Summary—Uranium(VI) can be quantitatively precipitated from aqueous solution in the pH range 2·1–6·9 with pyridine-2,6-dicarboxylic acid in the presence of tetraphenylarsonium chloride. This provides a new rapid gravimetric method for uranyl ion as an organic chelate complex of high molecular weight. Sodium, aluminium, copper and nickel as well as nitrate, chloride, sulphate and acetate ions, do not interfere, but iron(III) and thorium(IV) do.

Zusammenfassung—Uran(VI) kann aus wäßriger Lösung bei pH 2,1–6,9 quantitativ mit Pyridin-2,6-dicarbonsäure in Gegenwart von Tetraphenylarsoniumchlorid quantitativ gefällt werden. Dies liefert eine neue rasche Methode zur gravimetrischen Analyse von Uranylionen als organischer Chelatkomplex von hohem Molekulargewicht. Natrium, Aluminium, Kupfer und Nickel sowie Nitrat, Chlorid, Sulfat und Acetat stören nicht, dagegen Eisen(III) und Thorium-(IV).

Résumé—On peut précipiter quantitativement l'uranium (VI) d'une solution aqueuse dans le domaine de pH 2,1–6,9 avec l'acide pyridine 2,6-dicarboxylique en la présence de chlorure de tétraphénylarsonium. Ceci fournit une nouvelle méthode rapide pour l'analyse gravimétrique de l'ion uranyle sous forme d'un complexe chélaté organique de haut poids moléculaire. Les sodium, aluminium, cuivre et nickel, ainsi que les ions nitrate, chlorure, sulfate et acétate n'interfèrent pas, mais le fer (III) et le thorium (IV) gênent.

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QUANTITATIVE MEASUREMENT OF MIXTURES OF HALLUCINOGENS BY FLUOROMETRY AND PHOSPHORIMETRY*

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Currently, in forensic chemistry, most quantitative drug analyses are performed on as pure a sample as possible. This usually entails at least one chemical separation because most "street" drugs are mixtures. They usually contain one or two drugs and an inert matrix in the form of a tablet. There are many procedures to separate a drug from its matrix,[1] but fewer to separate a mixture of drugs from each other without significant losses. Therefore, it is of interest to look into methods of quantitative analysis not requiring separation of mixtures.

Lysergic acid diethylamide (LSD) has become one of the most widely used illicit drugs. It has also been mixed with many other drugs, either to enhance the physiological effect of the LSD or in order to be sold as some other drug. Many samples of "street" drugs which are examined contain mixtures of LSD and some other hallucinogen.

Fluorometry and phosphorimetry[2,3] offer the advantages of sensitivity, simplicity, accuracy, and relatively inexpensive equipment for the analysis of binary mixtures of LSD and some other hallucinogen. Recent improvements in phosphorimetry[4,5] allow its application to the measurements of analytes in aqueous, snowed matrices, *e.g.*, a predominately aqueous solvent (methanol/water 10/90 v/v). This has enabled workers to use the same solvent for both fluorometric and phosphorimetric measurements.

The present study was carried out to develop methods for the analysis of mixtures containing LSD and other hallucinogens, which are rapid, sensitive, and do not require physical separation (chromatographic) of components.

EXPERIMENTAL

Apparatus

All fluorescence and phosphorescence signals were measured with an Aminco-Bowman spectrophotofluorometer (American Instrument Company, Silver Spring, Maryland) with both fluorescence and phosphorescence cell assemblies and with an RCA 1P21 multiplier phototube powered by a model 244 high-voltage supply (Keithley Instruments Inc., Cleveland, Ohio). A 150-W Hanovia xenon arc lamp was powered by a Harrison model 6268A DC power supply (Hewlett-Packard, Palo Alto, California). The lamp was started by a circuit described by Zweidinger.[6] Signals were measured with a low-noise nanoammeter described previously.[7]

For fluorescence measurements at room temperature, a 1 × 1 cm quartz sample cell was used. Phosphorescence measurements were made at 77° K, using a rotating capillary tube (approximately 4·5 mm diameter and 1·0 mm bore) made from T21 Suprasil quartz capillary tubing (Amersil Inc., Hillside, New Jersey); this cell contained approximately 20 μl and was used under the conditions described in the work by Lukasiewicz, Rozynes, Sanders and Winefordner.[4]

Spectra were checked against available literature data.[8,9] An *X–Y* recorder (No. 1620–827, American Instruments Company, Silver Spring, Maryland) was used to record all spectra.

Reagents

The following hallucinogens were studied: lysergic acid diethylamide (LSD), 2-5-dimethoxy-4-methylamphetamine (STP or DOM), psilocybin (from NIMH, Center for Studies of Narcotics and Drug Abuse, Rockville, Maryland), mescaline hydrochloride (from Sigma Chemical Company, St. Louis, Missouri), and phencyclidine hydrochloride (from Philips Roxane, Inc., St. Joseph, Missouri). All drugs were used as received, *i.e.*, without purification.

