URANIUM DETECTION IN AEROSOL PARTICLES BY EMISSION SPECTRA OF LASER-INDUCED PLASMA

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Experimental data are presented on investigation of emission spectra of breakdown plasma induced by CO_2–laser radiation on solid and liquid aerosol particles containing UO_2F_2. Spectral lines of uranium ions have been identified. The technique is applicable for uranium detection in emissions of enrichment plants of nuclear industry.

In the last few years a problem of ecological monitoring of gas–aerosol emissions from plants of the so-called nuclear cycle involved in uranium enrichment and refinement of enriched and irradiated fuel for Atomic Power Station (APS) has become acute. The determination of chemical composition of such emissions is of interest in view of their dramatic effect on the environment.

Modern methods of monitoring connected with air sampling and subsequent chemical analysis are inefficient in view of much time required for preparation of samples. The impossibility of real-time remote analysis often makes them useless. In this connection it is of interest to use the method based on direct analysis of emission spectra of laser-induced plasma referred to as LIBS (Laser-Induced Breakdown Spectrometry). This method has been detailed in Refs. 1 and 2; moreover, in Ref. 2 the analysis of sensitivity of the method in comparison with other methods of chemical analysis of substance has been made. In this method, the analysis is made element-by-element and does not depend on the type of compound in which detectable element is included. Consequently, it is not necessary to prepare special samples. In addition, remote analysis is feasible, because a breakdown may be initiated at a distance from a radiation source.

The present work is devoted to the laboratory experimental investigations of plasma emission spectra of an optical breakdown induced by the CO_2–laser radiation on aerosol particles containing uranium. The problem was to identify uranium spectral lines and to study feasibility of their use for remote detection of uranium in gas–aerosol emissions from plants.

Analysis of technological process of uranium enrichment and refinement of irradiated fuel[3,4] as well as the data on a composition of gas–aerosol emissions from radio chemical plants[5] have shown that one of the probable compounds of emissions is uranium hexafluoride UF_6, which owing to its chemical activity undergoes hydrolysis with atmospheric moisture with formation of solid aerosol uranyl fluoride (UO_2F_2) particles with size ≤ 0.2 μm. As far as UO_2F_2 attracts well water molecules, its particles in a plume can be either in the form of hydrated solid aerosols or in the form of two-layer particles, formed in the damp atmosphere as drops grow on the uranyl fluoride particles making up condensation centers. In this case, partial dissolving of the solid nucleus of the two-layer particles is possible.

In our experiments the UO_2F_2 solid particles and drops of uranyl fluoride solution in distilled water were analyzed. They were detected by the spectral line of uranium ion with the wavelength $\lambda = 409.013$ nm. The line was chosen on the basis of spectrum analysis of elements usually contained in the atmospheric aerosol, such as Ca, Si, and Al, whose spectra may hinder identification of uranium lines under natural conditions.

The experiments on the spectral analysis of plasma induced by laser radiation on aerosol particles were conducted with the use of the experimental setup that is standard for the LIBS method and is shown in Fig. 1. The basic elements of the setup were:

– the pulsed CO_2 laser with a pulse energy up to 5 J and a pulse duration of 1.5 μs, possessing typical temporal energy distribution with a width of the front lasing peak ~300 ns at half maximum;

– the hermetically scaled cell having an input aperture with a mobile objective lens of focal length F= 13 cm to focus the laser radiation in the center of the cell and an output window made from LiF. The diameter of a focal spot was ~2 mm;

– the MDR–6 type monochromator with an input slit width of 60 μm. Instead of the output slit, the lens of the TV camera was placed;

– the TV camera with a built-in amplifier on microchannel plates and imaging system compatible with an IBM PC.

The image recording was triggered by external strobe pulse. The exposure time was 1.5 μs. Two frame fields were recorded on television standard. The image was digitized by a 6-bit high-speed ADC and was stored in a computer in the form of a bit image of 256×256 pixels.

