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PLASMA CAVITY RINGDOWN SPECTROMETER FOR ELEMENTAL AND ISOTOPIC MEASUREMENTS: PAST, PRESENT AND FUTURE

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INTRODUCTION

Cavity ringdown spectroscopy (CRDS)[1] has widely been accepted as a mature absorption spectral technique. Applications of CRDS are prosperously growing. One of the most interesting applications is elemental and isotopic measurements using CRDS combined with a plasma source, namely, plasma-CRDS. Since the first introduction of this newly developed technique,[2,3] plasma-CRDS has been successfully demonstrated as a promising technique for sensitive elemental and isotopic measurements. Several elements and isotopes have already been measured using the plasma-CRDS in a laboratory environment. The detection sensitivity has been shown to be as good as hundreds of parts-per-trillion.[4,5] Very recently, a new advancement in plasma-CRDS, including employing a compact diode laser as the light source and a low cost, compact microwave plasma as the atomization source, has been accomplished.[6,7] R & D towards a portable plasma cavity ringdown spectrometer is being vigorously implemented in our

laboratories. This paper presents a brief review on the plasma-CRDS technique, its applications, recent advancements and future development.

PLASMA-CRDS INSTRUMENT SYSTEMS

A plasma-CRDS instrument system typically consists of six major parts: a laser source, a plasma source, a ringdown cavity, a sampling device, an electronic control, and a data processing portion. Figure 1 shows the diagram of the plasma cavity ringdown spectrometer. The electronic control of the spectrometer as well as the associated optical system for the laser beam control are different and dependent upon which laser sources (pulsed or cw) are employed. In Figure 1, if a pulsed laser is used, then parts 1 and 2 will be the whole UV laser source and part 3 will be the telescope system used to approximately mode match the laser beam into the cavity. If a cw laser is used, then part 2 will be the laser driver and part 3 will the optical isolator, which is used to reduce the optical feedback effect. An additional electronic part is needed for the cavity mode excitation and shut-off when a cw laser is used; this part is incorporated into part 2 in Figure 1. Two different types of plasma sources, part 5 of Figure 1, have been used: an inductively coupled plasma (ICP) and a microwave induced plasma (MIP). The detailed description of each part in Figure 1 can be seen in our previous publications.[2-7]

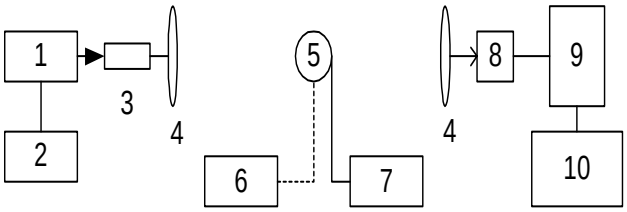

Figure 1. A diagram of the plasma cavity ringdown spectrometer. 1= laser source; 2= laser control system; 3= optical system for laser beam control; 4= ringdown mirrors; 5= plasma source; 6= sampling system; 7= plasma power supply; 8= detector; 9= oscilloscope; 10= computer.

THE INSTRUMENT PERFORMANCES

ICP-CRDS for elemental measurements

In the initial instrument configuration, a Nd:YAG pumped narrow linewidth (~ 0.06 cm^{-1} at 590 nm) dye laser with frequency doubling is used to provide a pulsed laser beam in the UV spectral region which covers the transition wavelengths of many elements. An ICP with a specially modified plasma torch, which is favorable for plasma stability and suitable for operating at low powers (200 - 450 w), is used as the atom/ion cell. Several elements have been measured in the system with the detection sensitivity up to hundreds ppt, *e.g.*, Pb(I) at 283.3 nm, 300 pg/ml; Hg(I) at 253.7 nm, 1 ng/ml; Mn(II) at 289.0 nm, 800 pg/ml.[4]

In addition to the feature of the high detection sensitivity, the system also shows high spectral selectivity. As observed in the experiment, the lead line at 283.3 nm is distinctively resolved from the strong spectral interference from the OH A-X (1-0) band. Furthermore, the extent of the spectral resolution can also be seen from the observation of the hyperfine structures of the mercury line at 253.7 nm under atmospheric pressure.

