Mass Spectral Studies of Ultraviolet Irradiated and Non-Irradiated Lysergic Acid Diethylamide Extracts from Illicit Preparations

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This report describes the analytical scheme used for the unequivocal confirmation of lysergic acid diethylamide (LSD) in forensic samples. The scheme includes the extraction procedure and subsequent spectral findings. Analytical techniques for LSD utilizing ultraviolet spectrometry (*1*), thin-layer chromatography (*2, 3*), fluorometry (*4*), gas chromatography (*5–7*), infrared (*8*), and mass spectrometry (*9–11*) have been reported. In this study, we report the ultraviolet spectral analysis including irradiation, with subsequent electron impact mass spectral analysis of both the non-irradiated and the irradiated samples. Samples containing as little as 15 micrograms of LSD have been successfully analyzed and confirmed.

EXPERIMENTAL

The mass spectra used in this study were obtained with a DuPont Instrument Type 21-491 double focusing mass spectrometer. The ionizing potential was 78 eV; the ionizing current was 250–300 μA; the accelerating potential was 1100 volts coupled with an electric sector voltage of 100 volts. The sample in the glass capillary was introduced into the mass spectrometer with a direct insertion probe. The temperature of the source was 175 °C. The temperature of the probe was adjusted from 180 to 195 °C. The mass spectra were recorded on a CEC 5-124 A recording oscillograph at a chart speed of 1 inch per second. A mass scan rate of 1000 seconds per decade in the linear scan mode was employed to produce the spectra. Peak assignment was made by using the DuPont digital mass marker which had been calibrated over the perfluorokerosene mass range.

The ultraviolet spectra were obtained with a Coleman Model EPS-3T Hitachi Ratio Recording Spectrophotometer. A scan speed of 50 nm/minute through the range of 210–360 nm with an automatic slit width of 0.005–2 mm was used. The amplifier sensitivity and photomultiplier sensitivity were set at 1 and 2, respectively.

A Helena Titan UV Lamp equipped with a mercury vapor lamp source and a 340-nm cut-off filter was used as the irradiation source.

Analytical Reagent, Mallinckrodt 1,2-dichloroethane and "Baker Analyzed" Reagent, Spectrophotometric quality chloroform were used.

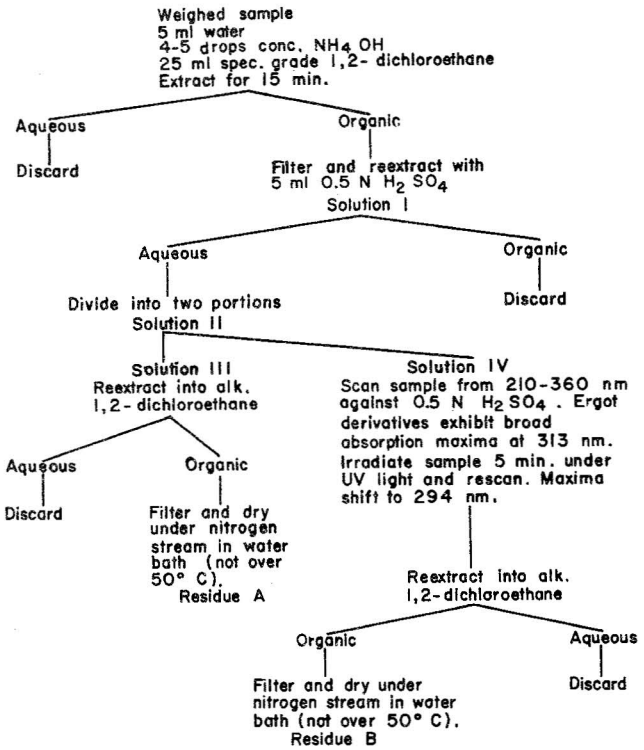
RESULTS AND DISCUSSION

An efficient and relatively simple extraction procedure is one of the most significant requirements in the analysis of LSD. Because of the numerous forms, sizes excipients, and dyes in illicit LSD preparations, the development of a single standardized extraction sequence is highly improbable. Martin and Alexander (*12*) and Sperling (*13*) describe column chromatographic techniques in the extraction and isolation of LSD from illicit preparations. We have found that acid–base partitioning with 1,2-dichloroethane as the organic phase best satisfies our extraction, isolation, and purification requirements. The 1,2-dichloroethane was superior to many solvents including other halogenated hydrocarbons and mixed alcohol systems. Greater than 90% recovery of LSD and the removal of highly colored excipients exhibiting ultraviolet spectral interferences were observed with 1,2-dichloroethane. Over 1000 samples have been extracted and analyzed, and no spectral interferences have been observed.

