

PAPER • OPEN ACCESS

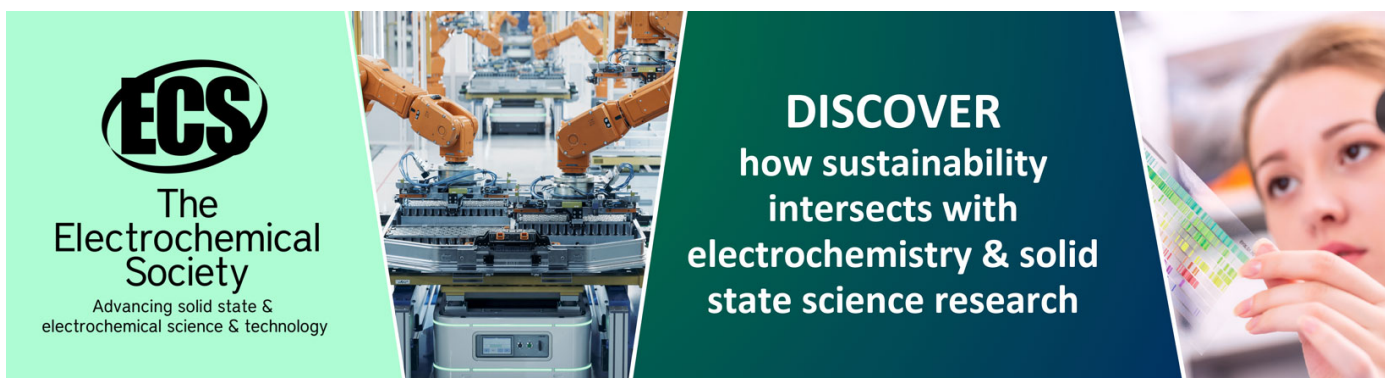
Study of arsenic resonance spectral lines in far UV region from a HFEDL for usage in Zeeman absorption spectroscopy

To cite this article: Natalja Zorina *et al* 2023 *J. Phys.: Conf. Ser.* **2439** 012013

View the [article online](#) for updates and enhancements.

You may also like

- [Reliability analysis of self-developed mechanical Meta action test-bed based on ETA](#)
Hongyu Ge, Yuan Liu, Baoqiang Liu et al.
- [Profile of elementary school teachers' ability in analyzing higher order thinking science question](#)
I R W Atmojo, R Tiana and K Karsono
- [DEM extraction and its accuracy analysis with ground-based SAR interferometry](#)
J Dong, J P Yue and L H Li



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Study of arsenic resonance spectral lines in far UV region from a HFEDL for usage in Zeeman absorption spectroscopy

Natalja Zorina¹, Anda Abola¹, Atis Skudra¹ and Gita Revalde^{1,2}

¹ Institute of Atomic Physics and Spectroscopy, University of Latvia, Riga, Latvia

² Institute of Technical Physics, Department of Materials Sciences and Applied Chemistry, Riga Technical University, Riga, Latvia

natalja.zorina@lu.lv

Abstract.

This work is focused on obtaining and analyzing the main spectral characteristics of a high-frequency electrodeless light source filled with arsenic for use in high-precision atomic absorption analyzers. We analyzed the relative intensities of the three arsenic resonance spectral lines 189.0 nm, 193.7 nm, and 197.3 nm in the far UV spectral region, the dependence of the intensity on the applied voltage, the impact of the instrumental function on the emission spectra, the influence of self-absorption and the stability of the radiation. Among others, a deconvolution procedure was implemented to obtain the real shapes of the emitted profiles.

1. Introduction

Atomic absorption spectrometry with Zeeman polarization modulation background correction (ZAAS) is a very sensitive method with exceptional detection limits, widely used to assess environmental pollution for various metallic elements. The most important component of an atomic absorption spectrometer is a light source. Typically, either hollow cathode lamps or high-frequency electrodeless lamps (HFEDLs) are chosen as light sources. In the case of such elements as arsenic, mercury, selenium, phosphorus, etc., electrodeless lamps offer significantly higher intensities, better stability, and longer lifetimes than hollow cathode lamps [1].

Arsenic is a toxic element that can be found in rocks, soil, water, and the air. Arsenic enters the environment because of natural processes and anthropogenic activities [2]. It is toxic if taken at higher doses and can cause various health problems, including skin lesions, cancer, cardiovascular disease, diabetes, and others [3;4]. Human exposure can occur via all three principal routes, that is, through the inhalation of air, through the ingestion of food and water, and via dermal. For example, a recent study found that the total arsenic in seafood samples consumed in the USA varied greatly in the range of 8-22200 ng/g (wet mass) [5].

