

DIFFERENTIAL SPECTROFLUORIMETER WITH A COPPER VAPOR LASER

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A spectrofluorimeter designed for recording the fluorescence spectra and their first derivatives is described. The spectra are differentiated instrumentally.

One of the techniques to increase the contrast and to reveal hidden components of the radiation spectra and, hence, to improve the spectrum informativeness is the instrumental differentiation of spectra and analysis of not only the wavelengths intensity distribution itself, but also the first and second derivatives of the distribution. This technique is widely used in the absorption spectroscopy, in particular, in the electron paramagnetic resonance (EPR) and laser spectroscopy because of a possibility to control frequency properties of the radiation source, for example, a semiconductor laser or a sample investigated, as it is with EPR technique, by simple hardware components.

In the case of photoelectric recording of the radiation spectra, in particular, recording of luminescence by monochromator and PMT periodic scanning within small limits of the monochromator output slit along the direction of the dispersion on the frequency ω with the subsequent recording of the PMT signals at the scanning frequency ω or at the doubled frequency 2ω of this signal is an analog of the differentiation technique. The component of the signal at the frequency ω is proportional to the spectrum first derivative, and the component of the signal at the frequency 2ω is proportional to the second derivative. The spectrum can be scanned periodically relative to the monochromator output slit by angular oscillation of the plane-parallel plate placed before the output slit inside the monochromator. The scanning frequency, vibrations and noise of mechanical gear are shortcomings of such an approach.

We made a spectrofluorimeter for recording the spectrum first and second derivatives with only electronic system of spectrum scanning. This device has no the above shortcomings. The dissector with a slit diaphragm whose deflecting system is connected with a sinusoidal signal generator at the frequency ω is used in the spectrofluorimeter as a radiation detector instead of a PMT. The value and amplitude of the sinusoidal signal determine a swing of oscillations of the dissector electronic slit and, hence, the frequency deviation over the optical range and level of the signals of the first and second derivatives.

A block diagram of the spectrofluorimeter is presented in Fig. 1. A copper vapor laser 1 is used as a radiation source. The choice of the copper vapor

laser has been determined by its high pulse repetition frequency ν . This allows the fluorescence signals to be processed by different electronic circuits over the well investigated sonic frequency range. The laser emitted at the wavelengths $\lambda = 510.6$ nm (green line) and $\lambda = 578.2$ nm (yellow line). For the pulse repetition rate $\nu = 8$ kHz the radiation mean total power was about 1 W. The focusing and deflecting systems of the dissector were oriented in such a way that the slit was scanned along the direction of dispersion of the spectral device 10. The dispersion element 4 and filters 2 and 3 provided a choice of one of the laser radiation lines to excite luminescence of the sample 6. Filter 8 absorbed the laser radiation scattered by the surface of the sample 6 under study. The luminescence radiation was directed by lenses 5 and 7 to the optical fibre 9 whose output end was an input slit of the polychromator 10. The spectrum formed by the polychromator is projected onto the input window of the dissector 11. The generator 15 operated at frequency $\omega = 41$ Hz powered the dissector deflecting system. The setup had three paths of signal recording at the dissector output: the direct-current amplifier 14, lock-in amplifier 12 at the frequency $\nu = 8$ kHz, and lock-in amplifier 13 at the frequency $\omega = 41$ Hz. This paths allowed the sample luminescence spectra as well as their first derivatives to be recorded simultaneously or consecutively. The spectra and their derivatives were recorded with a recorder 16.

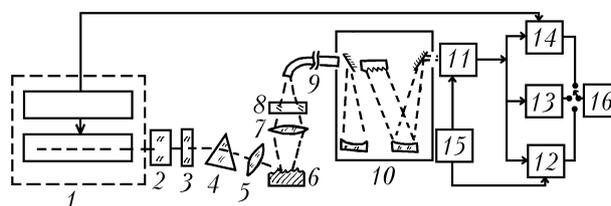


FIG. 1. Block diagram of the spectrofluorimeter.