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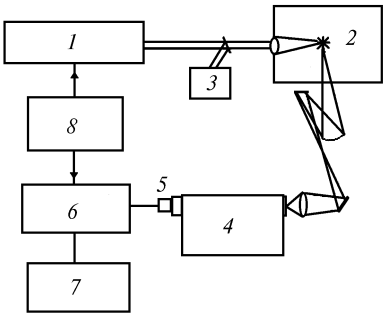

FIG. 1. The diagram of the experimental setup for spectrochemical analysis of the aerosols by breakdown plasma emissions spectra: CO_2 *laser 1, hermetically sealed cell 2, IMO-2 power meter 3, MDR-6 monochromator 4, TV camera 5, graphics digitizer 6, computer 7, and block of synchronization 8.*

The laser was started by framing pulse. The delay time of a strobe pulse relative to the framing pulse varied from 0 to 10 μs. The plasma emission was incident on a concave spherical mirror with a diameter of 3 cm located at a distance of 25 cm from the plasma focus. Thus, a receiving telescope used for remote sensing was modeled. In so doing, only ~ 0.09% of total energy from the plasma focus was incident on the mirror. The image was focused into a spot with a diameter of ~ 4 mm on the monochromator slit. Hence it follows that no more than 0.002% of total energy of plasma emission was incident on the input slit of the monochromator even disregarding significant losses due to imperfection of an optical train as well as losses due to mirrors and a final objective. Reducing the diameter of the focal spot on the slit down to ~1 mm it was possible to increase the intensity on the monochromator input four times. It corresponded to the distance no less than 20 meters from the telescope with a diameter of 0.5 m.

The examined particles were placed within the focal zone on an adhesive thread ~10 μm thick. First, the plasma spectrum induced by breakdown on the adhesive thread was recorded, as far as this spectrum was a main source of lines hindering identification of the uranium spectral lines.

In experiments with the solid aerosol, several UO_2F_2 particles whose total volume was no more than 10 μm^3 were placed within the focal zone. Their total mass was equal to ~ $6 \cdot 10^{-11}$ g given that the particle density was ~ 5.82 cm^{-3}. Thus, the concentration of the U atoms in the focal volume was no more than 5–6 ppm even under conditions of complete evaporation of particles. In Fig. 2, the image of the emission spectrum of plasma initiated on the UO_2F_2 particles is displayed from a monitor screen. Lines of the uranium spectrum are clearly seen. They are brightest in spectral ranges around λ = 409.013 and 411.610 nm. During processing, this image was filtered by low- and high-frequency linear filters to eliminate the TV camera noise without distortion of the image. At the last stage of processing, the summation of the bit image intensities row by row and the subtraction of average level of background were done. Such procedure has allowed us to increase sharply the signal-to-noise ratio.

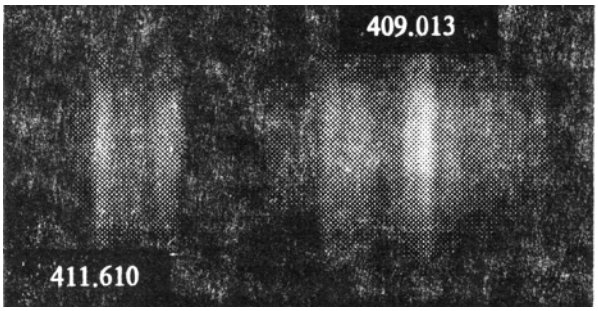

FIG. 2. The image of the plasma emission spectrum displayed on a monitor screen recorded by the TV camera for plasma initiated on uranyl fluoride particles at the delay time t_{del} = 4.2 μs. *The wavelength* (nm) *is indicated for the brightest lines of uranium.*

The resultant spectrum is shown in Fig. 3. Practically complete absence of the background has engaged our attention, which permits us to identify even comparatively weak lines of the uranium spectrum.

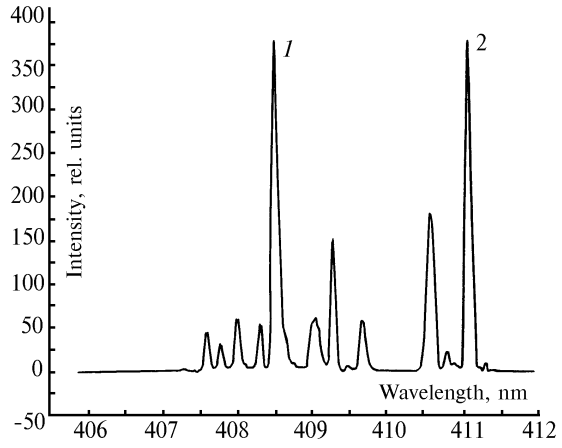

FIG. 3. The spectrum obtained by processing of the image shown in Fig. 2: spectral lines of uranium ions with λ = 409.013 *(1) and* 411.610 nm (*2*).

This is possible due to the fact that ionization potential of uranium is ~ 6.2 eV and the duration of a laser pulse is sufficiently long 1.5 μs. Under such conditions the plasma resulting from the breakdown remains sufficiently long so hot that it supports high concentration of excited ions with lower energy levels (energy of excitation is 3.82 eV for levels with λ = 409.013 nm and 3.01 eV for λ = 411.610 nm). The absence of lines of the adhesive thread spectrum is explained by an earlier breakdown on the particles of

UO_2F_2 distributed along the thread; as a result, the adhesive spectrum is shielded by that of plasma.