The purpose of this work is to continue the development of arsenic UV HFEDLs for their use in ZAAS for the detection of arsenic in low concentrations in the environment [6]. The focus of this work is to measure profiles and intensities of three poorly investigated As resonance lines of 189.0 nm, 193.7 nm, and 197.3 nm wavelength, lying in the far UV region. The aim is to find out experimentally which of the three resonance lines is the most suitable for use in ZAAS, considering that the 189 nm line has not



yet been studied. The requirement for ZAAS is to have an intense and not self-reversed resonance spectral line.

2. Theoretical background

In atomic absorption spectrometry, not only the intensity but also the spectral line shape is important. In such cases, diagnostics of line shapes is essential.

As it is well known [7;8] the measured (experimental) spectral line $f(\nu)$ is a convolution of the real line profile $y(\nu')$ of the emitted spectral line and the instrument function $A(\nu, \nu')$. It can be described by Fredholm integral equation of the first kind:

$$\int_a^b A(\nu, \nu') y(\nu') d\nu' = f(\nu), \quad c \leq \nu \leq d, \quad (1)$$

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

Reconstruction of the real line shape from the measured one is the so-called inverse ill-posed task because small uncertainties in the measurement give large deviations in the solution. Since it is a complicated task, sometimes the instrument function is neglected. In general, it is acceptable for high temperatures and dense plasmas. However, in the case of low-pressure inductively coupled plasma in HFEDLs, the instrument function is on the same order of magnitude as that of the experimental profile and it has to be taken into account [9].

The instrument function can cover the 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.

In our work, the solution of the ill-posed inverse task is implemented by a method based on Tikhonov regularization. According to Tikhonov's regularization algorithm [10,11], the initial, ill-posed task from equation (1) can be transformed into a task of the minimum searching of the smoothing functional:

$$M_\alpha[y, \tilde{f}] = \|\tilde{A}y - \tilde{f}\|_F^2 + \alpha\Omega[y], \quad (2)$$

where $\alpha > 0$ - regularization's parameter; $\|\tilde{A}y - \tilde{f}\|_F^2$ - discrepancy. Ω is stabilizing functional, described by the following expression:

$$\Omega[y] = \|y\|_Y^2. \quad (3)$$

By minimizing the functional (2), we obtain the solution of a correct inverse task instead of the incorrect one, for the further solution using the classical methods.

The main difficulty for the application of this method is the choice of the regularization parameter α , which determines the correspondence between the stability and reliability of the solution. Here we used the discrepancy minimization method [12].

3. Experiment

For measurements, we used a spherical HFEDL, with a bulb diameter of 1 cm, made of SiO₂ glass. The lamp was filled with arsenic as a working element and argon as a buffer gas of 3 Torr pressure. To ignite the discharge plasma, the lamp was placed in the coil of the excitation generator, working at 100 MHz frequency. The power of the generator was changed in the range from 11 W to 18 W. The spectral measurements were performed by a Fourier spectrometer Bruker IFS HR125 with a spectral resolution of 0.015 cm⁻¹.

We recorded and analyzed arsenic 197.3 nm (⁴P_{1/2} → ⁴S_{3/2}), 193.7 nm (⁴P_{3/2} → ⁴S_{3/2}), and 189.0 nm (⁴P_{5/2} → ⁴S_{3/2}) spectral line profiles and intensities, devoting more attention to the latter, as it has not been studied previously. All lines correspond to the resonance transition (ending on the ground level) which makes them suitable for use in AAS.

The stability of radiation was recorded by spectrometer Jobin Yvon SPEX 1000M, with a spectral resolution of 0.07 nm.

After the measurements, the deconvolution procedure was applied to retrieve the real spectral line shapes without the influence of the instrumental function.

4. Results

4.1. Intensity dependence on power

The spectra of arsenic in the range from 188 nm to 198 nm can be seen in Figure 1.

Figure 2 shows dependencies of the integrated areas of arsenic 189.0 nm, 193.7 nm, and 197.3 nm spectral lines on the excitation generator power values between 11 W and 18 W. As can be seen, all three lines have a maximum at power values of about 16.50 W. After that, intensities start to decrease.

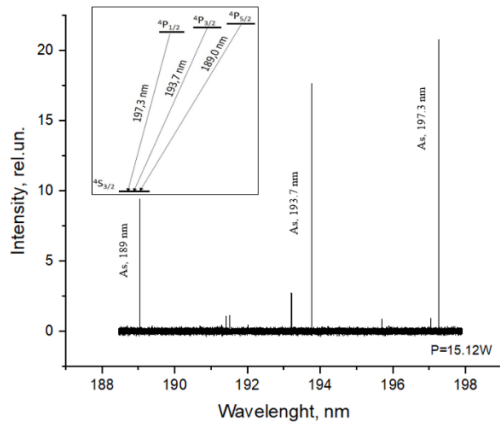


Figure 1. Arsenic HFEDL spectrum with three As resonance spectral lines. In the left corner, energy levels and transitions of the respective lines are shown.

