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Abstract

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INCREASING THE SENSITIVITY OF LUMINESCENT REACTIONS FOR CATIONS WITH ORGANIC REAGENTS UPON FREEZING SOLUTIONS

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In the works of Shpol' skii and co-workers ($^{1-4}$) on the investigation of the fluorescence spectra of organic compounds at the temperature of liquid air, the possibilities are shown for applying the frozen-solution method to the solution of specific analytical problems. Shpol' skii indicates (^{2}) the following possible directions: determination of carcinogenic substances in polluted air, in resins, tobacco smoke, smoked food products, and determination of heavy aromatics in petroleum oils and bitumens.

Both directions are oriented toward the determination of organic substances by their own fluorescence, using quasilinear spectra. Meanwhile, in works (^{5},^{6}) data are given concerning an increase in the fluorescence intensity of certain complex compounds when the temperature is lowered. It is noted (^{6}) that the complex compound of terbium with dibenzoylmethane does not fluoresce at temperatures of $-60°$ and above; at $-100°$ appreciable fluorescence is observed, the intensity of which increases 100-fold as the temperature is lowered to $-185°$.

It could be expected that the frozen-solution method, even without the use of quasilinear spectra, would prove very useful in the luminescent analysis of inorganic substances with the application of organic reagents.

In the present communication we give the results of an investigation of the possibilities of increasing the sensitivity of reactions for the determination of certain cations using two reagents with nonrigid structure, whose luminescence arises upon formation of complexes as a result of the elimination of internal nonradiative transitions (^{7}). One of them, 2,2′,4′-trioxy-5-chloro-(1-azo-1′)-benzene-3-sulfonic acid (lumogallion IREA), is known for the determination of gallium (^{8}) and niobium (^{9}) by the luminescent method; the other, 2-oxy-3-sulfo-5-chlorobenzene-(1-azo-1′)-2′-oxynaphthalene (magneson IREA), is known as a reagent for the colorimetric determination of magnesium (^{10}).

In our experiments the fluorescence spectra and intensities were measured with a spectrofluorimeter assembled on the basis of a Zeiss VSU-1 mirror monochromator. FEU-29 and FEU-27 photomultipliers were used as radiation receivers. The source of ultraviolet light was an SVD-120A mercury-quartz lamp with a

Fig. 1. Fluorescence spectra of the complex of lumogallion IREA with gallium: 1—at room temperature, 2—at liquid-nitrogen temperature, 3—fluorescence spectrum of lumogallion IREA at liquid-nitrogen temperature.

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UFS-3 light filter. The setup was calibrated with respect to wavelengths and sensitivity (^{11}). For measuring fluorescence spectra and intensities at low temperatures, the procedure described in (^{12}) was used. The solutions were frozen in quartz test tubes with an internal diameter of 4 mm. For visual observation of the fluorescence of frozen solutions, the test tubes were removed from liquid nitrogen and examined in ultraviolet light. Solutions of the complexes under study were prepared under conditions optimal for analysis and described

in works (8-10). The luminescence of the complex of lumogallion IREA with gallium was studied at pH 2.2—in this case the influence of aluminum is practically absent (8). The concentration of lumogallion IREA in the solution was 0.0004%, and that of gallium 4 μg in 1 ml. The complex was extracted with isoamyl alcohol 30 min after addition of lumogallion to the solution, and the fluorescence spectra were recorded.

Fig. 1. Fluorescence spectra of the complex of lumogallion IREA with gallium: 1—at room temperature, 2—at liquid-nitrogen temperature, 3—fluorescence spectrum of lumogallion IREA at liquid-nitrogen temperature.

The complex of lumogallion with niobium was obtained in solution at pH 5.8. The concentration of niobium was 2 μg in 1 ml, and that of lumogallion 0.0004%. Elimination of the influence of aluminum was achieved by adding ammonium oxalate to the solution. Its concentration in the buffer solution was 0.02 N. The excess reagent was extracted with isoamyl alcohol 30 min after adding lumogallion IREA to the solution. In both cases acetate buffer solutions were used.

The luminescence of the complex of magneson IREA with magnesium was studied in a water-acetone solution at pH 11.0, prepared with an ammonia buffer mixture. The acetone concentration was 32%, that of magneson IREA 0.0012%, and that of magnesium 200 μg in 1 ml.

