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Uranium emission spectra with a low power microwave plasma source

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Abstract

This work presents the first report of uranium spectra generated by a low power microwave plasma source to conduct emission measurements. Distinct uranium peaks in the wavelength range examined from 320 to 430 nm have been successfully obtained with a 200 W plasma utilizing low gas flow rates. The influence of temperature on the uranium behavior in the plasma source is discussed, and the intensity of the spectral lines obtained with this low power source is systematically compared with the results reported in literature, in which high power plasma sources were employed. Concentration effects are studied and the calibration curves are made for some strong spectral lines. The detection limits of uranium are also estimated to be at the 0.4 ppm level, with linear dynamic range at least two and half orders of magnitude. This research establishes a method to effectively generate uranium atoms and ions at a low power and low gas flow rate, which should be useful for uranium fundamental characteristic studies and on-site uranium monitoring work.

Keywords: Microwave plasma; Emission spectrometry; Uranium; Spectral line; Measurement

1. Introduction

Uranium, which is particularly important in nuclear production facilities, is one of the most important elements in the periodic table. Due to the complexity of the atomic structure and the abundance of energy levels, uranium, a member of the actinide family, presents a special challenge in spectral studies. It is estimated that there are over 300,000 spectral lines for uranium atoms (U I) and uranium ions (U II) alone [1,2]. Additionally, the particular chemical and physical properties of uranium make this element hard to handle in flames or plasma sources. Chemically, uranium can be easily combined with active species during the atomization process to form oxides at atmospheric pressure in hot sources and to form carbides in graphite furnace [3]. Physically, uranium has a relatively low ionization potential (∼6.08 eV), which results in almost complete ionization when it is introduced into a high power plasma source, such as an inductively coupled plasma (ICP) [4]. These chemical and physical features yield a poor atomization efficiency for uranium in high temperature plasma sources. Furthermore, low energy sources, such as flames or graphite furnaces cannot efficiently atomize uranium [5], thus preventing uranium detection to any useful degree by any flame or furnace with either atomic emission or absorption methods. With the most sensitive ion emission line, 385.957 nm, Winge et al. reported a detection limit of 250 ng/ml uranium in the early comprehensive studies of ICP emission spectrometry [6], and this detection limit was subsequently improved (16 ng/ml) by Boumans and Vrakking [7].

We have been working for years to design and develop new plasma sources for atomic emission and absorption measure-

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ments [8–10]. The notable stability and operational efficiency of these plasma sources has resulted in successful combinations with high sensitivity spectral techniques to further enhance detections limits. For example, an inductively coupled plasma, used as an atomization source, was successfully combined with cavity ringdown spectroscopy for sensitive elemental and isotopic measurements [10,21]. The results obtained from this union (plasma CRDS) show much promise towards the development of a plasma source cavity ringdown spectrometer. In order to design field portable instruments [11,12], compact plasma sources designed with low power, low gas flow rate, and high tolerance are particularly attractive. In the most recent studies, we have explored the combination of a low power microwave plasma source with cavity ring-down spectroscopy; and some elements that are readily atomized, such as lead and mercury, have been successfully measured [13,14]. We intend to further exploratory our studies on other refractory elements, such as uranium, using the low power microwave plasma source CRDS technique. However, there are very limited references reporting uranium measurements using a microwave plasma source (MIP) [15,16]. Furthermore, the uranium measurements reported in the literature were generated with a high power MIP. Prior to the introduction of the MIP into the plasma CRDS system for uranium measurements, the capability of the MIP to effectively generate uranium atoms and ions must be fully evaluated. Therefore, one of the major motivations of the present work is to systematically investigate whether such a low power microwave plasma source can be used as an effective uranium atomization/ionization source to be used for cavity ringdown spectroscopic measurements. A recently developed, well-tuned microwave plasma source [17,18] was selected to generate uranium atoms/ions, and the plasma's performance was evaluated by measuring the resulting uranium emission spectra.