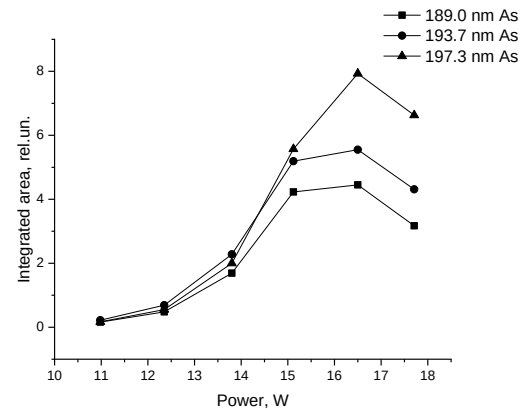


Figure 2. Integrated intensities of 189.0, 193.7, and 197.3 nm lines in dependence on excitation power on an HFEDL.

Figure 3a shows the dependency of the measured arsenic 189.0 nm spectral line profiles on the excitation generator power values, namely at 10.98 W, 12.35 W, 13.80 W, 15.12 W, 16.50 W, and 17.71 W. It agrees well with the results presented in Figure 2, illustrating, that a higher rate of self-absorption results in an intensity decrease.

Figure 3b shows an example of the measured and calculated real spectral line profiles of arsenic 189.0 nm in the case when the generator power was 15.12 W. As described previously, the instrumental function partially covers the dip in the real line shape.

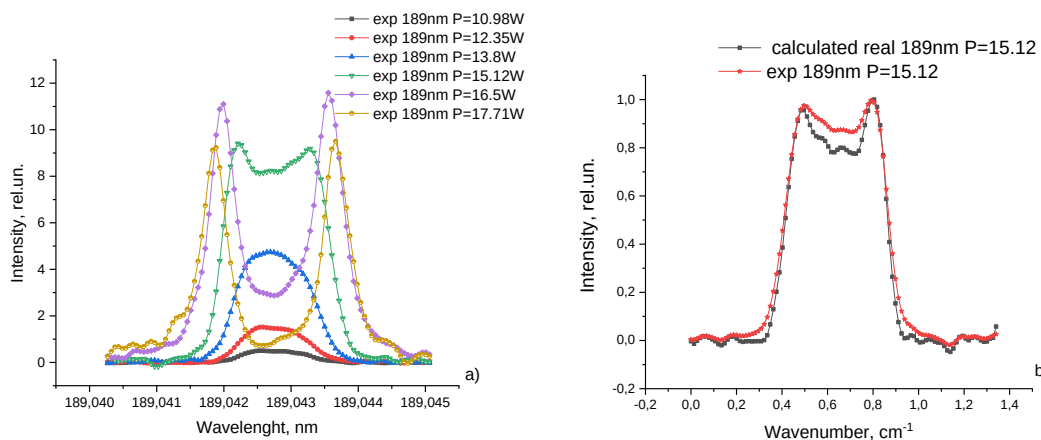


Figure 3. a) Dependence of intensity on power. b) The example of the measured As 189 nm spectral line (stars) and calculated real line (squares) when $P=15.12$ W.

4.2. $I_{\max}/I_0$ dependence on power

In this work, as a quantitative indication of self-reversal, the ratio of ($I_{\max}/I_0$) is obtained, where I_0 is the intensity of the spectral line profile at the center of the line; $I_{\max}$ is the intensity at the line maximum. In Table 1, we can see the obtained rates of ($I_{\max}/I_0$) for the three arsenic spectral lines as a function of generator power for calculated real (after implementation of deconvolution procedure) profiles.

Table 1. Obtained rate of self-absorption for calculated real profiles of As 189.0 nm, 193.7 nm, and 197.3 nm spectral lines by different values of excitation generator power.

Power, W	$I_{\max}/I_0$					
	10.98	12.35	13.80	15.12	16.50	17.71
189.0 nm line	1.10	1.10	1.03	1.22	5.40	31.01
193.7 nm line	1.00	1.00	1.00	1.53	7.17	38.61
197.3 nm line	1.00	1.00	1.00	1.09	2.80	8.88

As can be observed from Table 1, the spectral line of arsenic at 197.3 nm has the lowest levels of self-absorption, whereas the spectral line at 189.0 nm is the most self-absorbed. Self-reversal is nonexistent when the value of $I_{\max}/I_0$ is equal to 1. Comparing all three lines, the 197.3 line is less affected by self-absorption in wider power regions and is the most intense line compared to the other two (Figures 1-2). Considering that non-reversed and intense spectral lines are required, we can conclude that the 197.3 nm line is more suitable for use in AAS.

