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Elemental imaging method based on a dielectric barrier discharge probe coupled with inductively coupled plasma mass spectrometry

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ABSTRACT

An elemental imaging method based on a dielectric barrier discharge (DBD) probe as a sputtering source coupled with inductively coupled plasma mass spectrometry (ICP-MS) has been demonstrated. The DBD probe is simple to construct and the discharge power for producing micro plasma jet at ambient condition is as low as 3.75 W. To investigate the sputtering process, the major operating parameters of this technique are demonstrated by detecting ^{23}Na, ^{27}Al, ^{29}Si, ^{44}Ca, ^{55}Mn and ^{57}Fe in rock standard reference materials GBW07108. The reproducibility of the parallel detection was 1% ($n = 7$) for Hg in ABS sample was obtained. Based on these conditions, the elemental imaging is successfully obtained in the lead-based glaze ceramic with ^{206}Pb, ^{207}Pb, and ^{208}Pb, Chinese seal script with ^{202}Hg and siliceous stromatolites with ^{27}Al, ^{29}Si, and ^{44}Ca. When the 100 μm capillary was used to ablate the ABS sample, the washout time of 600 ms for Hg was obtained, and the spatial resolution of 106 μm was obtained. In addition, the potential quantitative analysis of this method has been studied, which provide the detection limits of ABS samples with 252 μg g^{-1} for ^{52}Cr, 24 μg g^{-1} for ^{202}Hg and 167 μg g^{-1} for ^{208}Pb, respectively. The present imaging method has the unique capabilities of multi-elemental analysis, easy set-up and low consumption, which may serve as a complementary technology for current elemental imaging technology.

1. Introduction

Elemental imaging technology is recognized as an important analytical method which provides elemental distribution of samples and it has brought forth a wide variety of different applications [1–4]. In order to achieve the sensitive analysis of increasingly complex solids, many innovations in analyzing equipment, dissociation and sample introduction methods have been developed. X-ray-based spectroscopy has been applied to the study of sample surfaces and their bulk compositions [5, 6]. However, these technologies are not sensitive enough for trace element determination owing to their low detection power and there are also difficulties in quantifying the analytical data [7]. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has demonstrated remarkable ability for elemental imaging [8, 9]. However, sample preparation is cumbersome and some samples cannot be directly analyzed due to high vacuum condition [10].

Glow discharge optical emission spectrometry(GD-OES) is a well-established and widely used analytical method for bulk and depth profile analysis which provides laterally resolved elemental information [11]. The application of acousto-optical imaging spectrometer (AOS) for different GD imaging tasks provides fast switching between different spectral lines in 200 ms time frames [12]. Although this barrier can be overcome using radio-frequency-powered GD, the lateral resolution is bad [13]. Further more, the size and shapes of the sample are limited by those of the vacuum chamber.

Laser ablation is an effective technique to generate significant energy leading the material ablated in melting or vaporization state by photon energy [14]. The laser ablation technique coupled with ICP-mass spectrometry (LA-ICP-MS) can be used in situ analysis and visualizing the elemental distributions of the solid samples. The technique offers minimal sample preparation, high analytical throughput and simultaneous lateral resolution at the micrometer and sub-micrometer levels [15]. A large number of works has been reported based on LA-ICP-MS imaging analysis, such as cultural heritage objects [16, 17] and geological solids [18, 19]. However, the laser energy is very high, which inevitably causes damage to samples [20]. Furthermore, the complex laser systems are reletively expensive to be equipped in normal labs for element analysis.

Recently, another trend on the development of ambient dielectirc barrier discharge(DBD) methods attracts much interest and it has been used in numerous applications [21–25]. DBD probe enables the ambient ionization and desorption of molecules from solid materials [26].

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Compared with LA, DBD probe contains a large number of charged particles and active ions simultaneously, which can remove mass from the surface of solid samples. DBD probe can operate at lower surface temperatures (~30 °C), which is in favor of detecting heat-sensitive materials [27]. In addition, DBD probe is simple to set-up with a quartz capillary as the dielectric barrier and two electrodes mounted outside of the capillary [28]. As an ambient ion source, investigating the authenticity of Chinese works of art demonstrated the usability of DBD-MSI for nondestructive imaging analyses [29]. As a sample introdution, rapid and sensitive method for elemental depth profiling [30] by the DBD probe coupled with ICP-MS has been reported. It is proved that the DBD probe can sputter the material from the surface of solid samples and then the sputtered aerosol can be efficiently transported to the ICP-MS for in-situ analysis. Therefore, the DBD probe coupled with ICP-MS will be considered as a new technology, which can obtain the real-time elemental signals at different positions of the sample for elemental imaging analysis.