2. Experimental

A schematic diagram of the experimental setup is shown in Fig. 1. The system consists of five primary parts: a plasma source, a monochromator with a CCD detector, a sampling device, the detection electronics, and a computer. The optical configuration of the cavity ringdown system is a simplified version of our previously reported setup [13,14]. The plasma source, also used in our previous work [18], has been freshly polished and finely tuned. The plasma source is mounted on a X–Y–Z three-dimensional adjustable stage for precise positioning of the optical beams to obtain the maximum signals. The microwave plasma takes a toroidal shape and can be operated with powers ranging from tens to hundreds of watts. The plasma torch, consisting of three coaxial tubes, is connected to a 2450 MHz microwave power supply through a 1 m coaxial cable. The plasma consists of three physically distinctive parts: the flame-like top portion, the thin cross point section where higher energies are accumulated, and the

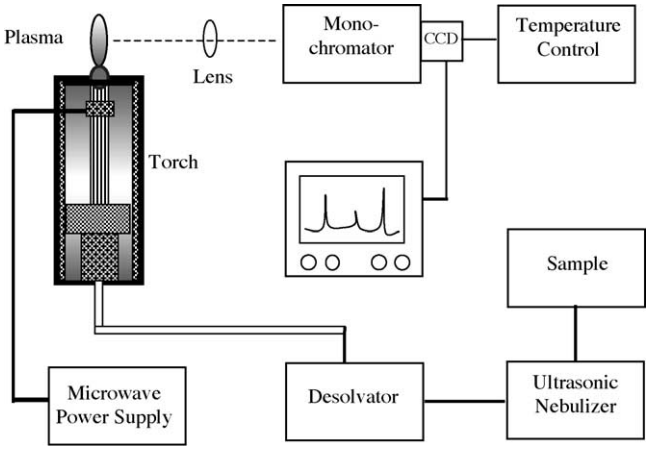

Fig. 1. Experimental set up.

bottom triangular part. The advantages of using this type of a microwave plasma source include low operating powers, low gas flow rates, high tolerance, and respectable plasma stability. Moreover, with this type of low power plasma, a cooling system is unnecessary. In the work presented here, the microwave power source operated at 200 W in the forward direction with a negligibly small reflection power. The plasma gas flow rate and carrier gas flow rate are controlled at about 0.5 L/min. Typical operational parameters for the instrument are summarized in Table 1.

The monochromator (ARC SpectraPro-500) used in this work has three gratings, 2400, 1800, and 1200 N/mm. The highest resolution of the monochromator with a grating of 2400 N/mm is approximately 0.1 nm in the UV spectral region. This instrument resolution is high enough to resolve the uranium emission lines under atmospheric plasma conditions. A CCD detector (Spectrum One CCD-200) is connected to the monochromator to record the emission spectra. The entrance slit of the monochromator is adjustable from 10 to 120 μm. Typical measurement times for the CCD detector are 0.01–0.1 s per spectrum, and 10–20 accumulations are obtained to enhance the signal-to-noise ratio. Due to strong plasma background emissions, such as the OH emission spectra around 308 and 315 nm, each uranium emission spectrum was subtracted from a background spectrum that was recorded under the same plasma operating conditions, except using a blank solution instead of the uranium sample solutions.

Samples are delivered through a commercial peristaltic pump into an ultrasonic nebulizer (U-5000 AT$^+$, CETAC), where the liquid samples are generated into fine, wet aerosols through contact with an ultrasonic transducer. The heating temperature inside the ultrasonic nebulizer is about 140 °C, and the cooling chiller operates around −5 °C at the aerosol outlet. The sample uptake rate is ∼0.75 ml/min. An additional desolvation device, a membrane desolvator, is employed to further control the solvent loading in the low power plasma source and to enhance the system performance. An argon gas stream with a flow rate of ∼0.5 L min^{-1} is introduced into the