PHOSPHORIMETRIC DETERMINATION OF BERYLLIUM WITH 2-(2'-HYDROXYPHENYL)BENZOXAZOLE

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Dedicated to Professor F. Čůta on the occasion of his 80th birthday.

Photoluminescence of 2-(2'-hydroxyphenyl)benzoxazole (BO) and 2-(2'-hydroxyphenyl)benzthiazole (BS) and their metal complexes was studied in aqueous alcoholic medium. The excitation and emission phosphorescence spectra were measured at the temperature of liquid nitrogen in dependence on pH and also on the presence of KI, and the phosphorescence lifetimes of the complexes of BO with Be, Zn, Cd, and Ga were determined; they decrease with the increasing atomic number of the metal from 1 s to 0·1 s. A procedure for the phosphorimetric determination of beryllium, concentrations $3 . 10^{-8} - 1 . 10^{-6} \text{ mol } l^{-1}$, with BO was worked out; the presence of alkali metals and of tenfold excess of Al, Ca, Cd, Ga, Fe(III), Mg, Pb, and Zn does not interfere. Beryllium can be determined directly *e.g.* in mineral waters. The relative standard deviation of the determination of 10^{-7}M beryllium solutions amounted to 7·8%.

In comparison with fluorimetry at ambient temperature, photoluminescence determinations at low temperatures are more sensitive and frequently also more specific owing to the more suitable emission spectral patterns or to different afterglow periods of the emitting moieties in the mixture. This is utilized in trace analysis particularly of organic substances or for the determination of elements in the form of complexes with inorganic ligands. Rather little study has been devoted to the application of phosphorescence of complexes with organic ligands to inorganic trace analysis[1]. So far, only phosphorimetric determinations of nanogram quantities of beryllium with dibenzoylmethane[2,3], boron with benzoylacetone[4], and niobium with 8-hydroxyquinoline[5] have been reported. The limited use of this technique is due to some experimental problems, not yet fully solved, such as the choice of appropriate medium, difficulties associated with the application of extremely low temperatures, or measurement of very short afterglow times[6].

In the present work we have studied the luminescence characteristics of two related organic reagents, *viz.* 2-(2'-hydroxyphenyl)benzoxazole (BO) and 2-(2'-hydroxyphenyl)benzthiazole (BS),

$$X = O \text{ or } S$$
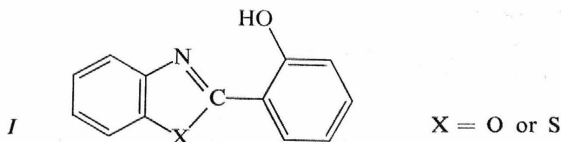
and their metal complexes at the temperature of liquid nitrogen. Attention was paid to the various factors affecting the reproducibility of the phosphorimetric measurements, choice of the solvent, and the adjustment of the pH of the reaction mixture prior to the cooling of the solutions; the possibility of the time resolution of the mixtures of the phosphorescing complexes according to their different afterglow was examined, too. We were able to develop procedure for selective phosphorimetric determination of beryllium with BO with the limit of determination of 0·1 ppb Be, which can be applied directly to, *e.g.*, analysis of mineral water.

EXPERIMENTAL

Chemicals

2-(2′-Hydroxyphenyl)benzoxazole[7,8] (BO) and 2-(2′-hydroxyphenyl)benzthiazole[9,10] (BS) were purified by chromatography on a layer of pretreated silica gel. Colourless crystals were obtained by recrystallization, m.p. (on a Kofler stage) of BO 123·5—124°C, of BS 131·5—132°C. The purity of the chemicals was checked by chromatography on layers of pretreated[11] Silufol[R] and by elemental analysis. For phosphorimetric measurements, 10^{-5}M solutions of BO and $5 \cdot 10^{-6}$M solutions of BS in 30% (v/v) methanol were usually employed; they are stable for at least 24 h and at 77 K form a microcrystalline snowy mass suitable for reproducible phosphorescence measurements.

The Al, Be, Cd, Ga, Sc, and Zn perchlorates used were prepared by dissolution of the pure metals (99·99%) in perchloric acid and double recrystallization of the products from deionized water. 0·1M stock solutions (pH ∼ 2) were prepared from the solid chemicals; they were diluted with deionized water to the desired concentration just before the measurements. The other chemicals used were Merck or Lachema, Brno, products, reagent grade purity.

The solvents for chromatography were redistilled prior to use. Methanol and ethanol for UV spectroscopy, Lachema, and deionized water were used for the photoluminescence measurements; these solvents or their aqueous solutions exhibited phosphorescence with rather long afterglow and with excitation maxima at 250 and 300 nm and an emission band at 430 nm. When, however, radiation of wavelength above 330 nm was used for the excitation, no emission signal was obtained even with the highest gain of the spectrofluorimeter.

