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Technical Note

Pulsed radio-frequency discharge inductively coupled plasma mass spectrometry for oxide analysis

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ABSTRACT

A direct solid sampling technique has been developed based on a pulsed radio-frequency discharge (RFD) in mixture of N_2 and Ar environment at atmospheric pressure. With an averaged input power of 65 W, a crater with the diameter of 80 μm and depth of 50 μm can be formed on sample surface after discharge for 1 min, suggesting the feasibility of the pulsed RFD for sampling nonconductive solids. Combined with inductively coupled plasma mass spectrometry (ICPMS), this technique allows to measure elemental composition of solids directly with relative standard deviation (RSD) of ~20%. Capability of quantitative analysis was demonstrated by the use of soil standards and artificial standards. Good calibration linearity and limits of detection (LODs) in range of 10^{-8}–10^{-9} g/g were achieved for most elements.

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1. Introduction

The multi-elemental analysis of oxides is gaining importance in environmental quality monitoring. Routine methods for oxide analysis are wet chemistry and direct solid sampling methods. Direct solid sampling is more popular with no need of tedious and time-consuming preparation. Well-known techniques, such as X-ray fluorescence spectroscopy (XFS) [1], laser-induced breakdown spectroscopy (LIBS) [2, 3], laser ionization mass spectrometry (LIMS) [4,5], direct current glow discharge mass spectrometry (DC-GDMS) [6], and ICPMS-based methods [7–9] have been applied for the elemental determination in oxide-rich samples. Generally, XFS, LIBS, and LIMS are used to analyze environmental samples, e.g., sediments and soils, but they cannot offer the requisite sensitivity to determine low-level elements of interest [9]. Application of DC-GDMS has been the method of choice for solid analysis [10–12], whereas the major restricting factor is that samples have to be electrically conductive in nature. The advent of RF-GDMS has played a complementary role in broadening the application field of GDMS as it allows most nonconductive samples to be analyzed directly [13–16].

Atmospheric-pressure source condition makes ICPMS-based techniques become an attractive option for direct analysis of solids [17]. Laser ablation (LA) ICPMS is now well established as a valuable tool in the analysis of both conductive and nonconductive materials [18]. It is also capable of providing elemental spatial information at micrometer scale. A plain flaw was its costly device. Electrothermal vaporization ICPMS (ETV-ICPMS) with LODs down to ng/g for solid analysis has been reported [19,20]. Facilitated by a matrix modifier, a better sensitivity and reproducibility can be achieved, but its memory effect cannot be ignored [7]. These two methods are playing significant roles in the direct analysis of solid samples. Atmospheric-pressure discharge coupled with ICPMS, such as arc discharge and spark discharge, is a well-accepted method for solid analysis [21,22]. In our previous investigation, pulsed direct-current discharge employed as an ablation source was coupled with ICPMS [23]. Compared to continuous DC discharge, pulsed discharge coupled to ICPMS demonstrates better performance in the determination of elements in different matrices [23]. Unfortunately, there is still a requirement that samples must be inherently conductive.

Despite the known benefits of RFD at reduced pressure, few applications of this mode were investigated at atmospheric pressure for the elemental determination in solid samples. Study here is intended to evaluate the applicability of pulsed RFD for sampling of oxide samples at atmospheric pressure. RF power source with frequency of 40.68 MHz was modulated and stable discharge can be achieved [24]. Capability of direct sampling was demonstrated with a crater formed on sample surface. Integrated with ICPMS, pulsed RFD offers good linearity of calibration curves for determining the elements in soils and artificial samples with LODs of 10^{-8}–10^{-9} g/g.

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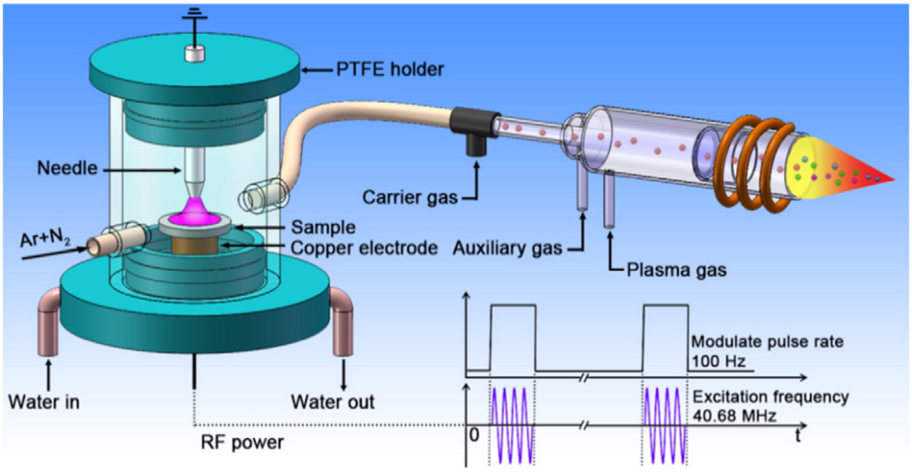

Fig. 1. Schematic diagram of pulsed radio-frequency discharge cell coupled to ICP source.