Methanol (Matheson, Coleman and Bell, Manufacturing Chemists, Norwood, Ohio, "Spectroquality" grade) and demineralized water were used as solvents.

Sodium iodide (Fisher Scientific Company, Fair Lawn, New Jersey, "Certified reagent" grade) was used for the heavy-ion effect in phosphorimetry.

Procedures

Stock solutions of the hallucinogenic drugs were prepared in a darkened room at concentrations of 10^{-2}–$10^{-3}M$ in methanol/water (10/90 v/v). For phosphorescence, drug mixtures containing LSD were also prepared in 0·75*M* sodium iodide. The stock solutions were prepared just before use because LSD was observed to decompose rapidly even when stored in darkness and at 5°. Because heavy-ion effect studies on mescaline hydrochloride and phencyclidine hydrochloride had not previously been performed, two stock solutions of each were prepared, one in methanol/water (10/90 v/v) and 0·75*M* in sodium iodide, the other in methanol/water (10/90) v/v.

The stock solutions were mixed and successively diluted to $10^{-9}M$ for preparation of the analytical curves. Each mixture was run at three different concentration ratios of LSD to the other hallucinogens: (*a*) 100:1; (*b*)1:1; (*c*) 1:100. The only exceptions were mixtures containing mescaline and phencyclidine, which were run at only two different concentrations because these species are only weakly fluorescent and phosphorescent.

The slit arrangement for fluorescence measurements was 3,2,2,3 (17 and 11 nm spectral half-band passes). A slit arrangement of 3,3,3,3 (17 and 17 nm spectral half-band passes) was used for phosphorescence measurements. In Table 1, the excitation and emission wavelengths at which measurements were made are given.

RESULTS AND DISCUSSION

Fluorometric and phosphorimetric analytical curves (luminescence signal *vs.* analyte concentration) for mixtures containing LSD and other hallucinogens at different concentrations were measured; the results are given in Table 2. All the hallucinogens except mescaline and phencyclidine (PCP) have fluorescence signals (and signal-to-noise ratios) high enough to be analytically useful. The phosphorescence signal of PCP is high enough to be analytically useful although the phosphorescence signal level of mescaline is too low.

Table 1. Excitation and emission wavelengths* (nm) used

Compound	Fluorescence†		Phosphorescence§	
	Excitation	Emission	Excitation	Emission
LSD	330	430	320	515
STP (DOM)	295	340	295	408
Psilocybin	283	352	—‡	—‡
Mescaline	—¶	—¶	281	418
Phencyclidine	—¶	—¶	265	385

* Peak wavelength error ±3 nm.
† In methanol/water (10/90 v/v).
§ In 0·75*M* NaI, methanol/water (10/90 v/v).
‡ Psilocybin was not measured by phosphorimetry.
¶ Mesacline and phencyclidine were not measured by fluorometry.

Table 2. Fluorometric analytical chacteristics of mixtures of hallucinogens

Hallucinogen	Fluorescence*				
	Slope of anal. curve§	Factor for concentration range of near linearity†		Limit of detection, *ng/ml*‡	
		Literature¶	This work	Literature¶	This work
LSD	0.96,0.94,1.09,1.28	10^3	10^4	6·5	3.6
STP	0·90	10^3	10^4	10	5
Psilocybin	0·89	10^3	10^3	23	23
Phencyclidine (PCP)	—	—	—	$2{\cdot}5 \times 10^4$¶	—
		Phosphorescence≠			
LSD	0·67,0·80,0·76,0·73	10^4	10^3	8	530
STP	0·99	10^3	10^4	10	33
Psilocybin	—	10^3	—	14	—
Phencyclidine (PCP)	0·98	—	10^2	—	320

* In neutral methanol/water (10/90 v/v) at 298° K.

§ The slopes of the analytical curves for LSD are for mixtures of LSD with STP, psilocybin, PCP, and mescaline, respectively.

† "Near linearity" means region over which analytical curve (log–log plot) deviates less than 1% from linearity. The absolute concentration range extends from the limit of detection to an upper concentration determined by the range factor times the limit of detection.

‡ Limit of detection is defined as the concentration giving a fluorescence of phosphorescence signal (located on the linear part of the analytical curve) that is twice the background noise.

¶ Reference 8.

≠ In 0·75*M* NaI solution in methanol/water (10/90 v/v) at 77° K.

Results for mescaline are therefore not reported. It was not possible to determine LSD and psilocybin by phosphorimetry. The excitation and emission peaks of the two were so close to each other that there would be severe spectral interference.