Apparatus and Measurement Techniques

The pH values of the studied aqueous methanolic solutions at 25°C were measured by means of a glass electrode combined with a calomel electrode using a pH-meter Radelkis OP-205. An aqueous methanolic succinite buffer, whose pH values in the mentioned mixed solvent of different compositions have been tabulated[12], were used for the standardization. The values found are denoted as pH* throughout this paper.

Qualitatively was the fluorescence monitored by employing a mercury lamp "Thelta-Sonne" (GDR) with a Wood filter.

The noncorrected excitation and emission photoluminescence spectra were measured on a spectrofluorometer SPF Aminco-Bowman equipped with a rotatory phosphoroscope (Fig. 1), a xenon discharge tube 150 W (source Aminco 422—818), and a photomultiplier 1P21 (spectral-characteristics S4). The emission intensity was measured with the photomultiplier voltage 720 V

on a microphotometer Aminco J10—280. The spectra were recorded by means of an X—Y plotter Aminco4-8909. The excitation and emission monochromators were calibrated using the mercury lamp lines.

The stationary cell resembled the commercial type (Aminco), its bottom part was manufactured from a quartz tube (outer diam. 3 mm, inner diam. 2 mm) and held in a frame Aminco. The rotatory capillary cell was represented by a quartz tube (outer diam. 5 mm, inner diam. 3 mm) to whose bottom a capillary 50 mm long (outer diam. 3 mm, inner diam. 0·9 mm) was sealed. The cell was coupled to the spinning device of an NMR spectrometer Tesla, driven by a stream of nitrogen.

Measurements of Photoluminescence Spectra and Phosphorescence Afterglow

The cells and all the vessels used were purified by treating with nitric acid 1 : 1 for 24 h. The Dewar flask was rinsed with liquid nitrogen, then the stationary cell containing the sample was inserted and the whole was placed always in the same position in a holder connected with the spectrofluorimeter. Prior to the application of the rotatory capillary cell, the solution was sucked into the bottom capillary end of the cell whose top end was then closed, and the cell was submerged in liquid nitrogen. For quantitative measurements of the phosphorescence intensity, the spectrofluorimeter was standardized with alkaline (0·08M-NaOH) aqueous methanolic solution (30% (v/v)) of BO, concentration $1 . 10^{-5}$ mol 1^{-1}. For the phosphorescence measurements of this solution in the stationary cell, temperature 77 K, excitation wavelength 350 nm and emission wavelength 490 nm, slit width 2 mm (entrance and exit slits of the cell compartment and the entrance slit at the photomultiplier), photomultiplier voltage 720 V, and gain 3, the deflection on the microphotometer was set to 1·60. The values thus obtained are denoted I_{rel}, those obtained in other conditions are denoted I'_{rel}.

The phosphorescence lifetimes τ (the time during which the initial emission intensity drops to its $1/e$ fraction) were determined from the record of the intensity decrease with the time after a rapid break of the excitation radiation. For this recording, a recorder Unicam SP 22 with a logarithmic converter was used with the maximum chart speed, 137 mm/min.

Purification of the Reagents by Chromatography on Silica Gel

50 g of silica gel L 100—160 was multiply eluted with hydrochloric acid 1 : 1, washed with water, and shaken with 100 ml of 0·1M Chelaton 3 (disodium salt of (ethylenedinitrilo)tetraacetic acid) for 5 min. After 30 min, the silica gel was decanted with water, sucked off, and dried at 105°C for 2 h. A 1·5 mm layer of this silica gel was poured on a glass plate, the total of 3 ml of 5% reagent in benzene was applied to the start and eluted with benzene. The spot positions were detected in UV light. The more rapidly migrating active components of the two reagents displaying intense fluorescence were prepared out of the chromatogram and washed with benzene; after evaporation of the solution to dryness, BO and BS were recrystallized from ethanol.

Qualitative Luminescence Reactions of the Reagents with Metal Ions

1 ml of a 10^{-3}M solution of BO or BS in 96% ethanol was mixed with several drops of an aqueous solution of the metal salt concerned, concentration about 1 mg metal/ml, and the luminescence of this mixture was observed in the UV light and compared with that of the blank, applying the ambient temperature as well as cooling in liquid nitrogen. The afterglow after screening the excitation source off was determined, too.

RESULTS AND DISCUSSION

Photoluminescence of the Reagents and Their Metal Complexes

The results of the qualitative observations are given in Table I. Rather strong phosphorescence at 77 K was found for the complexes of the two reagents with Be, Ga, and Zn, a weaker phosphorescence was observed with Al, Cd, and Sc. Alkaline or acidic solutions of the two reagents themselves (in contrast to neutral solutions) exhibit phosphorescence as well.

