Atomic Spectra from RF Electrodeless Discharge Sources for UV and VUV Spectrometry and Analytical Measurements.

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Abstract. *Electrodeless discharge lamps (EDLs) have been demonstrated to be an intense source of halogen atomic emissions in the ultraviolet (UV) and far UV (VUV) spectral region.*

Previously developed iodine resonance spectra source has been demonstrated as an intensive source of Iodine resonance lines. Iodine EDL has been successfully adopted in flash photolysis experiment. Quantitative measurements of concentration kinetics of iodine atomic species in an I_2+O_3 *system are possible. There are evidences that bromine sources could be used in similar way. A newly designed and developed bromine resonance source with high quality quartz window giving 163.36nm resonance line proves that bromine EDLs can be used in analytical spectroscopy. Further improvements in technology are necessary to increase the intensity of obtained 163.36 nm resonance line and to retrieve other resonance lines like 157.65nm and 153.19nm.*

Key words: *Atomic Spectra, Electrodeless discharge lamps (EDL), Flash photolysis (FP).*

Introduction

Electrodeless discharge lamps (EDLs) have been demonstrated to be intense sources of a variety of atomic emissions in the ultraviolet spectral region. A number of sources and applications of the atomic iodine spectrum have been reported. In spite of some success, production of halogen EDL has proven to be difficult[1,2,3]. Recently the development of inexpensive and convenient EDL iodine line source, powered by radio frequency was reported[3]. For optimized conditions, the radio- frequency EDL resonance radiation has line shapes close to Doppler profiles[4,5] and, therefore, the source may be used to measure absolute concentrations in resonance absorption experiments avoiding the problems of self-absorption[6,7]. EDL lamps show much better signal to noise ratio as commonly used hollow cathode lamps. The problem with Doppler profiles is solved in commercially available spectrometers, for example in Zeeman atomic absorption spectrometers[7].

Subject and Methods

Design of Iodine EDL. The principles of construction and exploitation of EDL lamps, usable in UV and VUV spectral regions are described in[8]. The above described need of iodine resonance spectra sources has lead to the development of an efficient iodine resonance lamp[2].

A schematic diagram of iodine resonance spectra source is given in figure 1. The EDL consists of a discharge volume of approximately 18mm outer diameter and 35mm in length. The discharge volume is connected to a side arm of approximately 6cm in length, which is placed in a thermo-stated copper block. By thermo-stating the side arm of the lamp volume, the vapour pressure of iodine inside the lamp is controlled. The optimum iodine partial pressure has been determined to be 2.5x10^{-3} mbar. This corresponds to the temperatures at the side-arm of about 246-248K. The lamp is supplied with high quality quartz window. The principal construction, technology and exploitation of the lamp are described elsewhere.[2]

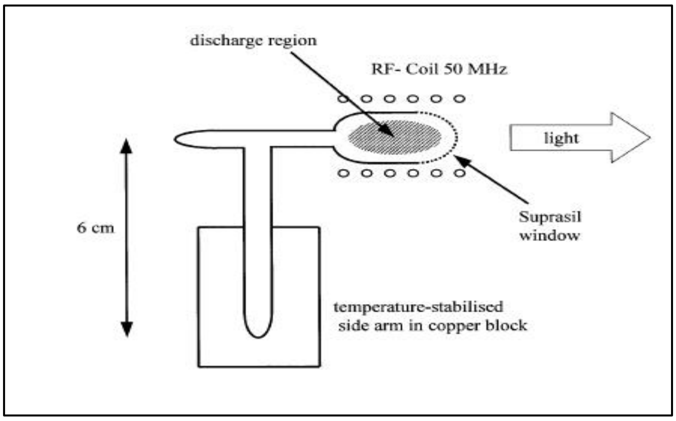

Figure 1. Iodine EDL with temperature stabiliser

Design of Bromine EDL. A newly designed bromine resonance source has been developed. Principles of construction, technology and exploitation of the bromine resonance spectra source are similar to principles used to develop an iodine resonance lamp[1, 2]. The bromine resonance line is more shifted to the VUV with the longest line being λ=163.36 nm. First developed test lamps have been supplied with a quartz window. Lamps fitted with MgF_2 window will be developed in future to enable other resonance lines down to 120 nm in VUV. Introduction of MgF_2 window will increase the intensity of resonance lines due to better transmission. However, this requires additional efforts to be made during the development phase in order to assure the stability of the lamp. Lamps supplied with a high quality quartz window can be used in FP experiments to monitor the Br atoms in the ground state. Previous experience[1] has shown that the high quality quartz available has a transparency limit at about 158nm.

Results

Figures 2 and 3 present the obtained emission spectra from the developed EDL for iodine and bromine respectively.

