

Application of excilamps to determination of iodine content in urine

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The XeBr excilamp (B–X transition, $\lambda = 283$ nm) was shown to decompose urine and organoiodine. In addition to decomposition of organic matter, the excilamp based on KrCl* molecules (B–X transition, $\lambda = 222$ nm) deactivates the dissolved oxygen and converts IO_3^- to I^- . The contents of I^- in a prepared sample was determined by the cathodic stripping voltammetry technique with formic acid admixtures.

The concentration of iodine in urine rather accurately reflects its intake with food and can serve a criterion for assessment of the iodine content in organism in order to reveal iodine deficiency disorders at early stages.¹

Different methods for determination of the iodine mass concentration are available in the literature.^{2–6} The iodine content in urine is determined by the photometric persulfate and cerium-arsenite methods with wet preashing of urine samples.¹ The application of chromatography and atomic absorption spectroscopy is limited by the high cost of the equipment.

The stripping voltammetry technique has found a wide utility in analytical laboratories due to its simplicity, availability, high speed, and the possibility to automate the measurement process. The sensitivity of stripping voltammetry enables measurements of the iodine concentration in diluted urine samples. However, analysis of even 1/100 diluted urine fails to reveal the analytical signal from iodide ions without pre-treatment of the sample, since the presence of organic constituents in urine leads to appearance of sharp adsorption peaks masking the analytical signal from iodine in voltammograms. The complete decomposition of organic substances can be achieved by ashing samples. However, this sample preparation method has some disadvantages, namely, a possibility of iodine volatilization or pollution of a sample by the reagents, as well as the long preparation process (up to 5 h).

The UV irradiation can be used to intensify the organic matter decomposition in a sample. The effect of UV radiation on a sample is based on decomposition of dissolved organic substances and metal complexes under their exposure to electromagnetic energy quanta. An advantage of the method is its applicability to different classes of organic substances. Since iodine can exist in different forms in urine, it should be converted into the electrochemically active form before measuring. The UV irradiation of aqueous solutions

allows the iodine compounds with the positive valence to be reduced to iodide ions.⁷

In recent years, the sources of spontaneous UV radiation that employ radiation of excimer and exciplex dimer molecules and halides of inert gases (excilamps) are being developed intensively,^{10,12} as well as searching for their new applications.^{11,14,15} First attempts were undertaken to use the new radiation sources to intensify the process of sample preparation.^{11–13}

The objective of this paper is to select optimal conditions for exposure urine samples to UV irradiation (UVI) in order to determine the total iodine content in urine by the cathodic stripping voltammetry method. Sealed-off capacitive-discharge KrCl* ($\lambda \sim 222$ nm) and XeBr* ($\lambda \sim 283$ nm) excilamps developed at the Laboratory of Optical Radiations of the Institute of High-Current Electronics (Tomsk, Russia)¹⁰ were used as sources of UV radiation. The excilamps provided $\Delta\lambda = 5–10$ nm and the power density of radiation up to 18 mW/cm^2 at the pulse repetition frequency $f = 200$ kHz and the pulse duration of about $1 \mu\text{s}$. The excilamp radiation spectra are shown in Fig. 1.

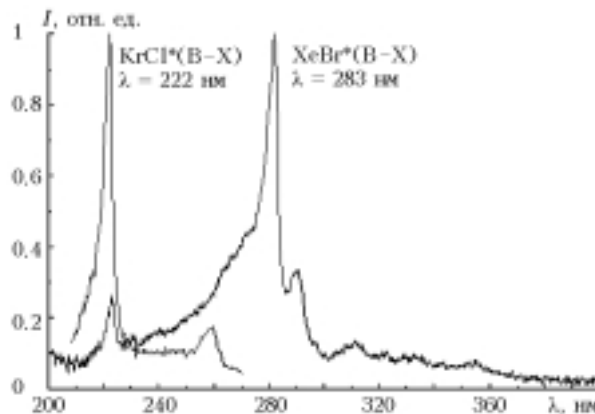


Fig. 1. Spectra of XeBr and KrCl capacitive-discharge excilamps.

It is seen in Fig. 1 that the UV spectrum differs from the spectra of low- and medium-pressure mercury lamps that are traditionally used for UVI in sample preparation.¹⁶ The excilamps emit more than 70% of the light energy within relatively narrow B–X band, which depends on the type of the working molecule. This provides a possibility to obtain near-, far-, and vacuum-UV sources emitting in a preset wavelength range. Since photochemical systems differently interact with radiation at different wavelengths, we can affect the rate of a photochemical reaction and the resulting photoproducts through a choice of working molecules.^{9,15} Among other things, this determines the urgency of investigations into the interaction of the excilamp radiation with solutions taken for sample preparation and gives hope for the decreasing number of reagents and increasing speed of the methods used.

The content of iodide ions in the prepared urine samples was measured with a TA-4 computer-aided voltammetric analyzer fabricated by the TomAnalit Company (Tomsk, Russia). The analyzer was equipped with three three-electrode electrochemical cells. A mercury film electrode (MFE), used as a test one, was prepared through electrolytic deposition of mercury onto a silver wire of 1.1 mm in diameter and 8–9 mm in length. The wire was molded in a polymer rod. The electrolytic deposition proceeded from a saturated $\text{Hg}_2(\text{NO}_3)_2$ solution at the direct current of 1.5 mA for 600 s. A glassy carbon electrode served as an auxiliary one; and a silver chloride electrode (in 1 M KCl) was used as a reference one. The analyzed solutions were mixed by means of vibrating the test electrode. All reagents were of high-purity grade and used as they were. All solutions were prepared with bidistilled water additionally stilled with sulfuric acid and potassium permanganate.

