrometry; Microwave induced plasma; Surface sampling; Matrix assisted; Environmental analysis

## 1 Introduction

The environment is a comprehensive and complex system which is formed by solid, liquid and gaseous matters. Typical examples of solid, liquid and gaseous samples in our natural environment are, in order, solid waste, soil and sediment, water and wastewater, air and exhaust from various pollution sources. Atomic spectrometry is an important technique for monitoring heavy metals in our environment. Conventional instrumental methods of atomic spectrometry are including inductively coupled plasma atomic emission spectrometry (ICP-AES)[1–3], atomic absorption spectrometry (AAS)[4,5] and atomic fluorescence spectrometry (AFS)[6–8]. They all have outstanding performance for elemental analysis. However, these conventional instruments are limited by their bulky volume, high power consumption, high maintenance and operational costs. As a result, they can only be used for laboratory-based applications. Environmental samples have the characteristics of complex components and various interfering substances. Therefore, in most cases, sample pretreatment is essential in environmental analysis, which consumes a lot of time of analysts. In environmental pollution incident investigations and regional/watershed scale ecological risk investigations, due to the large sample amount

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and wide investigation range, the high-throughput and on-site detection technology becomes an urgent need. Therefore, investigation of small size atomic spectrometer which enables high-throughput analysis of environmental samples is of great importance.

Plasma surface sampling technique, due to its advantages including simple device, high analysis speed and little sample pretreatment, has attracted more and more attentions in recent years. So far, more than ten different kinds of plasma techniques have been developed for ambient ionization methods for surface sampling mass spectrometry[9–15]. Nevertheless, all of these techniques focus on the analysis of organic compounds with mass spectrometry. Few works has done in atomic spectrometry with plasma based surface sampling techniques. This was mainly due to the fact that the excitation energy and gas temperature of the plasma tail plume was too low to catch the atomic spectral information.

In this work, matrix assistance was utilized to couple with plasma atomization emission spectrometry for surface sampling. Simple and low cost quantitative filter paper was used as sample matrix. The filter paper matrix was served as the partial energy producer to promote the atomization and excitation process and the sample substrate to adsorb sample solution or powder. This analytical system was successfully applied to analysis of 13 metal elements in water, soil, sediment and other environmental samples, and the detected content of each element was well in agreement with the certified values. The proposed method took advantages of fast analysis for multiple elements, little sample consumption, without complex sample pretreatment, which was promising for high-throughput analysis. Moreover, the whole system was small in size, and simple in structure, which provided a possibility to design a portable instrument for environmental analysis.

## 2 Experimental

### 2.1 Instruments and reagents

The following instruments were used in the work: YY1-50W-2045 solid-state microwave generator (Najing Yanyou Electronic Science and Technology Co. Ltd., China), AvaSpec-2048-4-DT four channel fiber optic spectrometer system (Avantes Science and Technology Co. Ltd., Netherlands), and D07-19B mass flow controller (Beijing Sevenstar Electronics Co. Ltd., China).

All reagents used in this work were of at least analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a UP water purification system was used throughout this work. High-purity argon was used as plasma discharge gas (99.999%, Qiaoyuan Gas Co.). Stock solutions (1000 mg $L^{-1}$) of Ag, Au, Ba, Cd, Cr, Cu, Eu, La, Mn, Ni, Pb, Sr and Y were purchased from the National Research Center for Standard Materials (NRCSM) of China. The working standards were prepared by diluting stocking solution with nitric acid (5%). Both liquid and solid reference materials, including simulated natural water sample (GBW(E)08607), soil sample (GBW07428), marine bottom sediment sample (GBW07313), gold ore sample (GBW07801) (NRCSM, China), were used to validate the method accuracy.

### 2.2 Experimental setup

The schematic diagram and photograph of the experimental setup are shown in Fig.1a and Fig.1b, respectively. The main components include home-built microwave-induced plasma source, solid-state microwave generator, carrier gas system, sample plate and CCD-array spectrometer system.

#### 2.2.1 Microwave-induced plasma source

The microwave-induced plasma source used here was a Surfatron structure, which employed surface wave for energypropagation. The microwave coaxial cavity was cylinder- shaped and made of copper with a fused-silica tube (1 mm i.d., 6 mm o.d., and 200 mm long) centered axially. The discharge gas (argon) was fed through the fused-silica tube to facilitate discharge. The radio frequency power from the solid-state microwave generator (2450 MHz, power of 0–150 W) was input into the cavity via a standard N-type

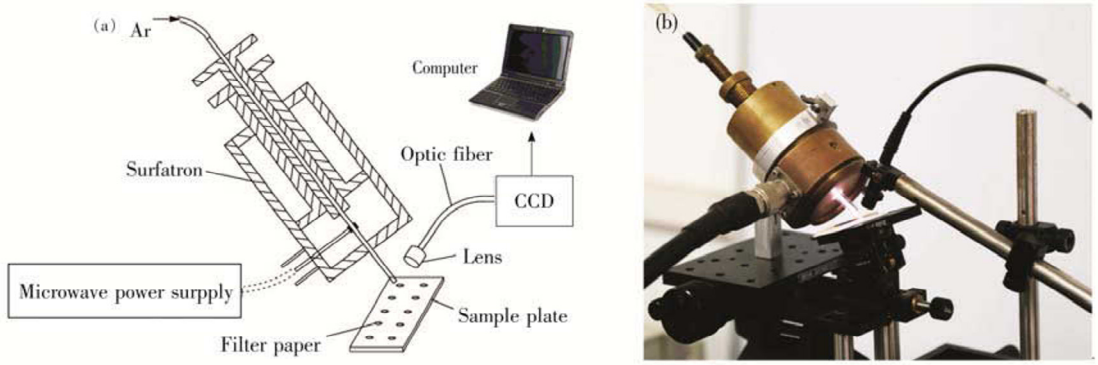


Fig.1 Schematic diagram (a) and photograph (b) of experimental setup