TABLE I

Photoluminescence Reactions of the Reagents BO and BS

Abbreviations: w. weak, m. medium, s. strong; b. blue, g. green, y. yellow, v. violet.

Metal	BO			BS		
	fluorescence		phosphorescence	fluorescence		phosphorescence
	298 K	77 K	77 K	298 K	77 K	77 K
Ag	w. b.	m. g.		w. b.	m. gy.	
Al	s. b.	s. b.	s. gb.	w. b.	m. y.	w. g.
Ba	m. b.	m. g.		w. b.	s. y.	
Be	s. b.	s. b.	s. g.	s. b.	s. b.	s. g.
Bi	w. b.	m. g.		w. b.	s. b.	m. y.
Cd	s. b.	s. b.	w. gb.	w. b.	s. y.	
Co		w. g.		w. b.	m. y.	
Cr(III)	w. b.	m. g.		w. b.	s. y.	
Cu		w. g.			s. y.	
Fe(II)				w. b.	s. y.	
Ga	s. b.	s. b.	s. bg.	s. b.	s. y.	s. g.
Hg(I)				w. b.	s. y.	
Hg(II)	w. b.	w. b.		w. b.	s. y.	
Mg	s. b.	s. b.		w. b.	s. b.	
Mn	w. y.	m. b.	w. b.	w. b.	s. y.	
Ni	w. b.	w. b.		w. b.	s. y.	
Pb	w. b.	s. b.		w. b.	s. b.	w. y.
Sb(III)	w. b.	s. g.		w. b.	s. b.	
Sc	s. b.	s. b.	w. gb.	s. b.	m. bg.	w. g.
Sm	w. b.	m. g.		w. b.	s. b.	
Sn(IV)	w. b.	m. b.		w. b.	s. b.	w. y.
Sr	w. b.	w. b.		w. b.	s. y.	
Zn	s. b.	s. b.	s. gb.	s. b.	s. b.	s. y.
Reagent	w. b.	m. b.		w. b.	s. y.	
+ NaOH	s. b.	s. b.	s. yg.	s. b.	s. bv.	s. g.
+ HClO$_4$	w. b.	s. b.	m. b.	m. b.	s. b.	s. yg.

Reproducibility of Phosphorimetric Measurements

The differences in the procedure during the freezing of the samples and the alignment of the cell with the sample in the Dewar flask containing liquid nitrogen on the measurement precision was investigated statistically by using the F-test[13] for the 95% probability and for 10 repeated measurements. Nitrogen stored for a longer time is bluish owing to its gradual enrichment with oxygen during the condensation of the latter from the air. The temperature of the cooling bath varies thus in dependence on its composition, which affects unfavourably the reproducibility of the measurements.

The scatter of the phosphorescence intensity measurements[14] of 10^{-5}M aqueous methanolic solutions (30% methanol) in 0·08M-NaOH indicated that a careful alignment of the cell with the sample in the Dewar flask and the whole in the apparatus is of great importance for precise results of the phosphorimetric measurements, whereas the rate of freezing does not affect the precision appreciably.
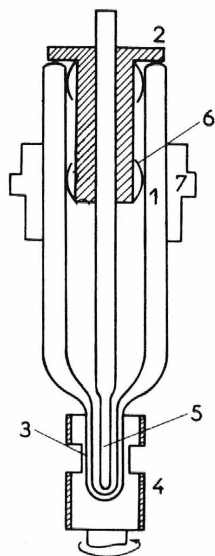

FIG. 1

Low-Temperature Phosphorimetric Arrangement

1 Dewar flask with liquid nitrogen, 2 cell holder, 3 silver-uncoated part of the Dewar flask, 4 rotatory cylindrical phosphoroscope, 5 bottom part of the cell with the sample, 6 strip spring, 7 outer cell holder.
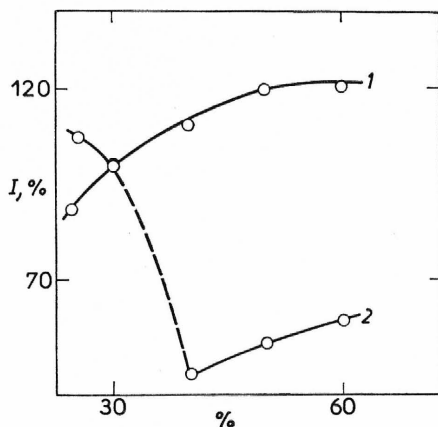

FIG. 2

Dependence of the Photoluminescence Intensity of the Reagent BO in Alkaline Medium on the Composition of the Aqueous Methanolic Solvent