The electrodeposition of iodide ions onto the MFE surface was conducted in the form of poorly soluble mercury compound Hg_2I_2 at the potential of -0.05 V, at which electrosolution of metal mercury occurs.⁸ Then the sediment was dissolved at the alternating-current or differential-pulse scanning of the polarizing voltage from -0.05 to -0.95 V with the rate of 100 mV/s. As this took place, the voltammogram showed a cathodic peak at the potential of $-(0.35 \pm 0.05)$ V. This peak served the analytical signal of iodide ions. The content of iodide ions in a sample was determined by the method of additions.

The interfering influence of dissolved oxygen is traditionally removed by bubbling nitrogen through the analyzed solution. The use of the $0.2\text{--}0.5$ mol/dm³ formic acid solution as a base electrolyte allows deactivation of dissolved oxygen due to the photochemical reaction under exposure of the analyzed solution to UV radiation. The time of the exposure and the corresponding degree of removal of the interfering effect of oxygen is different for different lamps. When the solution is exposed to the XeBr lamp radiation for 20 min (at the chosen optimal conditions for mixing the irradiated solution), only a 70–80% suppression of the oxygen wave recorded at the voltammetric curve takes place. Further increase of the exposure time does

not change the form of voltammograms. Upon irradiation by the KrCl lamp for 5 min, the oxygen wave is not observed in voltammograms. This allowed us to replace the bubbling of the analyzed solution by an inert gas with irradiation by the KrCl lamp, when determining the content of iodide ions.

To remove the interfering effect of the organic matrix, the urine sample was diluted by bidistilled water and irradiated by the excilamp until obtaining a reproducible analytical signal from iodide ions during the polarographic analysis of the obtained solution. To intensify the process of decomposition of organic matter, different amounts of formic acids and hydrogen peroxide were added to the diluted urine samples before irradiation; the oxidizing ability of hydrogen peroxide was improved by adding 1 M of potassium nitrate solution. Three quartz glasses containing the analyzed solution were irradiated simultaneously from one side by the excilamp located at a distance of 0.5–2 cm from them. The increase of the distance led to significant increase of the exposure time. After irradiation, 0.2 ml of the concentrated formic acid was added in the glasses. The resulting solutions were irradiated by the KrCl lamp or bubbled by nitrogen for 5 min, and then the analytical signal from iodide ions has been measured.

The efficiency of conditions for the urine sample irradiation was assessed from the possibility of obtaining the analytical signal (AS) allowing a quantitative estimate of the total iodine in the urine. The estimate correctness was checked by the method of additions and through comparison with the results obtained from the analysis of the mineralized sample. The exposure time that is needed for decomposition of organic matter and obtaining the reproducible peak of iodide ions is tabulated below. All the values are obtained for 10 ml diluted urine sample with addition of the optimal amount of oxidants. The results tabulated correspond to the cases that the error of determination of the introduced iodide ion addition did not exceed 50% and the spread between the results obtained from the analysis of the irradiated and mineralized samples did not exceed 50% as well.

The tabulated data indicate that the both lamps can be used for sample preparation. The minimal exposure time for both the KrCl and XeBr excilamps is 20 min. However, when determining iodine in urine, the XeBr lamps can be used for photooxidation of organic matter only provided that the oxidants are added to the solution, the solution is mixed intensely, and the lamp is spaced from the glass containing the solution by no more than 0.5 cm. If the distance between the lamp and the glass is about 0.5 cm, the needed UVI time is 20 min; at the distance of about 1 cm, the needed time is 60 min; and at the distance of about 1.5 cm, it becomes as long as 150 min. At the distance of 2 cm, we failed to obtain the analytical signal from the irradiated solution.

The application of the KrCl lamp has two advantages, namely, the possibility of decomposing organic matter without oxidant additions and the photochemical removal of the interfering effect of oxygen, when recording the analytical signal of iodine.

Table. Effect of UV irradiation on the degree of decomposition of organic matter and on obtaining the reproducible peak of iodide ions

Urine concentration	Addition	UVI time, min	
		KrCl lamp	XeBr lamp
1:100 (0.1 ml urine/ 10 ml water)	No additions	180	No AS recorded
	0.2 ml H ₂ O ₂ 30%	120	H ₂ O ₂ does not decompose
1:200 (0.05 ml urine/ 10 ml water)	No additions	120	No AS recorded
	0.2 ml H ₂ O ₂ 30%	60	H ₂ O ₂ does not decompose
	0.5 ml conc. HCOOH	60	No AS recorded
	0.1 ml H ₂ O ₂ 30% + + 0.05 ml 1 M KNO ₃	40	120
0.03 ml urine/ 10 ml water	No additions	90	No AS recorded
	0.5 ml conc. HCOOH	60	Nonreproducible AS
	0.1 ml H ₂ O ₂ 30% + 0.05 ml 1 M KNO ₃	20	20

Our results indicate that the application of excilamps allows the time for determination of the iodine content in urine to be reduced to 30 min. The use of the KrCl lamp makes the analysis easier and cheaper. In our opinion, the application of the KrCl lamp in devices for preparation of samples of water, biological objects, and some foodstuffs to quantify heavy metals, iodine, mercury, and selenium in them is quite promising, therefore, the studies should be continued.

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