Studies of Thallium Line Spectra in Thallium – Mercury Discharge

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Abstract. In this paper, we present a study of broadening of thallium emission spectral line shapes in the Tl-Hg discharge. The spectral lines were emitted from high frequency electrodeless lamps, containing Tl, Hg, Ar mixtures and measured by means of Fourier transform spectrometer. The deconvolution procedure, by means of ill posed inverse task solution, was performed to obtain the real (without instrumental function) profiles for further analyze. The solution was implemented using Tikhonov regularization algorithm. The Tl 276.8 nm, 351.9 nm, 352.9 nm spectral lines were analyzed in detail in dependence on the discharge power. The additional broadening of Tl 276.8 nm and 351.9 nm lines were observed due to the excitation transfer in collisions of ground state Tl atoms with excited Hg atoms.

1. Introduction

An electrodeless lamp (EDL) consists of a quartz bulb filled with an inert gas, typically argon gas, at low pressure and the element or a salt of the element for which the lamp is to be used. The bulb is inserted into a coil that is generating an electromagnetic high frequency (HF) field, resulting in a low-pressure inductively coupled discharge in the lamp. HFEDLs are known to be bright radiators with the line spectrum characterized by high intensities and narrow line shapes. Detection limits in graphite furnace Atomic Absorption Spectrometry with HFEDLs were better by a factor of 1.5–8 depending on the element in comparison with the hollow cathode lamps. If isotope enriched HFEDLs are used, spectral line widths are found to be several times narrower giving an increase in AAS sensitivity by factors of 1.5–3.2 [1]. Emitting spectral line shape measurement and modelling for plasma diagnostics was made [2]. If lamps are filled not only with one working element but with several metals or working elements, lamps are called multi-element HFEDLs. In the multi-element HFEDLs, two or more working elements are alloying without overlapping emitting spectra. Multi-element HFEDLs are promising since they provide advantages of cost and speed for atomic absorption analysis. However the interactions between elements, in this case, thallium and mercury, have to be investigated to optimize the filling and working conditions. One of the possible interactions in the Hg-Tl HFEDLs could be energy transfer, observed in the metal vapors.

The first observation of energy transfer between mercury and thallium was made by Cario and Franck in their classical experiments on sensitized fluorescence of metal atoms in the vapor phase [3]. A mixture
of mercury and thallium vapor, when irradiated with the light of the mercury resonance line, shows the emission spectra of both atoms. Thallium atoms do not absorb the exciting light thus they can get excited only by an excitation transfer from mercury atoms [3]. Earlier, in our laboratory, the sensitized fluorescence was investigated and the broadening of Tl lines shapes was observed in mercury-thallium vapor [4]. More recent spectroscopic studies of Tl containing high frequency electrodeless lamps and the discharge plasma temperature measurement were made in [5,6]. However, the spectral line shape broadening was not studied in this work.

In this paper we present the results of an investigation and diagnostics of high-frequency electrodeless discharge lamps, containing Hg and Tl (enriched with Tl-205 isotope), developed in our laboratories as light sources for their use in atomic absorption spectrometry (AAS). The spectral diagnostics include line intensity and spectral line shape measurements and modelling [7]. To study the possible Tl spectral line broadening due to the energy transfer effect between Hg-Tl atoms, the spectral line shapes were measured and deconvoluted [in detail [8,9]] from the instrumental function, allowing getting the real spectral lines.

2. Experiment

For this study, the lamp was prepared, filled with thallium isotope: Tl205+Hg+Ar. The buffer gas was argon with the pressure of about 3 Torr. The plasma was excited by placing the lamp in the electromagnetic field of 100 MHz frequency. Lamps were operated at the excitation generator power values from 13 W to 24 W. The spectral line profiles were recorded using a Bruker IFS-125HR Fourier Transform Spectrometer. For the real spectral line calculations, the instrumental function was approximated by the Lorenz function with the full widths at half maximum (FWHM) of 0.03 cm⁻¹.

The deconvolution procedure of the measured profiles was implemented. The profile obtained by convolution is compared with the measured profile in figure 1(a).

![Figure 1](image)

Figure 1. (a) A comparison between the measured (red line) profile and the profile, obtained by means of the ill posed inverse task solution. (b) The estimated FWHM, depending on power, for thallium 352.9 nm, 351.9 nm and 276.8 nm spectral lines.

In figure 1(b) we can see the thallium spectral line FWHM, depending on power, for the 352.9 nm, 351.9 nm, 276.8 nm lines. To obtain the FWHM, the real spectral line profiles were used after deconvolution procedure. The temperature of plasma, obtained from the FWHM of the Doppler broadening of Ar lines, is 1115 K. According to our previous measurements, the electron density of plasma is about 10¹² m⁻³ [10].

3. Results and discussion

Analysis of the 351.9 nm (6²D₃₂-6²P₃₂) and 276.8 nm (6²D₃₂-6²P₃₂) spectral line profiles in dependence on power showed that these lines are broader than 352.9 nm (6²D₃₂-6²P₃₂) line. The simplified diagram of the energy levels of thallium can be seen in figure 2 [11]. The additional broadening indicates that there is an energy transfer process from the excited mercury atoms (Hg*(6²P₀₁)) to thallium atoms in ground state like (see figure 2):
\[ Hg^*(6^3P_{0,1}) + Tl (6^3P_{3/2}) \rightarrow Hg(6^3S_0) + Tl^* (6^2D_{5/2}) + \Delta E, \]  

where \( \Delta E \) is the kinetic energy difference.

The kinetic energy difference \( \Delta E \) gives rise of the observable broadening of the spectral line shape. Similar excitation takes place also for the level \( Tl^* (6^2D_{3/2}) \) but because this level is connected with the \( Tl \) ground state via resonance transition (276.8 nm, \( 6^2D_{3/2}-6^2P_{1/2} \)), radiative relaxation and subsequent re-absorption takes place and the additional broadening of the line 352.9 nm (\( 6^2D_{3/2}-6^2P_{3/2} \)) was not observed.

![Figure 2](image)

This result proves that also in the HFELDs plasma similar process takes place like observed earlier in metal vapours for thallium spectral line broadenings [12]. When an excited mercury atom collides with an thallium atom in its ground state, the part of the excitation energy can be transferred into kinetic energy or internal energy of thallium, which leads to the broadening of the spectral line. The elaboration of a detailed theoretical model will be the next step of our work.

**Conclusions**

In our study of the \( Tl \) and \( Hg \) high frequency discharge plasma we observed an additional broadening of the \( Tl \) 276.8 nm and 351.9 nm lines due to the excitation transfer from the excited \( Hg \) atoms in collisions with the ground state \( Tl \) atoms. This effect is similar as observed earlier in vapour phase fluorescence experiments without discharge plasma. This effect has been taken into account in the case of preparing multi-element HFEDLs for atomic absorption spectrometry.

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