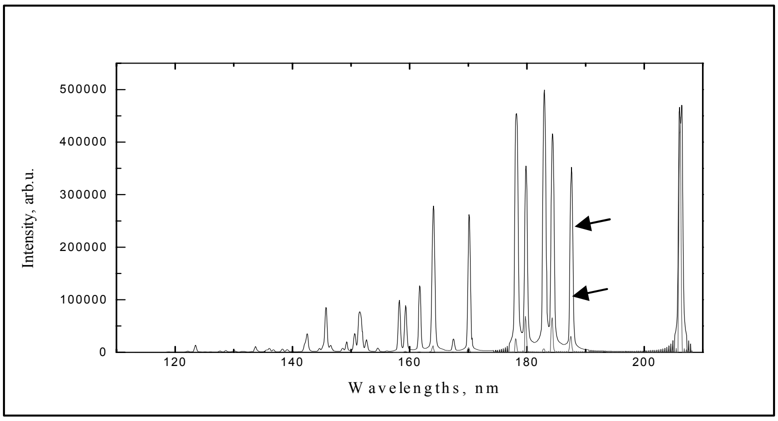

Figure 2. Spectra of an iodine EDLs with MgF window -(a) and high-quality quarz window - (b).

With a special set-up described in[9], the iodine resonance spectra sources can be used in flash photolysis experiment for quantitative measurements of concentration kinetics of iodine atomic species in an I_2+O_3 system. Figure 4 gives an example of time resolved intensity measurements as usually required in FP experiments.

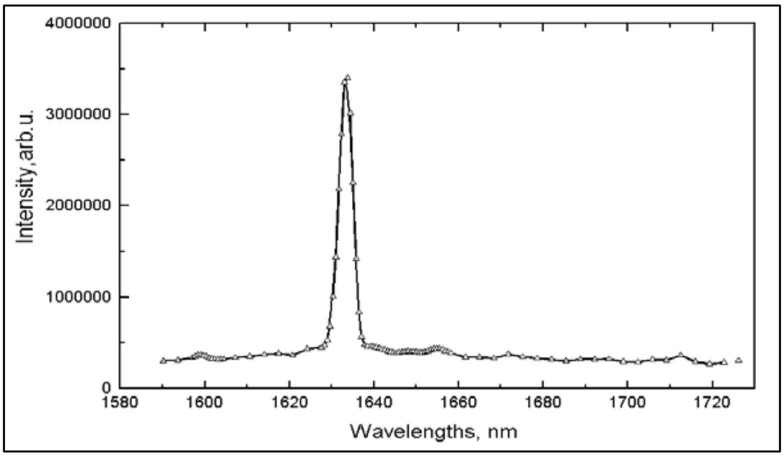

Figure 3. Spectra of one of the newly developed Br EDL

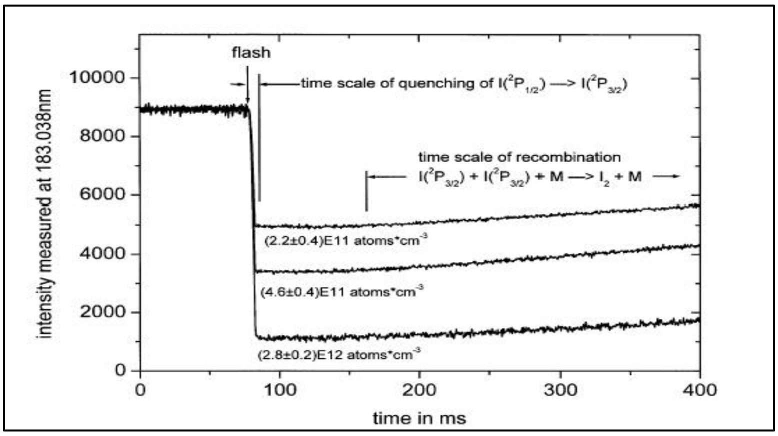

Figure 4. Three time-resolved intensity measurements of signals from the 183.038nm line at three different I_2 concentrations. Time scales of fast quenching $I(^2P_{1/2})+M \rightarrow I(^2P_{3/2})+M$ and recombination $I(^2P_{3/2})+ I(^2P_{3/2}) \rightarrow I_2+M$ are indicated.

Discussion

Halogen EDLs are relatively simple to use intensive light sources giving atomic emission spectra in VUV.

Previously developed RF-powered iodine EDL resonance spectra source has been tested in a flash photolysis (FP) experiment. The optimal operating conditions with minimized self-absorption of emission lines and sufficient intensity have been determined.

With a relatively simple set-up (compared to commercially available spectrometers), the iodine resonance spectra sources can be used in flash photolysis experiment for quantitative measurements of concentration kinetics of iodine atomic species in a I_2+O_3 system, which gives the opportunity to improve the experimental data of iodine-ozone system that will allow better simulation of the chemistry of this complex system in the computer experiment. It also means better understanding of processes with iodine oxides involved in the stratosphere and troposphere of our Earth's atmosphere. Due to the actuality of the bromine in the atmosphere the FP experiment with Br_2+O_3 is on the agenda. The bromine resonance sources will be used to get relevant picture on atomic bromine temporary behaviour.

Conclusions

- There is still a demand for high quality, high intensity resonance iodine and bromine sources in analytical spectroscopy
- Under optimized conditions the developed Iodine and Bromine EDLs can be used for quantitative determination of the atom concentrations, for example in a flash photolysis experiment
- The developed bromine EDL with high quality quartz window is an intensive source of the bromine resonance line 163.36nm

- Development of bromine EDL with MgF_2 or sapphire window is underway
- Adoption of the bromine resonance sources in different applications for determination of the atomic concentrations is underway

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