$c_{BO} = 1 . 10^{-5}$ mol l^{-1} in 0·08M-NaOH; 1 fluorescence at 298 K, 2 phosphorescence at 77 K; λ_{exc} 350 nm, λ_{em} 490 nm.
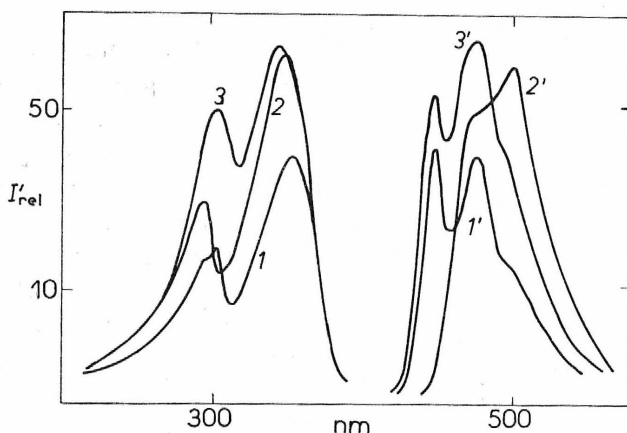
FIG. 3

Phosphorescence Spectra of BO and Its Beryllium Complex in Solvent Water–Methanol (30% v/v Methanol) at 77 K

Slit width 2 mm; $1-3$ excitation spectra, $1'-3'$ emission spectra; $1, 1'$ $c_{BO} = 1 . 10^{-5}$ mol l^{-1}, $c_{Be} = 1 . 10^{-6}$ mol l^{-1}, pH* 9·0, gain 3, λ_{exc} 350 nm, λ_{em} 448 nm; $2, 2'$ $c_{BO} = 1 . 10^{-5}$ mol l^{-1}, 0·08M-NaOH, gain 1, λ_{exc} 346 nm, λ_{em} 496 nm; $3, 3'$ $c_{BO} = 4 . 10^{-6}$ mol l^{-1}, 0·08M-HClO$_4$, gain 1, λ_{exc} 342 nm, λ_{em} 478 nm.
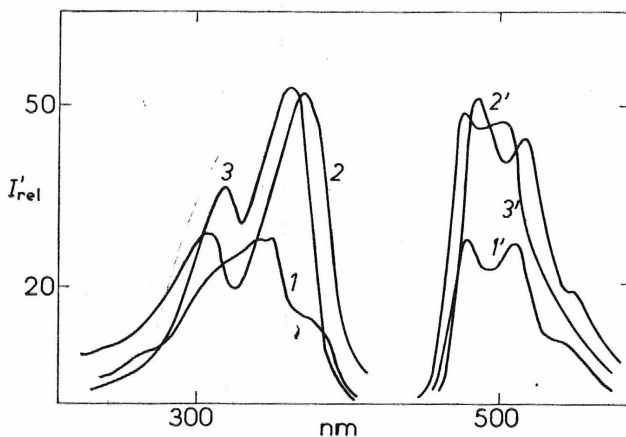

FIG. 4

Phosphorescence Spectra of BS and Its Beryllium Complex in Solvent Water–Methanol (30% v/v Methanol) at 77 K

Slit width 2 mm; $1-3$ excitation spectra, $1'-3'$ emission spectra; $1, 1'$ $c_{BS} = 1 . 10^{-5}$ mol l^{-1}, $c_{Be} = 1 . 10^{-6}$ mol l^{-1}, pH* 9, gain 1, λ_{exc} 345 nm, λ_{em} 480 nm, $2, 2'$ $c_{BS} = 4 . 10^{-6}$ mol l^{-1}, 0·08M-NaOH, gain 0·3, λ_{exc} 366 nm, λ_{em} 486 nm; $3, 3'$ $c_{BS} = 4 . 10^{-6}$ mol l^{-1}, 0·08M-HClO$_4$, gain 1, λ_{exc} 360 nm, λ_{em} 480 nm.

The application of the rotatory cell brings about a considerable improvement of the measurement precision in comparison with the stationary cell. However, with the rotatory cell the measurements are occasionally precluded due to evolution of bubbles in the liquid nitrogen or formation of condensed solid ice particles; while in the stationary cell these particles deposit on the bottom of the Dewar flask, in the rotating cell they whirl, which results in variations of the phosphorescence signal. For this reason only the stationary cell was employed for the measurements.

Solvent Effect on the Photoluminescence of BO

This effect is shown in Fig. 2. The structure of the frozen sample changes essentially as the concentration of methanol in the aqueous solution increases; as the most suitable from the point of view of the measurement reproducibility and the phosphorescence intensity appeared the solvent with 30% (v/v) methanol. For the measurements of the phosphorescence spectra, solvents with higher alcohol contents were used occasionally, too.