It was found that the magnesium complex with magneson IREA fluoresces with red light, but the fluorescence intensity in the unfrozen solution is so low that it does not seem possible to use this reaction as a luminescent one. The fluorescence spectra of the investigated complexes in unfrozen and frozen solutions are given in Figs. 1-3, from which it is evident that at room temperature the complexes have structureless fluorescence spectra with $\lambda_{\max}$ for the complex of lumogallion IREA with gallium at 580 mμ, with niobium at 610 mμ, and for the complex of magneson IREA with magnesium at 613 mμ. At the temperature

Fig. 2. Fluorescence spectra of the complex of lumogallion IREA with niobium: 1—at room temperature, 2—at liquid-nitrogen temperature.

Figure 2: Fig. 2. Fluorescence spectra of the complex of lumogallion IREA with niobium: 1—at room temperature, 2—at liquid-nitrogen temperature.

Fig. 3 and Fig. 4: fluorescence spectra and calibration curves

Figure 3: Fig. 3 and Fig. 4: fluorescence spectra and calibration curves

of liquid nitrogen the fluorescence spectra of the complexes are also structureless, but have two maxima. One of the maxima is close to the maximum for the unfrozen state, while the second is shifted into the short-wavelength region. The second maximum for lumogallion IREA with gallium lies at 546 mμ, with niobium at 565 mμ, and for magneson IREA with magnesium at 577 mμ.

Fig. 2. Fluorescence spectra of the complex of lumogallion IREA with niobium: 1—at room temperature, 2—at liquid-nitrogen temperature.

As is seen from Figs. 1-3, the fluorescence intensity of the complexes increases sharply upon freezing the solutions: in aqueous and water-acetone solutions, for the complexes of lumogallion IREA with niobium and magneson IREA ···

with magnesium by more than 100 times, and in isoamyl alcohol for the lumogallion IREA complex with gallium—by 10 times. On freezing, lumogallion IREA fluoresces with a weak red light with λ_{max} equal to 618 mμ.

Such a sharp increase in the fluorescence intensity of the complexes upon freezing the solutions made it possible to increase the sensitivity of the luminescent reaction for determining niobium with lumogallion IREA by an order of magnitude,

Fig. 3. Fluorescence spectra of the magnezon IREA complex with magnesium at room temperature (1) and at the temperature of liquid nitrogen (2)

Fig. 4. Calibration curves for the determination of niobium by the luminescent method, obtained at room temperature (1) and at the temperature of liquid nitrogen (2); for the determination of magnesium by the colorimetric method at room temperature (10) (3) and by the luminescent method at the temperature of liquid nitrogen (4)

from 0.05 to 0.005 μg in 1 ml, and to use the colorimetric reagent magnezon IREA as a luminescent reagent, with an increase in the sensitivity of the reaction by 20 times, from 0.04 to 0.002 μg in 1 ml of solution. This point is illustrated by the calibration curves shown in Fig. 4.

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CITED LITERATURE

[1] É. V. Shpol' skii, A. A. Il' ina, L. A. Klimova, DAN, **87**, 935 (1952).
[2] É. V. Shpol' skii, *Uspekhi fiz. nauk*, **71**, 215 (1960).
[3] É. V. Shpol' skii, *Uspekhi fiz. nauk*, **68**, 51 (1959).
[4] É. V. Shpol' skii, R. I. Personov, *Zav. lab.*, **18**, 428 (1962).
[5] W. E. Ohnesorge, L. B. Rogers, *Spectrochim. Acta*, **15**, 27 (1959).
[6] V. V. Kuznetsova, *Dokl. AN BSSR*, **5**, 203 (1961).
[7] E. A. Bozhevol' nov, *Izv. AN SSSR, ser. fiz.*, **24**, 762 (1960).
[8] A. M. Lukin, E. A. Bozhevol' nov, *ZhAKh*, **15**, 43 (1960).
[9] V. V. Klimov, O. S. Didkovskaya, *Zav. lab.*, No. 2 (1963).
[10] A. M. Lukin, G. B. Zavarykhina, *Tr. Inst. reaktivov*, issue 24 (1961); G. G. Karanovich, *Tr. Inst. reaktivov*, issue 24, 54 (1961).
[11] E. A. Bozhevol' nov, in: *High-Purity Substances and Reagents*, 1959, p. 124.
[12] É. V. Shpol' skii, L. A. Klimova, É. A. Tirdniyauskaitė, in: *Proceedings of the 10th All-Union Conference on Spectroscopy*, 1, Lviv, 1957, p. 24.

Note: Figure translations are in progress. See original paper for figures.