Unfortunately, the 6-bit ADC applied in a recording unit does not permit to obtain more than 64 gradations of the intensity. For this reason, the most intensive lines of the spectrum were cut off, and the uranium ion lines with wavelengths λ = 409.013 and 411.610 nm have nearly the same intensities in Fig. 3.

It should be noted that strobing permits us to cut off lines of excited atoms by the choice of the delay time of strobe pulse (in this case, t_{del} = 4.2 μs) and to optimize the interval to obtain a sufficiently high signal-to-noise ratio for the ion spectral lines. It is vividly illustrated by Fig. 4, in which the same spectrum is shown but at t_{del} = 3.8 μs. A large number of foreign atomic lines are seen, and the intensity of the uranium lines drops appreciably.

It should be emphasized that all results were obtained for a single laser pulse. Statistical processing of spectra for a pulse series to increase the signal-to-noise ratio was not conducted. Nevertheless, sensitivity obtained in our experiments on uranium detection in solid particles is twice the limiting sensitivity of 10 ppm specified by Radziemski et al.[2] In the study of spectra of plasma induced on drops of the uranyl fluoride solution in distilled water, the size of drops varied from 100 μm up to 1 mm. Because UO_2F_2 is practically insoluble in water, the concentration of solution was not measured, however, the insoluble residue was measured, and its amount allowed us to conclude that the concentration of the uranium atoms in the breakdown zone was less than 2 ppm. In the experiments with drops of water solution the spectra difficult for identification were obtained. An example of this spectrum is displayed in Fig. 5. The spectrum congestion can be explained by the presence of the spectral lines of adhesive thread. For unambiguous detection of uranium ion lines, additional experiments with distilled water drops were performed. Then computer analysis of the number and position of their spectral lines was conducted. From these experiments, it is possible to make the conclusion that the concentration of the uranium atoms at a level of 2 ppm is the lowest threshold of sensitivity of the equipment for the given spectral range.

Thus, our results suggest that the given method be very promising not only for detection of solid and liquid aerosols containing uranium, but also for the quantitative analysis of the uranium concentration in plumes. In spite of the fact that in remote sensing of plumes the intensity of a useful signal will be decreased, we can state that the use of a spectrochemical lidar described in Ref. 1 will allow us to receive consistently a signal from distances up to 150 - 200 meters. Therewith, the signal attenuation by the atmosphere will be insignificant, as far as coefficient of radiation extinction by the aerosol atmosphere at wavelengths ~ 0.4 μm is of ~ 0.1 km^{-1}.

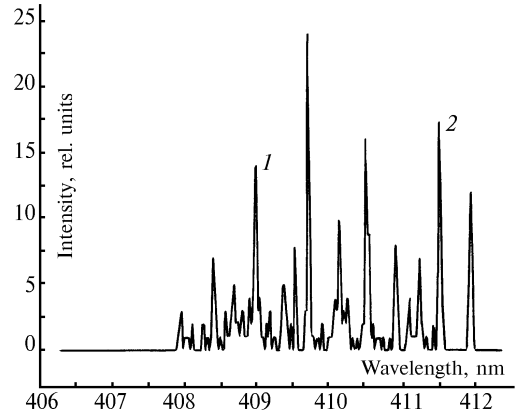

FIG. 4. The plasma spectrum at t_{del}=3.8 μs *:* λ = 409.013 *(1) and* 411.610 nm *(2).*

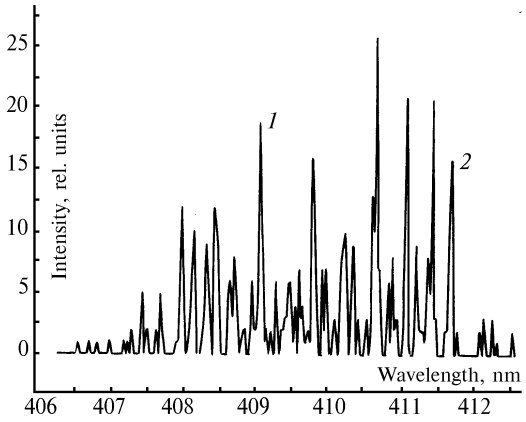

FIG. 5. The plasma spectrum initiated by the laser radiation on a drop of UO_2F_2 *in water solution:* λ = 409.013 *(1) and* 411.610 nm *(2).*

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