Limits of detection (defined as the concentration giving a fluorescence or phosphorescence signal twice the background noise) were approximately the same as reported by Aaron, Sanders and Winefordner[9] except for LSD by phosphorimetry (see Table 2). The limit of detection of LSD in this work was approximately 66 times that obtained by Aaron, Sanders and Winefordner.[9] This was a result of a much higher background, which for low concentrations of LSD effectively hid the phosphorescence signal in the noise. However, the high limit of detection for LSD does not present a problem because the normal dose in "street" tablets of LSD is 2–400 μg.[1] The phosphorimetric limit of detection for PCP was found to be about 250 ng/ml. Sodium iodide, which was added to enhance the signal intensity of LSD by the heavy-ion effect, was also found to enhance the phosphorescence signals of PCP and mescaline. The phosphorescence signal level for PCP was increased by a factor of four and for mescaline by a factor of ten. The presence of LSD in a mixture also containing mescaline of PCP prevented reliable measurement of fluorometric signals from either mescaline or PCP, owing to the high background noise level. However, in phosphorimetry, if sodium iodide is present, it would be possible to determine low concentrations of phencyclidine (but not mescaline).

There were no severe fluorescence interferences between the two compounds in the mixtures (see Table 2) *i.e.*, neither component affected the analytical curve for the other. However, in phosphorimetry, there were several cases of rather severe interference and analytical curve slopes appreciably below unity were obtained. It should be stressed, however, that in these cases the slopes were the same whether the ratio of LSD concentration to the other hallucinogen concentration was 100, 1, or 0·01, The reason for the departure from linearity is not known to the authors. However, by proper calibration procedures, such non-linear curves could be used for analytical purposes. The linear dynamic ranges of the analytical curves (see Table 2) compare well with those reported by Aaron, Sanders and Winefordner.[9] The standard deviation of the slopes for all analytical curves was 5%.

Because of the low limits of detection, lack of severe spectral interference, simplicity of procedure, and versatility of application, a combined fluorometric and phosphorimetric method seems appropriate for the quantitative analysis of hallucinogenic drugs in mixtures. It is sensitive, rapid, and does not require separation of the mixture. An examination of the spectra of the mixture can also give information on the identity of the hallucinogens.

The use of fluorometric and phosphorimetric methods for the analysis of hallucinogenic mixtures should be extended to other drug mixtures. A possible example would be quantitative analysis of a morphine–strychnine mixture by phosphorimetry.[10]

This study was done under ideal conditions in which the drugs were pure and did not have to be extracted from a real sample. A study should be performed on regular "street" drugs to determine if the extraction of the hallucinogens will be satisfactory and which solvents are compatible with the background requirements of fluorescence and phosphorescence. A useful further extension of this work would be the analysis of hallucinogenic mixtures by time-resolved phosphorimetry.[11,12] Such studies are currently in progress.

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Summary—Room temperature fluorometric and low-temperature phosphorimetric analytical curves of hallucinogens in methanol/water solution have been prepared to demonstrate the absence of interference in common binary mixtures of hallucinogenic drugs. Limits of detection and linear dynamic ranges have been determined for drugs in mixtures. Mixtures containing LSD and another hallucinogen such as STP (DOM), psilocybin, mescaline, and phencyclidine have been studied. Detection limits are low, and analytical curves are linear over wide concentration ranges.

Zusammenfassung—Es wurden bei Zimmertemperatur fluorimetrische und bei tiefer Temperatur phosphorimetrische analytische Kurven von Halluzinogenen in Methanol-Wasser-Lösung aufgenommen, um die Abwesenheit von Störungen in gängigen binären Gemischen halluzinogener Drogen zu zeigen. Für Drogen in Gemischen wurden Nachweisgrenzen und lineare dynamische Bereiche ermittelt. Gemische, die LSD und ein anderes Halluzinogen wie STP (DOM), Psilocybin, Mescalin und Phencyclidin (1-(1-Phenylcyclohexyl)-piperidin) enthielten, wurden untersucht. Die Nachweisgrenzen sind niedrig und die analytischen Kurven sind in weiten Konzentrationsbereichen linear.

Résumé—On a préparé des courbes analytiques fluorimétriques à température ambiante et phosphorimétriques à basse température d'hallucinogènes en solution méthanol/eau pour démontrer l'absence d'interférence dans des mélanges binaires communs de drogues hallucinogènes. On a déterminé les limites de détection et les domaines dynamiques linéaires pour des drogues en mélange. On a étudié des mélanges contenant du LSD et un autre hallucinogène tel que STP (DOM), psilocybine, mescaline et phencyclidine. Les limites de détection sont basses, et les courbes analytiques sont linéaires dans de larges domaines de concentrations.