Comparison of As, Hg and Tl High-Frequency Electrodeless Lamps for Detection of Environmental Pollution

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Abstract - **Nowadays, there is an increasing necessity to determine the concentration of different substances in the environment in low concentrations, as more and more attention is paid to environmental pollution. This work is devoted to the comparison of main characteristics of high-frequency electrodeless light sources with different fillings for their use in high precision atomic absorption analysers.**

The spectral line intensities and profiles were studied in special design light sources, manufactured at Institute of Atomic Physics and Spectroscopy, with arsenic, mercury and thallium filling. Special attention is devoted to the UV lines of 193.7 nm and 197.2 nm of As, 276.8 nm, 377.6 nm of Tl and 253.7 nm of Hg spectral lines. The intensities and profiles were measured by means of a Fourier transform spectrometer.

The deconvolution procedure was implemented to obtain the real form of emitted profiles for further analysis, since in the case of low –pressure or cold plasma, the instrumental function is on the same order that experimental profile and it has to be taken into account. The instrumental function can distort the real spectral line shape significantly, for example, it changes the width of the spectral line that leads to the uncertainties in the determination of such important plasma parameters like temperature. The instrumental function can conceal a detailed structure of the spectral line, like the dip in the line center caused by the self-absorption (self-reversal) and characterizing the radiation trapping.

The integrated areas, values of self-absorption, and other parameters were obtained and compared for all fillings as a function of working regimes.

Keywords - detection of heavy metals (As, Tl, Hg) in environment, electrodeless light sources, UV spectral lines shapes, self-absorption.

I. INTRODUCTION

Since thallium, mercury, and arsenic exposure even at small doses can have adverse effects on humans and environment, their monitoring is of high importance. As with any highly toxic element, it is imperative to detect concentrations as low as possible.

The spectral line shape studies are necessary, to find appropriate spectral line for the application of high frequency electrodeless light sources (HFEDLs) in atomic absorption spectrometry (AAS) for determination of environmental pollution, as well as to optimize the HFEDLs operation. The main requirements for use of the line in AAS are the narrow and intense spectral line without self-absorption [1].

In this work we test in laboratory conditions high-frequency electrodeless lamps with arsenic, mercury and thallium fillings for their use in atomic absorption

spectrometers for detection of arsenic, mercury and thallium in low concentrations in the environment.

II. MATERIALS AND METHODS

A. Experimental

The spectral characteristics, such as accurate line positions, transition intensities, line shapes, and hyperfine structure patterns are very important for atomic absorption spectrometry.

For this study, special design light sources were manufactured at our laboratory, filled with working element (As, Hg or Tl) and Ar as a buffer gas. In Fig. 1 one may see the lamps used in this study, (a) - the example of Tl lamp and (b) – As lamp.
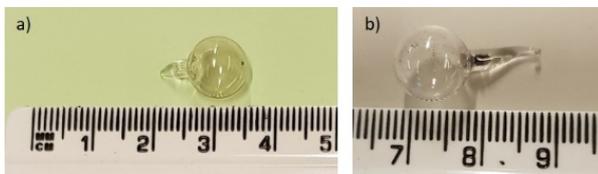

Fig. 1.   Examples of Tl and As lamps.

Tl light source has been filled with Tl 205 isotope; the As and Hg light sources were filled with natural mixture of isotopes. Pressure of argon in all types of lamps was about 3 Torr. The plasma was excited by placing lamp in electromagnetic field of 100 MHz frequency. HFEDLs filled with Tl were operated with excitation generator power values between 13.7 W and 22.8 W, however for As lamps the range was from 4.7 W till 8.68 W and Hg lamps from 2.63 W till 9.05 W.

In the present work, the emission spectra from high frequency electrodeless discharge of Tl, As and Hg were studied in a spectral range from 190 nm till 400 nm   The spectral line profile and intensity registration was performed using Fourier Transform spectrometer Bruker IFS-125HR (spectral resolution 0.015 cm^{-1}).

From spectra with more than 2 500 000 points about 100 points were selected for each wavelength for further calculation.

B. Theoretical approach

As well known, the measured profile f(x) is the convolution of the real spectral line y(s) and instrumental function A (x, s). It can be described by Fredholm integral equation of the first kind:

$$\int_a^b A(x,s)y(s)ds = f(x), c \leq x \leq d \qquad (1)$$

where: a, b and c, d - the limits of the real and measured (experimental) profiles accordingly.

