RAPID LASER ANALYSIS OF BERYLLIUM CONTAINING AEROSOLS

E.B. Belyaev, Yu.D. Kopytin, S.T. Penin, and S.A. Shishigin

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
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In this paper we present the experimental results on studying a possibility of measuring beryllium content in aerosols using an optical breakdown in air initiated with a pulsed CO_2 *laser radiation at* 10.6 μm *wavelength.*

The problem of detecting the content of beryllium and its compounds in air of industrial premises is very urgent. This is a result of extremely high toxicity of beryllium containing aerosols. Existing techniques of analysis, namely, chemical and techniques using an electric arc with hollow electrode require too much time that leads to the results depreciation. The technique of direct spectral analysis of the beryllium emission lines of laser spark allows one to essentially speed–up the obtaining of results.

The feasibility of remote analysis is one more advantage of this technique. Moreover, high accuracy of measurements is achieved even for extremely small concentrations of detected element.[1,2,3]

Plasma generated in a volume of a laser spark is significantly nonequilibrium one. The electron temperature T_e approximately equals $10^4 - 10^5$ K. This causes the maximum of spectral intensity to move to lines with high excitation potential. Hence it is not necessary to work in the vacuum ultraviolet range in many cases, and this fact allows an essential simplification of the equipment to be reached.

The intensities of emission spectra of neutral atoms and ionized ones reach maximum values at different periods after plasma formation. This makes it possible to maximize the signal–to–background ratio and minimize the spectral interference of the atomic and ion lines as well as the interference of lines of different elements.

The most difficult problem occurring in the case of analysis of the beryllium and its compounds containing solid–phase aerosols is the calibration. Variations of size and shape of particles hamper the data processing, while low maximum permissible concentration of beryllium lowers the probability of the beryllium containing particles coming into focal volume. Analysis of aerosol with filters (see Ref. 1) makes it possible to lower the difficulties connected with calibration. The measurement accuracy in this case is approximately 10 – 20%. The lowest detectable amount of beryllium equals 0.06 μg. To excite the spectrum, a Nd laser with 1.06 μm wavelength is used in this technique.

In Ref. 2 the analysis of the beryllium containing aerosol in air has been carried out. In this study the lowest level of beryllium content detection reached was 0.5 ng/g ($\sim 5 \cdot 10^{10}$ of particles mass). Aerosol has been created with an aerosol generator. The breakdown has been initiated with a Nd laser radiation at 1.06 μm wavelength.

In this paper we consider some results of measuring the beryllium content in aerosol using a pulsed CO_2 laser radiation at 10.6 μm wavelength. Radiation of such a wavelength has some advantages over laser radiation generated in the visible or near infrared ranges for high efficiency of the cascade ionization processes in vapors, which is proportional to λ^2. This causes an essential (1–2 orders) lowering of the threshold values of intensities of the pulse optical breakdown initiated by a suspended particles of aerosol for radiation at the wavelength $\lambda = 10.6$ μm compared to radiation in short–wave spectral range. In case of sub–microsecond laser action the excitation of optical spectrum of matter has the electroluminescence nature, that essentially raises the signal–to–noise ratio in comparison with the emission spectroscopy of the arc discharge.

We carried out measurements using ordinary procedure from emission analysis of laser–induced plasma. Block diagram of measuring setup is presented in Fig. 1.

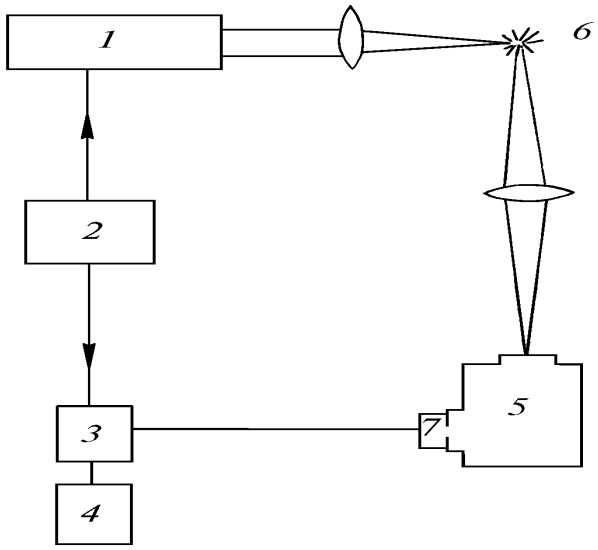

FIG. 1. Block diagram of a setup for analysis of laser spark. For spectrum recording we use the photodiode array operating during a fixed period after the breakdown initiation that allows the recording of the spark emission solely. Shown in the figure are a pulse laser (1), a control timer (2), a PD controller (3), an oscilloscope (4), a spectrograph (5), a laser spark (6), and a photodiode array (7).