Phosphorescence Characteristics of the Reagents and of Their Complexes

The excitation and emission phosphorescence spectra of the two reagents and their beryllium complexes in different conditions are reproduced in Figs 3 − 5. The maxima in the spectra of BS are shifted to longer wavelengths with respect to the corres-
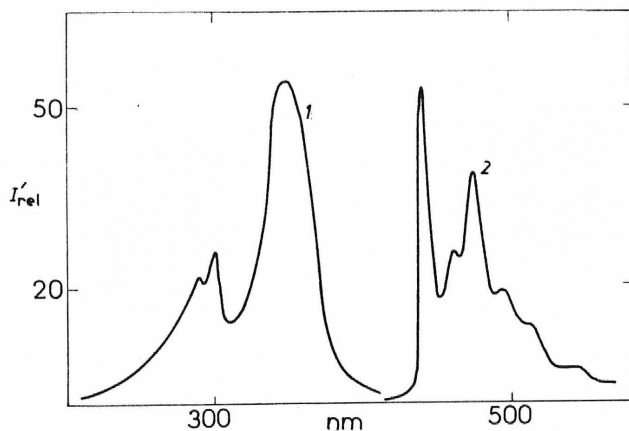

FIG. 5

Phosphorescence Spectrum of the Beryllium Complex of the Reagent BO in 96% Ethanol at 77 K

Slits: 1, 0·5, 0·5 mm; $c_{BO} = 5 \cdot 10^{-5}$ mol l^{-1}, $c_{Be} = 5 \cdot 10^{-4}$ mol l^{-1}; spectrum: *1* excitation, *2* emission.

ponding maxima for BO. The spectra of the reagents in neutral aqueous methanolic medium are virtually identical with those of the solvent itself.

The spectral characteristics and lifetimes of some BO complexes are given in Table II.

The emission spectra of the complexes exhibiting the shortest-wavelength vibrational band at about 450 nm differ considerably from those of the reagent anion. An excess of the reagent suppresses strongly the emission of the zinc complex. The phosphorescence lifetimes of the complexes decrease with the increasing atomic number of the central metal in the order $Be > Zn > Ga > Cd$.

The phosphorescence lifetimes of the reagent BS and its complexes in the conditions applied are much shorter than those found with the reagent BO, and could not be measured by means of the technique employed.

TABLE II

Phosphorescence Spectral Characteristics and Lifetimes of Some BO Complexes in Mixed Water–Methanol (30% v/v Methanol) at 77 K

$c_M = 8 \cdot 10^{-5} \text{ mol} \cdot l^{-1}$, $c_{BO} = 8 \cdot 10^{-6} \text{ mol} \cdot l^{-1}$ (excess metal), $c_M = 1 \cdot 10^{-6} \text{ mol} \cdot l^{-1}$, $c_{BO} = 1 \cdot 10^{-5} \text{ mol} \cdot l^{-1}$ (excess reagent).

Metal	Z^a	λ_{exc}^b nm	λ_{em}^c nm	I_{rel}^d %	τ^e s
		Excess metal			
Be	4	352	448, 478	100	$1 \cdot 34 \pm 0 \cdot 10$
Zn	30	357	457, 488	155	$0 \cdot 50 \pm 0 \cdot 10$
Ga	31	350	452, 480	39	$0 \cdot 40 \pm 0 \cdot 10$
Cd	48	356	456, 488	30	$0 \cdot 15 \pm 0 \cdot 08$
		Excess reagent			
Be	4	350	448, 480	100	$1 \cdot 00 \pm 0 \cdot 10$
Zn	30	(350)	456, 488	14	$0 \cdot 56 \pm 0 \cdot 10$
Ga^f					
Cd	48	(350)	458, 488	6	$0 \cdot 15 \pm 0 \cdot 10$
H^g	1	342	450, 478		$1 \cdot 09 \pm 0 \cdot 08$
OH^h		346	(475), 494		$0 \cdot 20 \pm 0 \cdot 10$

[a] Atomic number of the metal; [b] the longest-wavelength excitation maximum; [c] the most pronounced vibrational bands; [d] relative intensity, emission percentage of the beryllium complex for measurements in the longest-wavelength emission maximum; [e] lifetime with the confidence interval for 95% probability; [f] emission of the gallium complex not observed; [g] the reagent BO in acidic medium (0·08M-HClO$_4$); [h] the reagent BO in alkaline medium (0·08M-NaOH).

Dependence of the Phosphorescence Intensity of the Reagent BO *and Its Beryllium Complex on the* pH* *Value*

This dependence in nonbuffered medium is shown in Fig. 6. The phosphorescence intensity maximum of the complex lies at pH* 9.2. When buffers (ammonium, phosphate, diethylbarbituric) are employed to adjust the pH of the solutions prior to their freezing, the pH* region in which the phosphorescence intensity of BO is increased shifts to lower values as compared to nonbuffered medium. This might be explained in terms of changes in the rate of the establishing of the equilibrium between the various reagent species in the excited state, which the presence of the buffer affects.