ICP-CRDS for uranium isotopic measurements

The plasma-CRDS system described above has also been used to measure the uranium isotopes at the three different transition lines, 286.6, 358.5 and 409.0 nm. Isotopic-resolved spectra of uranium, with a ratio of 1:1 ($^{235}U/^{238}U$, 2.5 µg/ml) and a ratio of 0.714% ($^{235}U/^{238}U$, 1.25 µg/ml ^{235}U) at the natural abundance, were successfully recorded. The measured isotopic shifts of the three lines are in the range of 3 - 9 ($\pm$ 2) pm; the detection limits are in the range of 70 - 300 ng/ml for the three different lines. This system undoubtedly can be used for other isotopic measurements, such as Pu, *et al*.[5]

ICP-CRDS for plasma diagnostics

Atmospheric plasmas have wide applications. However, many fundamentals, such as the plasma thermodynamics, the temperature and the electron density profiles and the lineshape broadening mechanism, still need to be explored. The performance of a plasma is strongly dependent on multiple parameters, such as gas flow rate, plasma power, and torch geometry; therefore, when different plasmas or the same plasma operating under different conditions is employed, the physical and the chemical characteristics could be different. The gas kinetic temperature of the plasma used in this system is in the range of 1800 - 4000 K, determined from the Doppler component of the broadened lineshape measured by CRDS. The electron density in the plasma is ~ 10^{15} cm^3, as derived from the Lorentzian component of the lineshape.[4] From the ringdown measurements of the $S_{21}(1)$ line of the OH A - X (0-0) band, the OH radical density in the plasma is determined to be 1.7 - 8.5 $\times 10^{20}$ m^3 at different plasma locations. The plasma used with this system has been validated to be approximately in LTE.[8] These fundamental studies on the plasma diagnostics are essential to effectively optimize the parameters of a plasma source and will prove to be valuable for the new plasma design, specifically, plasma-CRDS.

THE IMPROVED INSTRUMENT CONFIGURATION—DIODE LASER MIP-CRDS

The over arching goal of the plasma-CRDS project is to develop a new generation, field deployable, cost-effective instrument to be used to monitor U.S. DoE contaminated sites and environmental management processes. Toward this end, our very recent effort has been focused on the improvement of the instrument configuration of the plasma-CRDS, using a compact diode laser as the light source and a low cost, compact MIP as the plasma source, to yield diode laser MIP-CRDS. The system performance in the areas of stability and detection sensitivity has been demonstrated by using strontium (Sr) as an example. The detection limit of Sr at 680 nm, where the wavelength can be covered by a commercially available external cavity diode laser, is 375 ng/ml based on the 3σ criteria.The research demonstrates that the modified configuration not only improves the physical features of the instrument (cost, size and weight) but also the instrument performance (detection sensitivity).[7]

A novel tube-shaped MIP has been designed and fabricated very recently in our laboratories. The plasma's capability of generating atoms/ions has been evaluated by obtaining emission spectra of numerous elements, including uranium. The estimated laser beam path-length in this plasma is up to ~80 mm, which is ~ 15 times longer than

that in the MIP currently used and the plasma can efficiently operate at powers as low as 15 watts.[9]

Future developments

The plasma-CRDS technique has shown much promise in applications involving elemental and isotopic measurements. The R & D towards field deployable instrumentation using this technique has been vigorously processing in our laboratories. Future developments will focus on following major aspects:

(1) Development of a low cost, compact, new MIP source with an elongated laser beam path-length in the plasma.

(2) Utilization of diode lasers as the light source, *e.g*. an external cavity diode laser operating at 409 nm and 424 nm for isotopic measurements of uranium.

(3) Improvement of the sampling system's performance, including efficiency and gas tolerance.

(4) Study of matrix effects on the measurement accuracy and repeatability as well as selectivity (simulation testing on the real site samples).

(5) Preliminary design of the instrument blueprint.

Some hurdles exist ahead. However, they will definitely be overcome with the experience gained from our many years of continuous efforts in this area. We believe that a new generation of plasma cavity ringdown spectrometers for elemental and isotopic measurements will be available within the next few years.

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