2. Experimental

2.1. Instruments

Fig. 1 is the schematic diagram of experimental setup. Briefly, the discharge cell consists of a tungsten needle tip, copper electrode, sample, PTFE holder, and quartz glass chamber (18 mm i.d, 32 mm height). Shown in Fig. 2 was image of tungsten needle tip with diameter of ~50 μm. It was fabricated via mechanical method using tungsten wire (99.9999%) with a diameter of 1 mm (Yiji Co., Shanghai, China), serving as the ground electrode. Cooled by chilling water, the copper electrode was placed between the sample and the pulsed RF power supply source. The gap between the front end of tip and sample surface was about

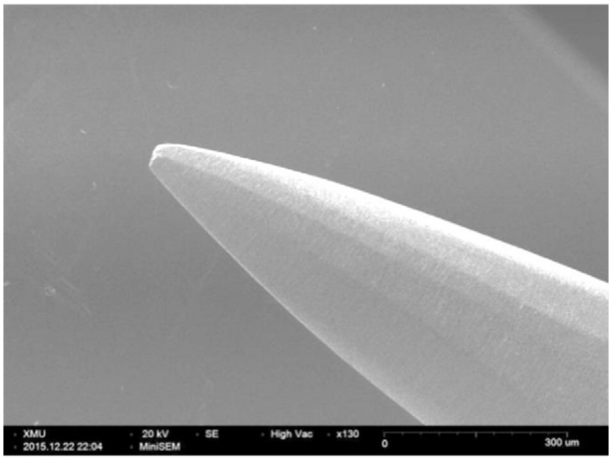

Fig. 2. Scanning electron microscope image of needle tip fabricated via mechanical method.

Table 1
Operating parameters used for pulsed radio-frequency discharge and ICPMS.

Pulsed radio-frequency discharge	
Averaged input power	65 W
Modulate pulse rate	100 Hz
Pulse width	4 ms
Distance between needle tip and sample	~ 50 μm
Flow rate of N_2 and Ar	50 mL/min and 250 mL/min
ICPMS	
RF power	1350 W
Carrier gas flow	0.75 L/min
Auxiliary gas flow	1.0 L/min
Plasma gas flow	16.0 L/min

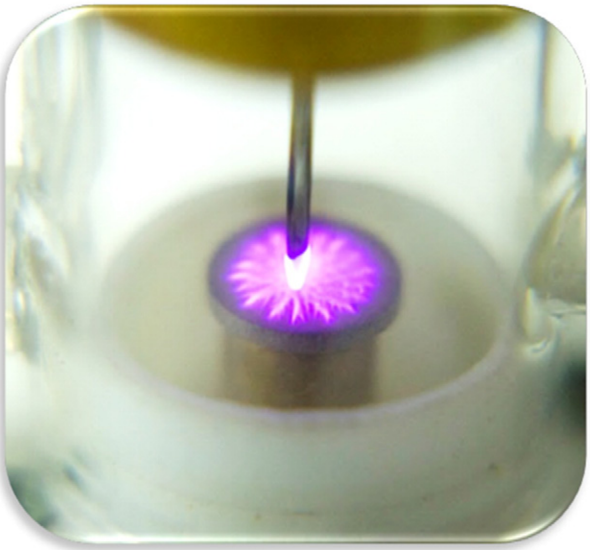

Fig. 3. Image of pulsed radio-frequency discharge.

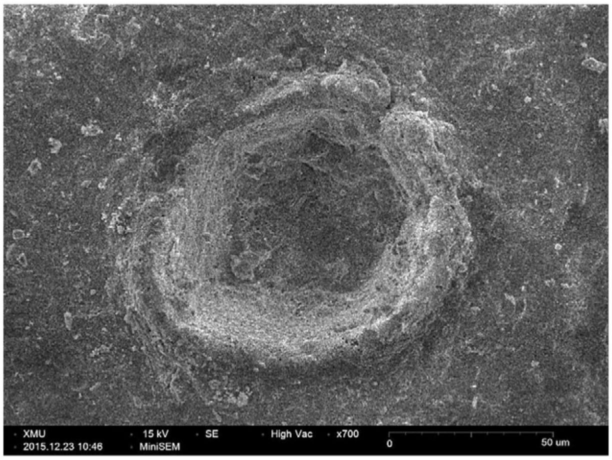

Fig. 4. Scanning electron microscope image of crater after 60 s discharge.

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