The deconvolution of the real profile of the measured spectral lines is ill-posed inverse tasks and can't be solved directly. As shows our previous experience [2]-[6], the Tikhonov regularization approach is one of the most efficient methods regarding calculation time, stability, and accuracy of solution, as well as the amount of needed additional information. And method of deconvolution of spectral line based on it can be used for multicomponent spectra deconvolution as well. Using minimum of prior information, we will get a stable and accurate solution of the inverse ill-posed problem. The most important step in the Tikhonov regularization method is to find the regularization parameter α, which establishes the correspondence between the requirement of the stability of solution and its reliability, since inaccurate determination of α leads to major solution errors. Choosing the regularization parameter is the main difficulty of the regularization methods applying in practice.

In this work the regularization parameter was obtained by means of discrepancy minimization and the instrumental function was approximated by the Lorenz function with the FWHM (full width at half of maximum) of 0.03 cm^{-1}.

More detailed description of instrumental function approximation can be seen in [6].

III. RESULTS AND DISCUSSION

A. HFEDL filled with thallium

Fig. 2 and Fig. 3 show the profile examples of thallium 377.6 nm and 276.8 nm spectral lines depending on excitation generator power values, namely 15.44 W, 19.3 W, and 22.8 W.
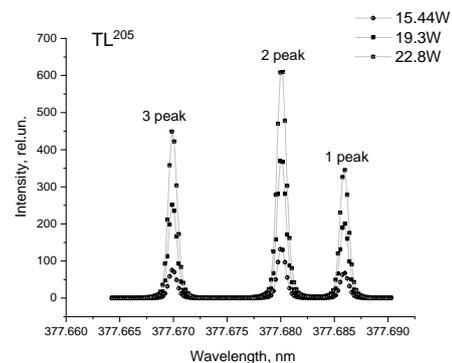

Fig. 2.   Examples of Tl 377.6 nm line forms in dependence on power.
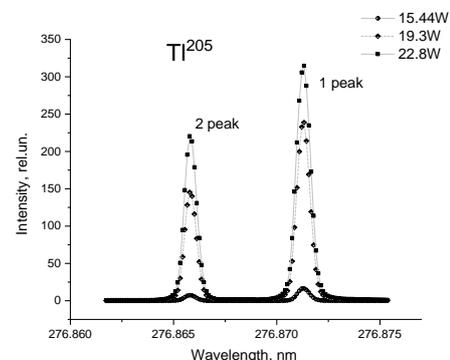

Fig. 3.   Examples of Tl 276.8 6nm line forms in dependence on power.

In the Fig. 4 and Fig.5, we can see changes in relative intensities of thallium 377.6 nm and 276.8 nm spectral lines depending on excitation generator power values. Both spectral lines correspond to resonance transition (ending on the ground level) which makes them suitable for use in absorption spectrometers.
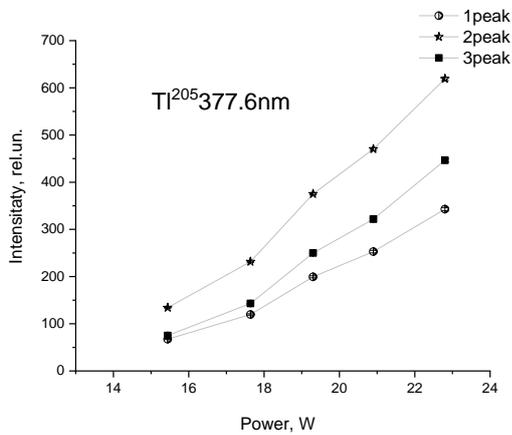

Fig. 4.   Tl 377.6 nm line relative intensities dependence on power.
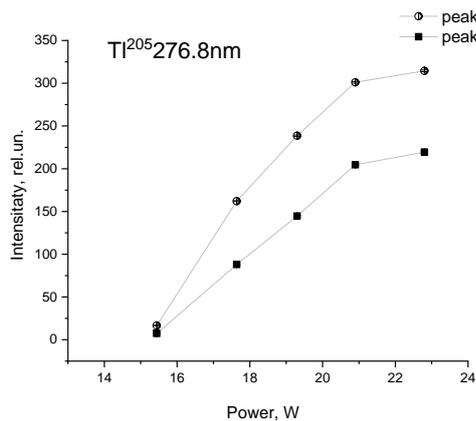

Fig. 5.   Tl 276.8 nm line relative intensities dependence on power.