Here, we develop a new DBD-probe-ICP-MS imaging system, which can perform two-dimensional surface elemental imaging of solid samples. The DBD probe based on imaging system shows low consumption and high stability. In addition, the effects of operating parameters of the DBD probe and detection system on the achievable imaging resolution are investigated. At the same time the important elemental mapping in different solid samples are evaluated. This method offers the advantage of operating at atmospheric pressure, without chemical pretreatment, multi-element analysis, simple construction and such a probe is surprisingly economical and easy. It may be considered as a complementary multi-elemental imaging method to existing techniques.

Table 1
Operating Conditions of ICP-MS Instrument for imaging.

Parameters	Values
RF Power (W)	1200
plasma gas flow rate (L/min)	13
auxillary gas flow rate (L/min)	1
measurement mode	time-resolved, TRA
dwell time per isotope(ms)	10
quadrupole settling time (ms)	1.5–10 (depending on isotope)
isotope measured	^{23}Na, ^{27}Al, ^{29}Si, ^{44}Ca, ^{55}Mn,^{57}Fe, ^{52}Cr, ^{202}Hg, ^{206}Pb, ^{207}Pb, ^{208}Pb
the discharge gas	He
the discharge power (W)	3.75–30
the discharge gas flow rate (L/min)	0.06–0.08
the discharge tube diameter (μm)	100–318
the carrier gas flow (L/min)	0.7
the plasma distance (mm)	1–2

2. Experimental section

2.1. DBD-probe-ICP-MS setup

As shown in Fig. 1(a), the DBD-probe-ICP-MS setup comprises the DBD probe, sputtering chamber and three-dimensional (3D) movement stage. The DBD probe utilizes a quartz capillary coated with silica (Polymicro Technologies) as the dielectric barrier between two metal electrodes (20 mm-long Al films), which are separated by 15 mm and wrapped around the capillary. The plasma is generated between the two electrodes by a power supply (CTP-2000 K, Colona Co. Ltd., Nanjing, China) at atmospheric pressure. The power supply can produce 2–25 kV at an adjustable frequency of 1–30 kHz without a

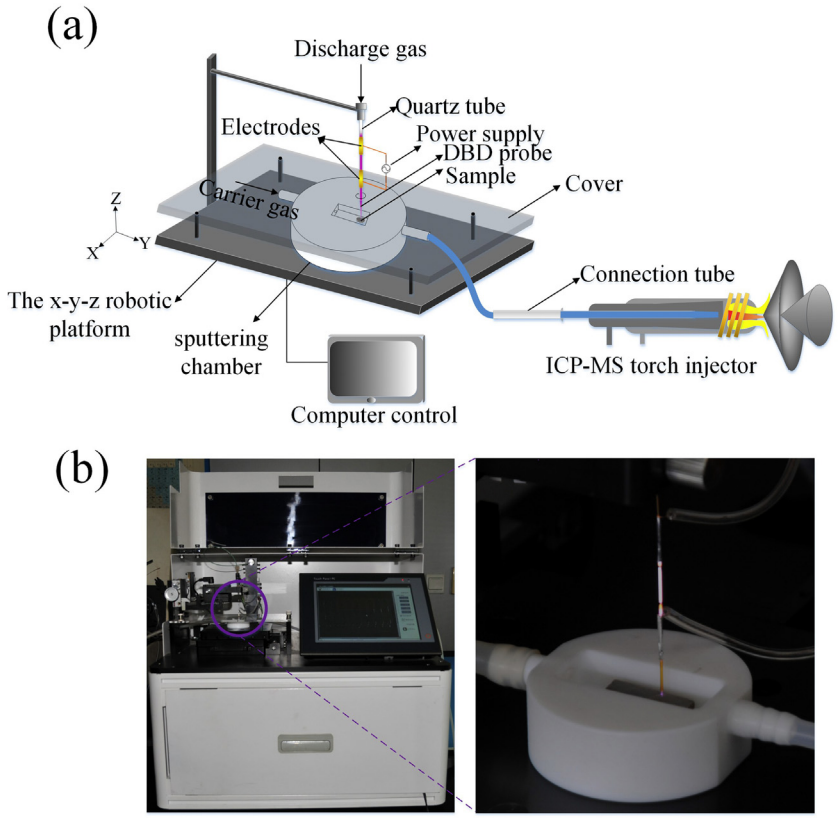

Fig. 1. (a) Schematic diagram of the DBD-probe-ICP-MS-imaging instrument. (b) Photo of the DBD probe instrument.