Effect of Potassium Iodide on the Phosphorescence of BO *and Its Beryllium Complex*

We examined this effect as we attempted to raise the phosphorescence intensity by introducing a heavy element in the solvent[15-18]. We found that the introduction of potassium iodide brings about an increase of the phosphorescence intensity not only of the beryllium complex, but also of the reagent itself in alkaline medium,
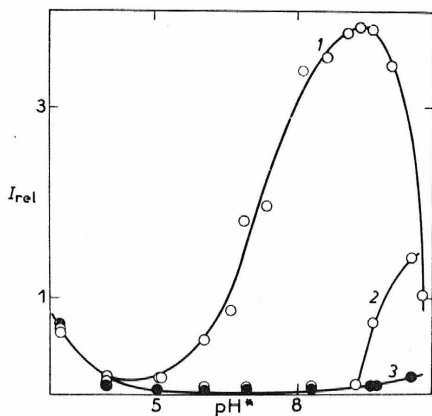

FIG. 6

Dependence of the Phosphorescence Intensity of BO and Its Beryllium Complex on pH* in Solvent Water–Methanol (30% v/v Methanol) at 77 K

λ_{exc} 350 nm, λ_{em} 448 nm (*1, 3*), 490 nm (*2*); *1* beryllium complex, $c_{BO} = 1 . 10^{-5}$ mol l^{-1}, $c_{Be} = 1 . 10^{-6}$ mol l^{-1}; *2, 3* the reagent, $c_{BO} = 1 . 10^{-5}$ mol l^{-1}.
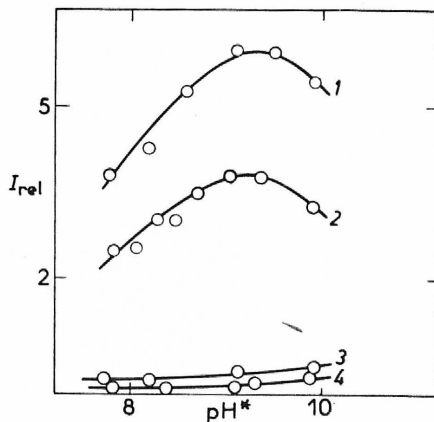
FIG. 7

Dependence of the Phosphorescence Intensity of BO and Its Beryllium Complex on pH* in the Presence of KI in Aqueous-Methanolic Solvent (30% v/v Methanol) at 77 K

λ_{exc} 350 nm, λ_{em} 448 nm, $c_{BO} = 1 . 10^{-5}$ mol l^{-1}; *1, 2* beryllium complex, $c_{BO}/c_{Be} = 10$; *3, 4* the reagent; *1, 3* $c_{KI} = 0.8$ mol . l^{-1}, *2, 4* $c_{KI} = 0$.

approximately in the same ratio (Fig. 7). The phosphorescence lifetime of the complex shortens with increasing concentration of KI (Fig. 8). An opposite effect on the phosphorescence intensity to that of KI was found with NaCl.

Phosphorimetric Determination of Beryllium with BO

Calibration curve. Based on the preliminary results, we chose medium without any addition of a buffer (which increases the value of the blank) and of potassium iodide which − though increasing somewhat the phosphorescence signal − lowers the emission lifetime below the limit of measurable values.

Different volumes of the standard solution of beryllium perchlorate and always 0·50 ml of 10^{-3}M methanolic solution of BO were pipetted in 50 ml volumetric flasks, and the mixtures were brought to the volume with aqueous methanol solutions such that the resulting methanol concentration was 30% (v/v). The pH* of the mixture was adjusted with small additions of 2M- -NaOH to the value of 9·2. After thermostating to 20°C for 10 min, the pH* of the solution was checked. The resulting beryllium concentration made $3 . 10^{-8}$ to $1 . 10^{-6}$ mol l^{-1}. The solution was placed in the stationary cell and the phosphorescence (λ_{exc} 350 nm, λ_{em} 448 nm) was measured immediately after freezing in liquid nitrogen. Three parallel samples with the same beryllium concentration were always prepared and the phosphorescence of each of them was measured three times.