4.3. The stability of the radiation of the lamp

Short- and long-term stability of radiation is a very important factor for applications, being one of the main advantages of HFEDLs over hollow cathode lamps. Figure 4 shows the integrated intensity of arsenic resonance lines over a period of time. The measurements were performed at a power value of 14.9 W, registering the line intensity every 15 seconds for an hour. To evaluate the stability of radiation, we implemented a ratio $\Delta I/I_{\text{avg}}$, where ΔI is the standard deviation and I_{avg} is the average value of spectral line intensities. Our calculations showed that, after a short warm-up time, the stability of the spectral lines is at the level of 0.4% for As 193.7 nm and As 197.3 nm, and because of lower intensities - approximately 0.7% for As 189.0 nm, which are very good values [13].

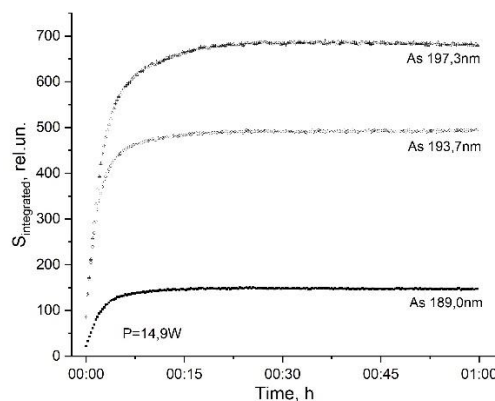


Figure 4. Integrated spectral line intensity over a period of time for the three As resonance lines.

5. Conclusions

In this work, we investigated spectral line shapes and intensities of the arsenic far UV 189.0 nm, 193.7 nm, and 197.3 nm spectral lines, emitted from a HFED lamp, manufactured in our laboratory. The spectral line profile of the far UV As line 189 nm has been studied for the first time. The measurements made by the Fourier spectrometer in dependence on the excitation power showed that intensities reach a maximum at 16.50 W for all three lines, but self-reversal occurs already at 14-15 W. Relative

intensities start to decrease for higher excitation power values. This behavior can be explained by self-absorption.

Along with the increase of excitation generator power self-absorption's influence on the line shape leads to self-reversal and thus becomes clearly visible.

We also examined the stability of radiation of HFEDL. The results show that after the initial warm-up time, the lamp has a high level of stability fluctuations around the average intensity not exceeding 0.4-0.7%, depending on spectral line intensity.

To conclude, the arsenic 197.3 nm spectral line has the highest intensity and also the lowest values of self-absorption, which makes it the best choice for usage in ZAAS. Of the three resonance lines being studied, the 189.0 nm spectral line has the highest level of self-absorption, making it unsuitable for use in ZAAS.

Acknowledgments

The research was supported by projects: ERAF 1.1.1.5 project LU No. ESS2018 / 270 University of Latvia and Institutes in the European Research Area -Excellence, Activity, Mobility, Latvian Council of Science No. lzp-2020/1-0005, ESF project No. 8.2.2.0/20/I/006, and UL IAPS.

References

- [1] Welz B and Sperling M 1998 *Atomic Absorption Spectrometry* 3rd edition Weinheim: Wiley-WCH p 109
- [2] Nordstrom D K 2002 *Science* **296** (5576) 2143-45
- [3] Hong Y S, Song K H and Chung J Y 2014 *J Prev Med Public Health* **47** (5) 245-252
- [4] Ratnaike R N 2003 *Postgrad Med J* **79** 391-396
- [5] Wolle M M, Stadig S and Conklin S D 2019 *J. Agric. Food Chem.* **67** (29) 8253-67
- [6] Zorina N, Skudra A, Gavare Z and Revalde G 2021 *Proc. of the 13th Int. Practical and Scientific Conf. Environment. Technology. Resources. (Rezekne)* vol 1 (Rezekne: Rezekne Academy of Technologies) p 275-80
- [7] Lebedeva V 1977 *The technique of the optic spectroscopy* (Moscow: Moscow university) p 353 (in Russian)
- [8] Sizikov V S 1999 *Stable methods of processing of the results of measurement* (St.Petersburg: SpetsLit) (in Russian)
- [9] Zorina N, Skudra A and Revalde G 2019 *J. Phys. Conf. Ser.* **1289** 012045
- [10] Tikhonov A N 1963 *Rep USSR Acad Sci* **153** N 1 (in Russian)
- [11] Petrov G M 2002 *J Quant Spectrosc Radiat Transf* **72** 281-87
- [12] Verlan F and Sizikov V S 1986 *The integral equations: the methods, algorithms, program* Kyiv: Naukova Dumka (in Russian)
- [13] Kazantsev S A, Khutorschikov V I, Guthohrlein G H and Windholz L 1998 *Practical Spectroscopy of High-Frequency Discharges* New York: Plenum Press