On the Fig. 6 and Fig. 7 we can see thallium 377.6 nm and 276.8 nm spectral line FWHM value dependences on the excitation generator power. The values of FWHM were obtained before deconvolution from measured profiles and after deconvolution procedure implementation.
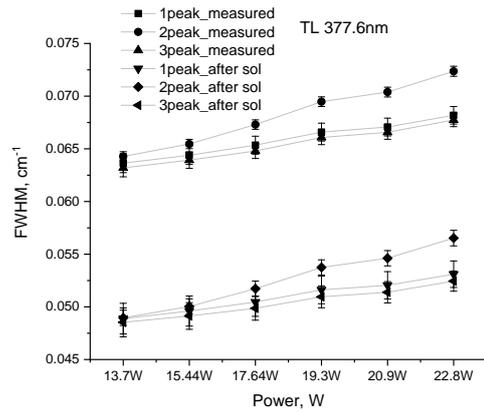

Fig. 6.   Dependence of FWHM of measured and deconvoluted profiles on generator power for Tl 377.6nm.
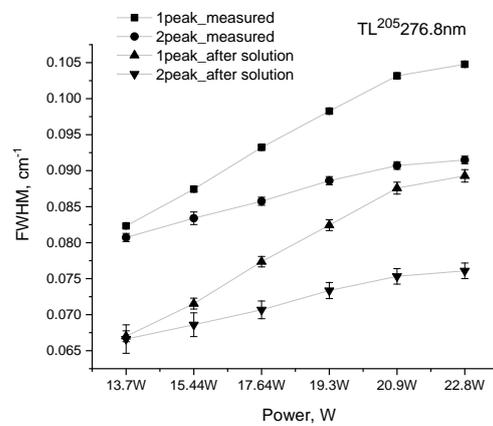

Fig. 7.   Dependence of FWHM of measured and deconvoluted profiles on generator power for Tl 276.8nm.

For Tl lines we did not observe the self-reversal, so we can estimate the discharge temperature from the Doppler broadening of the deconvoluted lines. On the Fig. 8, the dependence of obtained values of the gas temperature on power is shown.
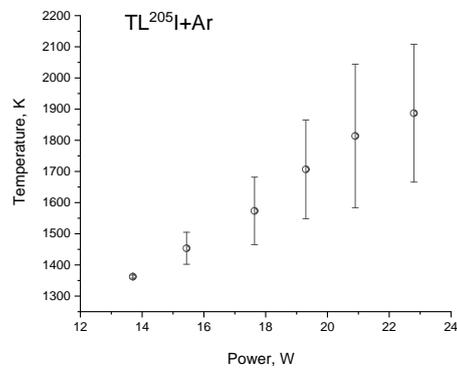

Fig. 8.   Temperature dependence on power.

The gas temperature determined from the thallium spectral lines 377.6 nm and 276.8 nm was in the range from 1300 K to 1800 K, indicating the origin of the emission to be localized in the central part of the HFEDL. Similar results were reported in the previous study of the same type of discharge with the same filling [7] in which the analysis of the molecular emission of OH and C_2 molecules showed that the temperature in the central part of a thallium HFEDL can reach 1450 K while the gas temperature near the walls is significantly lower (by approximately 400 K).

B. HFEDL filled with arsenic

In the frame of this work, the dependence of the relative intensities of arsenic spectral lines on the power of the excitation generator was measured. The studied spectral lines were 193.7 nm and 197.2 nm. As in the case with thallium lines, these spectral lines of arsenic correspond to resonance transitions.

Fig. 9 shows the dependence of relative intensities at the line centre of As 197.2 nm and 193.7 nm spectral lines on generator power.
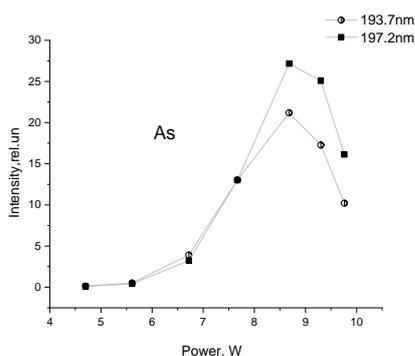

Fig. 9. Relative intensity values of As 197.2nm and 193.7nm lines in dependence on power .

Analysis of the arsenic 193.7 nm and 197.2 nm spectral line profiles in dependence on power showed that when increasing excitation generator power up to 8 W, relative intensities of these spectral lines are increasing, but afterwards the relative intensities decrease.