The results were processed statistically by using the least squares method[13] and the equation of the regression straight line was calculated to be

$$I_{rel} = 4\cdot088 . 10^6 \, c_{Be} + 0\cdot031 , \tag{1}$$

where c_{Be} is the molar concentration of beryllium. The standard deviation of the abscissa was $s_a = 9\cdot47 . 10^{-3}$, that of the regression straight line slope was $s_s = 4\cdot92 . 10^4$.
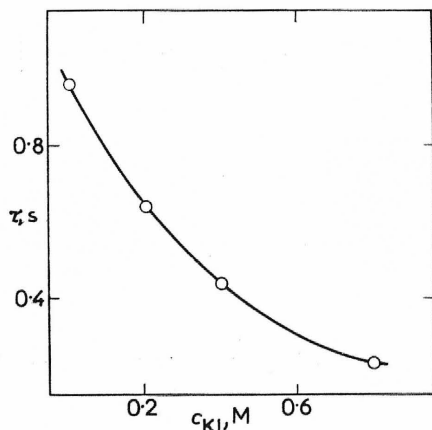

Fig. 8

Dependence of the Phosphorescence Lifetime of the Beryllium Complex of BO in Aqueous–Methanolic Solvent (30% v/v Methanol) at 77 K on the Content of Potassium Iodide

$c_{BO} = 1 . 10^{-5}$ mol l^{-1}, $c_{BO}/c_{Be} = 10$, pH* 9·2; λ_{exc} 350 nm, λ_{em} 448 nm.

The calibration curve was linear in the span of two orders of magnitude, up to 10^{-6} mol . l^{-1}. The upper limit is dictated by the demand that a sufficient excess of the reagent be present, which in turn is limited by the low solubility of BO. The correlation coefficient was 0·999. The T-test evidenced that the magnitude of the signal at $c_{Be} = 0$ was not significantly different from zero. As follows from the F-test[13], the reproducibility of the measurements in the range of low beryllium concentrations $(3 . 10^{-8}$ mol . $l^{-1})$ was constant.

The limit of determination as calculated from the relation $y_d = \bar{y}_0 + 4s_a$ was 0·069. To this corresponds $c_{Be} = 1·02 . 10^{-8}$ mol . l^{-1}, hence approximately 0·1 ppb. The measurement precision with 10 parallel samples of 10^{-7}M beryllium could be expressed by the relative standard deviation of 7·8%.

Effect of Foreign Ions on Phosphorimetric Determination of Beryllium

This effect was examined for $c_{Be} = 1 . 10^{-7}$ mol . l^{-1} and concentration of associate ions 10^{-6} mol . l^{-1} by applying the same procedure as during the calibration measurements. The extent of interference of the associate ions was considered from the Student t-test[13] for three parallel measurements. As follows from the comparison of the calculated values with the critical t_k value, it can be assumed with 95% probability that random errors solely account for the differences between the results for solutions containing beryllium only and those for beryllium solutions containing in addition Al^{3+}, Ca^{2+}, Cd^{2+}, Fe^{3+}, Ga^{3+}, Mg^{2+}, Pb^{2+}, or Zn^{2+} ions.

Determination of Beryllium in Model Samples of Mineral Water

Model water samples were used containing ions in concentrations as follows (mg/1): Na^+ 2000, K^+ 100, Ca^{2+} 150, Mg^{2+} 50, Al^{3+} 0·1, Fe^{3+} 1·3, and SO_4^{2-} 2000. The beryllium concentration was $4 . 10^{-6}$ to $1 . 10^{-5}$ mol . l^{-1}. The composition of the

TABLE III

Results of the Determination of Beryllium in Mineral Water Model Samples

The values found represent averages of three parallel determinations with the confidence intervals for 95% probability.

Be introduced 10^{-6} mol . l^{-1}	Be found 10^{-6} mol . l^{-1}
4·0	4·35 ± 0·95
6·0	6·37 ± 1·18
10·0	9·54 ± 1·13

samples approached that of the mineral water "The Millspring" in Carlsbad, where the content of beryllium has been determined by atomic absorption spectrometry[19].

Working procedure. To 5 ml of the acidified model sample was added 0·5 ml of 10^{-3}M methanolic solution of BO and the whole was diluted to 50 ml with an aqueous solution of methanol such that the resulting solution contained 30% (v/v) methanol. After adjusting the pH* with microadditions of 2M-NaOH to the value of 9·2, the phosphorescence was measured as during the calibration measurements. The results of three parallel measurements are given in Table III. They do not involve a systematic error, the reproducibility of the determination is, however, markedly poorer than that of the AAS determination[19].