The energy emitted from the breakdown area of vapor–gaseous halos in the neighbourhood of absorbing particles is determined by the emission at all spectral lines, recombination continuum, and thermal radiation from radiatively heated particles

$$J_R = \sum_{k,\,m} N_k^* A_{km}^* (\varepsilon_m - \varepsilon_k) + N_e^2 \sum_m A_{em}\, \varepsilon_m +$$

$$+ 4\pi \bar{a}^2 \sigma \alpha_g (T^4 - T_\infty^2)\,, \qquad (1)$$

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where N_k^* is the population of the kth level; A_{km}^* is the effective probability of radiative transition $k \to m$; $\varepsilon_m - \varepsilon_k$ is the energy of emitted photon; A_m is the coefficient of radiative recombination to the level m; $\overline{a}$ is the rms size of plasma initiation core; σ is the Stefan–Boltzmann constant; α_g is the grayness coefficient; and, N_e is the concentration of free electrons. For quantitative spectral analysis we used the technique[3,4] based on the relation of the form

$$n_d \approx n_r (J_d / J_{d.r.})\, C_{d.r.} (J_{r_1} / J_{r_2}) , \qquad (2)$$

where n_d and n_r are the concentrations of detected element and reference one (with respect to this element the content of other substances is estimated); $J_d/J_{d.r.}$ is the ratio of intensities of homologous pairs of spectral lines of corresponding substances; $C_{d.r.}$ is the calibration coefficient obtained for controlled concentrations of detected and reference substances; J_{r_1}/J_{r_2} is the ratio of the fixed pair of lines of a reference substance, which indirectly characterizes the conditions of excitation in plasma, whose random variations are caused by fluctuations of the radiant energy density of a laser from pulse to pulse and the particles size.

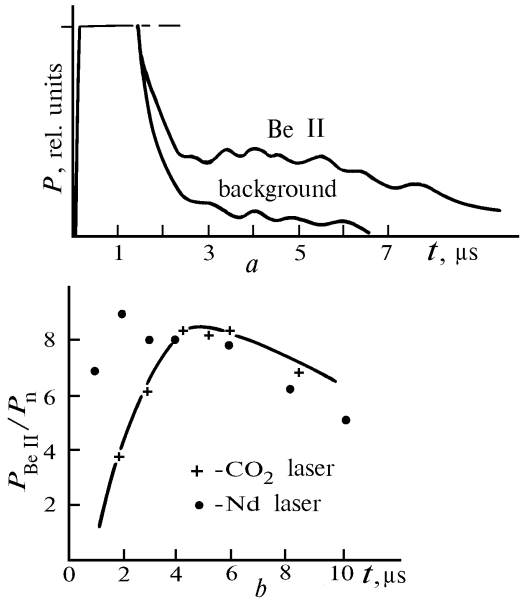

FIG. 2.

The results of studying on rapid laser analysis of the beryllium containing aerosols using emission line at the wavelength $\lambda = 313$ nm are shown in Fig. 2; the background was near the emission line Be II and the beryllium concentration was 2 μg/m^3. Figure 2*a* presents the time behavior of signal P from single ionized Be II. The initial period of the breakdown plasma formation (approximately up to 1.5 μs) is not shown, because this period is characterized by a strong continuous luminescence connected with electron–electron interaction. The long "tail" of signal from beryllium should be noted as against the rapidly falling off background.

Figure 2*b* presents the time dependence of the signal–to–noise ratio both for Nd laser[2] and CO_2 laser. The noise was calculated as a standard deviation from mean background. It is easy to see from the figure, that the ratio for CO_2 laser is not less than ratio for Nd laser, in general. In both cases there exists a pronounced maximum in 2 – 4 μs range for Nd laser and 4 – 6 μs range for CO_2 laser.

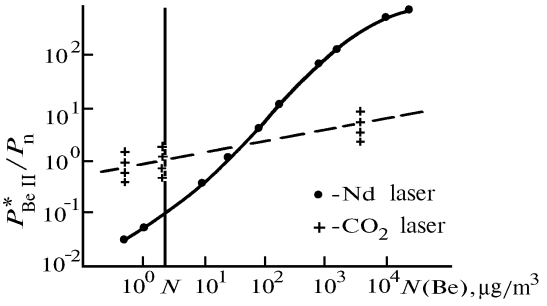

FIG. 3.

The calibration nomograms for quantitative estimation of the beryllium content in air are shown in Fig. 3. Here the vertical solid line marks the maximum permissible concentration (MPC) of beryllium in air of industrial premises according to standards of the Russian Ministry of Public Health. Time of delay for spectra recording is $\Delta t = 4$ μs both for experiments with Nd and CO_2 lasers. Level of signal from Be II P^* was calculated against the background level (i.e. signal minus background). One can easily see the advantage of using CO_2 laser over Nd laser in the range of extremely small concentrations of beryllium. For MPC level we achieved the ratio

$$P^*/\overline{P}_b \sim 2 .$$

As follows from Fig. 3, after constructing a detailed calibration curve the reliable detection of the beryllium content within MPC level is possible using a CO_2 laser.

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