Fig. 10 shows the profile examples of As 197.2 nm spectral line at four different values of excitation generator power, namely 7.67 W, 8.68 W, 9.3 W and 9.76 W. As we can see, the dip in the line centre caused by the self-absorption is increasing with the rising of generator power, and it is also the explanation for the decrease of spectral line intensity for excitation generator power values starting from 8 W.
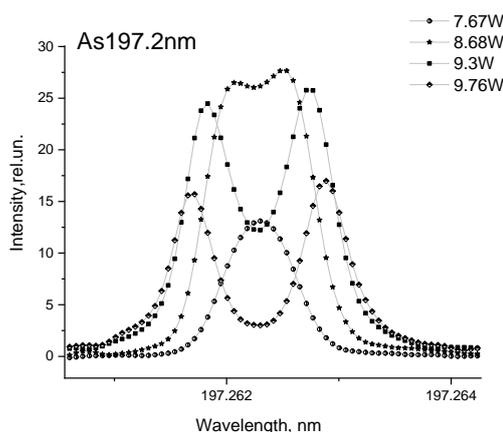

Fig. 10. Examples of As 197.2 nm line forms in dependence on power.

Analysis of deconvoluted As lines shows that the mean value of I_{max}/I_0 is larger compared to measured ones. The I_o is the intensity of the spectral line profile at the centre of the line; I_{max} is the intensity at the line maximum.

It means, that the self-absorption is better visible in profiles, obtained from solution of ill-posed inverse task, thus illustrating the concealing of detailed spectral line structure by the instrumental function. On Fig. 11 and Fig. 12 one may see the dependence of obtained rate of qualitative self- absorption of arsenic spectral lines on the excitation generator power for measured and deconvoluted (after implementation of deconvolution procedure) profiles, accordingly.
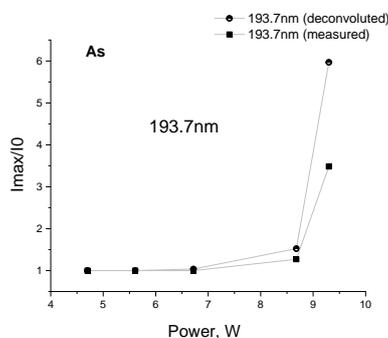

Fig. 11. The obtained qualitative rate of self- absorption of As 193.7 nm spectral line dependence on the excitation generator power for measured and calculated profiles.
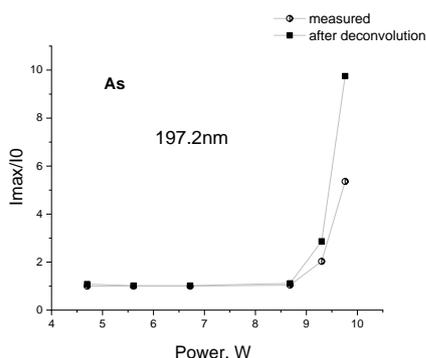
Fig. 12. The obtained qualitative rate of self- absorption of As 193.7 nm spectral line dependence on the excitation generator power for measured and calculated profiles.

On the Fig. 13 we can see an example of the comparison of integrated areas of measured and deconvoluted profiles of arsenic 197.2 nm spectral line.
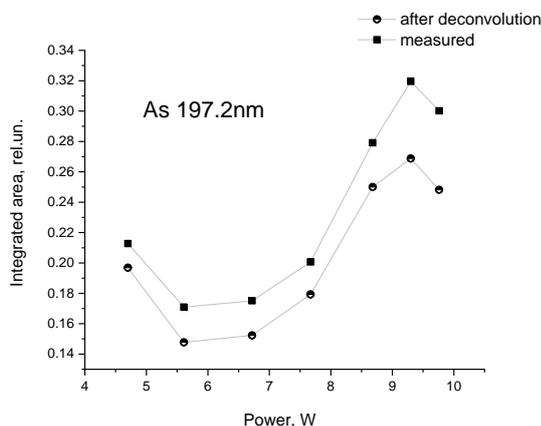

Fig. 13. The comparison of normalised integrated intensities of measured and deconvoluted profiles of As 197.2 nm on dependence of power.

As can be seen, values of integrated areas of calculated profiles are smaller than the measured ones. This shows that instrumental function changes the width of the spectral line, meaning that the appearance of the self-absorption in the light source increases the broadening of the spectral line, at the same time increases also the dip in the centre of the line, leading to the decrease in area. That is the explanation for the slow decrease of integrated spectral line area starting at around 8 W