Determination of Metal Complexes in Mixture Based on the Difference in Their Phosphorescence Lifetimes

a) *Choice of the speed of rotation of the phosphoroscope.* O'Haver and Winefordner[20] have derived for a cylindrical phosphoroscope a relation for the α_p value representing the ratio of the phosphorescence intensities obtained with the phosphoroscope and during the continuous measurements:

$$\alpha_p = \tau[\exp(-t_D/\tau)][1 - \exp(-t_E/\tau)]^2/\{t_C[1 - \exp(-t_C/\tau)]\}, \qquad (2)$$

where t_D is the period during which neither excitation nor emission recording occurs in the course of one revolution of the phosphoroscope, t_E is the duration of the excitation or emission, t_C is the duration of one complete cycle, hence $t_C = 2(t_D + t_E)$, and τ is the phosphorescence lifetime. For the rotatory phosphoroscope Aminco–
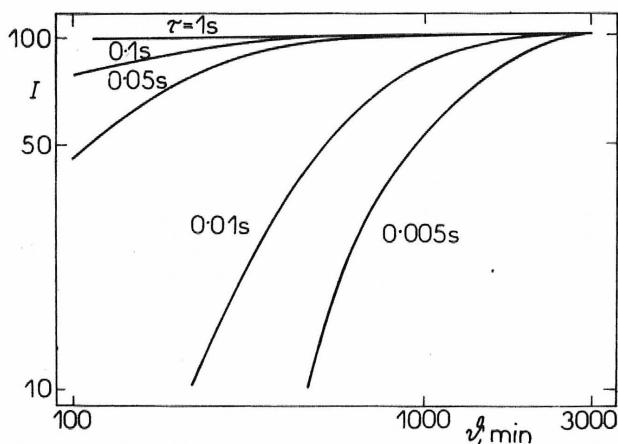

FIG. 9

Dependence of the Relative Intensity of Phosphorescence on the Speed of Rotation of the Phosphoroscope for Different Emission Lifetimes

‒Bowman employed, $t_C = 30/\vartheta$, $t_D = (0.5\pi r - L) \cdot 30/\pi r\vartheta$, and $t_E = 30L/\pi r\vartheta$, where ϑ is the speed of rotation of the phosphoroscope (rpm), r is the radius of the phosphoroscope cylinder (1·18 cm), and L is the arc length of the cut-out section of the phosphoroscope (1·4 cm).

Fig. 9 shows the dependence of the relative extinction of the emission on the speed of rotation of the phosphoroscope for various lifetimes; for lifetimes longer than 1 s the intensity of emission is seen to be virtually independent of variations in the speed. A pronounced decrease of the emission by at least one order of magnitude can be achieved by appropriate choice of the speed of rotation for emission with the lifetime shorter than 0·01 s.

In accordance with this theoretical conclusion, the mutually only slightly different phosphorescence lifetimes of the various BO complexes did not permit to determine beryllium, zinc, and cadmium in a mixture on this principle.

b) *Record of the emission after once-through breaking of the excitation.* Assuming that the emissions of the two constituents A and B of a two-component mixture do not affect each other and that the decrease of the emission intensity is exponential for both of them, it is possible to express the emission intensity I of the mixture in time t as[21]

$$I = I_A \exp\left(-t/\tau_A\right) + I_B \exp\left(-t/\tau_B\right), \qquad (3)$$

where I_A and I_B are the phosphorescence intensities of the respective components before the breaking of the excitation. Assuming for the case $\tau_A > \tau_B$ that $t \gg \tau_B$, we obtain on conversion to the logarithmic form the relation

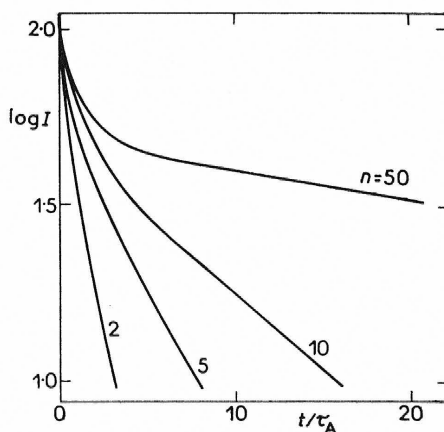$$\log I = \log I_A - \left(t/2.303\tau_A\right). \qquad (4)$$

Fig. 10

Dependence of the Logarithm of the Phosphorescence Intensity of Two-Component Mixture after the Breaking of Excitation on the Value of the Parameter t/τ_A

t Time elapsing after the breaking of the excitation, n ratio of the lifetimes τ_A/τ_B.

Extrapolating the linear part of the semilogarithmic dependence $\log I$ vs time to $t = 0$ we obtain I_A and from this in turn also I_B.

Fig. 10 depicts the dependence of the logarithm of the phosphorescence intensity of a two-component mixture after the breaking of the excitation on the t/τ_A value for various lifetime ratios τ_A/τ_B. If the emission in dependence on time can be recorded rapidly enough, it is possible to solve the analysis of the binary mixture with various accuracy also for low values of the lifetime ratio of the two constituents.

Inasmuch as the equipment employed did not enable sufficiently rapid recording of the drop of the emission intensity after the breaking of the excitation, we were not able to utilize the above method for the determination of beryllium and zinc in a mixture.

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