To study properties and possibilities of the spectrofluorimeter, the samples of minerals and petroleum products having wide and low contrast fluorescence spectra^{1,2} were chosen as typical fluorescent objects.

Figure 2 presents the fragments of the luminescence spectra of the Naryn-Kunta amazonit and plagioglass from the mica-bearing pegmatites of Mamsko-Chuiskii region (lower curves in Fig. 2). The spectra of roentgeno-luminescence^{3,4} and photoluminescence^{4,5} were pre-recorded for this samples. The spectra in Fig. 2 in the range of 520–540 nm have been distorted by absorption of the filter 8. It is impossible to avoid using this filter in the given optical scheme because the laser radiation scattered by the sample causes fluorescence of the optical waveguide 9.

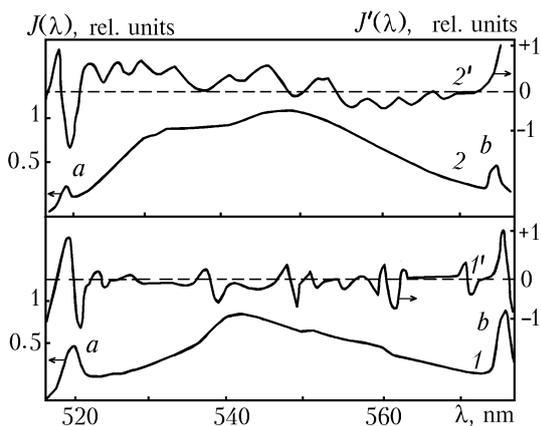


FIG. 2. The plagioglass fluorescence spectrum $J(\lambda)$ (1) and its first derivative $J'(\lambda)$ (1'), the amazonit fluorescence spectrum (2) and its first derivative (2'). Dashed lines show the zero level of the spectrum derivative signals.

Upper curves in Fig. 2 are the signal records at the frequency ω , i.e. the derivatives of the corresponding spectra of amazonit and plagioglass. The spectra fragments marked in Fig. 2 by the letters *a* and *b* are the bench marks ($\lambda = 510.6$ and $\lambda = 578.2$ nm of CuI).

As one can see from the signal records in Fig. 2 the spectra differentiation allows the peculiarities imperceptible in the records of the spectral curves to be revealed. These peculiarities can be useful to solve different problems of the luminescent analysis of minerals.

Figure 3 presents the record of the fluorescence spectrum of oil and its first derivative.

Note, that many substances fluoresce only under an intense ultra-violet irradiation only. When developing this spectrofluorimeter, the essential progress in lasing of radiation harmonics of the copper-

vapor laser was taken into account. In particular, the ultra-violet radiation level attained about 1–3 W (Ref. 6). The differential spectrofluorimeter based on the same UV laser can be used in industry and scientific research.

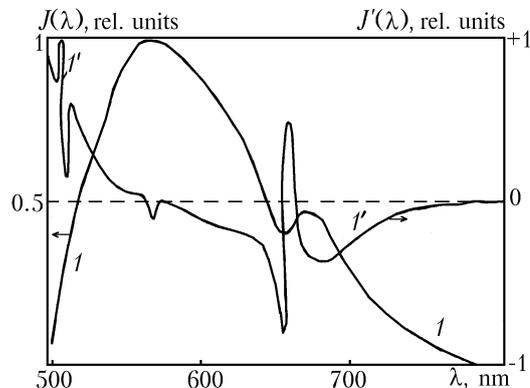


FIG. 3. The petroleum oil fluorescence spectrum (1) and its first derivative (1'). Pronounced peculiarities over the range of 500–600 nm are conditioned by superposition of bench mark atomic lines of copper; a minimum on the fluorescence spectrum at the wavelength of 660 nm is connected with the radiation absorption in the optical waveguide.

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