C. HFEDL filled with mercury

On Fig. 14 we can see some examples of the complex structure of the Hg spectral line 253. 7 nm in dependence on excitation generator power. It is due to hyperfine splitting and isotopic shifts of the Hg isotopes in the natural composition of mercury in the filling. We can clearly observe that by small discharge power 2.626 W 4.16 W and 5.25 W still the resulting five components can be resolved but at 9.05 W power, the reabsorption starts to play, and the lines structure is becoming complex.
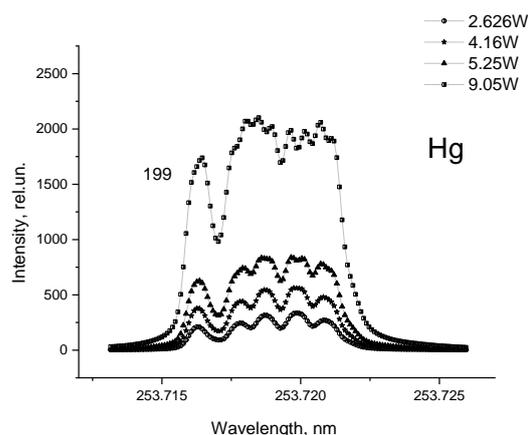

Fig. 14. Examples of measured Hg 253.7 nm line forms in dependence on power.

On the Fig.15 is shown the comparison of form of spectra of measured and deconvoluted profiles of Hg 253.7 nm at 2.62 W of generator power.
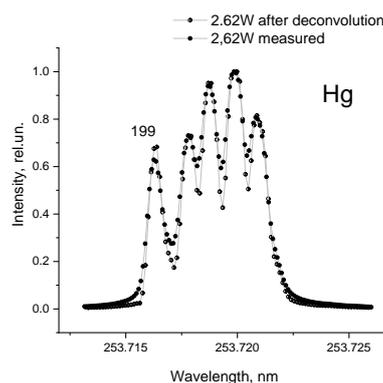

Fig. 15. The comparison of form of measured and deconvoluted spectral profiles of Hg 253.7 nm at 2.62 W of generator power.

After deconvolution procedure implementation the components of spectra, corresponding to different isotopes can be seen clearly, especially 199 isotope.

Fig. 16 shows the examples of form of natural composition of the Hg spectral line 253.7 nm in dependence on excitation generator power after deconvolution procedure implementation. There are three different values of excitation generator power: 2.62 W, 4.16 W and 9.05 W.
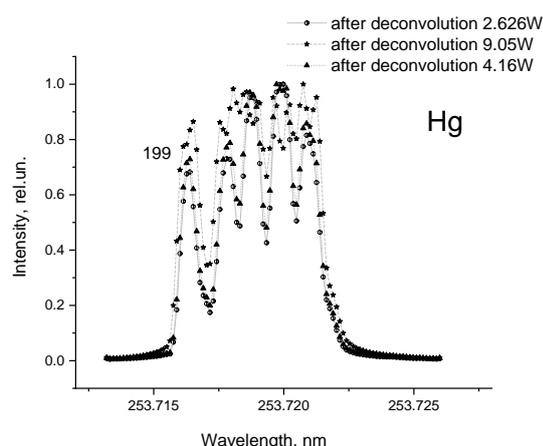
Fig. 16. The Examples of Hg 253.7 nm line forms after deconvolution in dependence on power .

It is interesting to observe that the five resulting components can be seen clearly after the deconvolution for the 2.62 W, 4.16 W power regimes that means that the self-absorption has small influence but by the 9.05 W, the individual components are becoming self-reversed and can't be resolved. That means that for the use of 253.7 nm line, the power regime not more than 4 W should be used.

Conclusions

The analysis has shown that the ratio of the intensity at the line centre to maximal line intensity, estimated from the deconvoluted spectral line profiles is a robust indicator of self-absorption and it can be easily used to detect the optimal power regimes for selected lines. In addition, the measurements of integral intensity should be taken into account to estimate the optimum working conditions with the right balance of brightness of line and influence of self-absorption.

The analysis of arsenic and mercury resonance spectral lines revealed the appearance of self-absorption at quite small values of excitation generator power, meaning that the working regime for this HFEDL needs to be chosen very carefully in order to use it in absorption spectrometers

We can conclude that for arsenic 197.2 nm line the optimal discharge power is about 8 W, for 193.7 nm about 7 W. For mercury 253.7 nm line the operating power

should be not more than 4 W. However, we did not observe the self-absorption of thallium lines of 377.6 nm and 276.8 nm. Thus, they can be operated at power from 20 to 23 W.

The obtained results of temperature in thallium HFEDL correspond to the previous study of the same type of discharge with the same filling [7], where values of temperature were obtained by another independent method. To investigate further the distribution of emitting atoms inside the thallium HFEDLs, it is necessary to use tomographic approach as demonstrated in [8].

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