In addition to the different forms of LSD preparations, differences in the chemical composition of the ergot content are often encountered. It is general experience that many samples submitted for analysis contain small amounts of iso-LSD (a stereoisomer of the more common *N,N*-diethyl-*d*-lysergamide) and LSD degradation products in addition to the parent LSD. In many cases, the separation of LSD from iso-LSD is not necessary. The Controlled Substances Act of 1970 or, more appropriately, the Comprehensive Drug Abuse Prevention and Control Act of 1970 places lysergic acid diethylamide and all its isomers, including optical, position, and geometric, in the controlled or regulated category of Schedule 1. However, in certain cases where the requirement for separation does exist, infrared spectrometric (*8*) and paper chromatographic (*14*) procedures are available. The analytical scheme presented here describes the extraction, isolation, and confirmation of LSD from illicit preparations where LSD refers to all stereoisomeric species.

Figure 1 outlines the extraction and isolation procedure. In this sequence, Solution II (5.0 ml) containing the LSD as the amine acid sulfate salt in 0.5*N* H_2SO_4 is divided in half. The LSD in one half, Solution III, is made just basic with NH_4OH, re-extracted into 1,2-dichloroethane and recovered as Residue A. The second half, Solution IV, is scanned from 210–360 nm with 0.5*N* H_2SO_4 as reference. A broad absorption band with the maximum at approximately 313 nm is observed (Figure 2). After scanning, the solution is irradiated with long wave ultraviolet light for five minutes and re-scanned from 210–360 nm. A shift of the broad absorption maximum from 313 nm to approximately 294 nm is observed. The reaction product is re-extracted and recovered as Residue B.

The ultraviolet spectral phenomenon of LSD as well as other alkaloids of the ergot family was first explicitly described by Stoll and Schlientz (*1*). They attributed the shift of the absorption maximum to a photochemically induced hydration reaction at the $C_{9,10}$ double bond of the parent ergot alkaloid (Figure 3). This phenomenon has since been utilized by many forensic laboratories in the analysis of illicit street preparations of LSD. In addition to UV analyses, Anderson (*2*) identified LSD by the irradiation degradation pattern using thin layer chromatography. It has been our courtroom experience, however, that ultraviolet spectral analyses with thin layer chromatography is subject to legitimate criticism on the basis of specificity. In order to unequivocally confirm the presence of LSD and to



The residues (A and B) are dissolved in 5 drops of chloroform and transferred to glass capillaries and evaporated to dryness under reduced pressure. The capillaries are stored for mass spectral analyses.

Figure 1. Extraction and isolation of LSD from illicit preparations

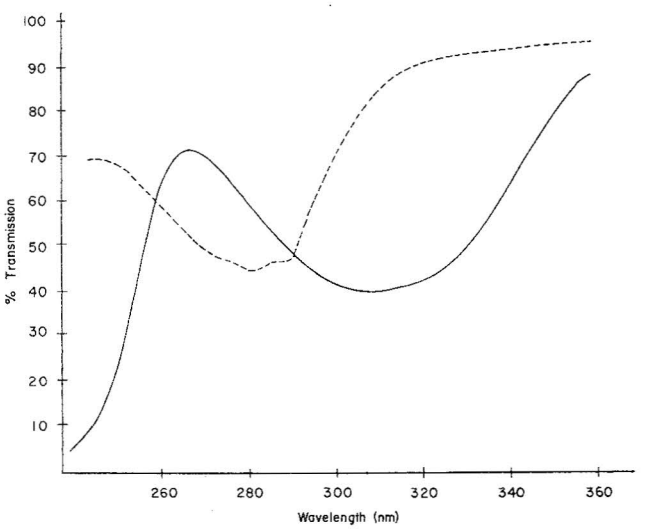


Figure 2. Ultraviolet spectra of LSD (solid curve) and irradiated LSD (dotted curve)

eliminate other possible non-controlled ergot alkaloids, we have found that electron impact mass spectral analyses of the non-irradiated extract (Residue A), *i.e.,* parent LSD, as well as the irradiated product (Residue B), *i.e.,* hydrated LSD, provides the specificity for forensic purposes.

In an endeavor to obtain the most characteristic electron impact mass spectrum of LSD, *i.e.,* molecular ion as base peak at m/e = 323, the intensities of the observed ions at different probe temperatures were measured. The sum of the intensities of all peaks greater than 5 mm, in the most sensitive galvanometer tracing, was determined, and the percentage of each m/e peak with respect to the sum was calculated. The m/e peaks at the lower temperatures are

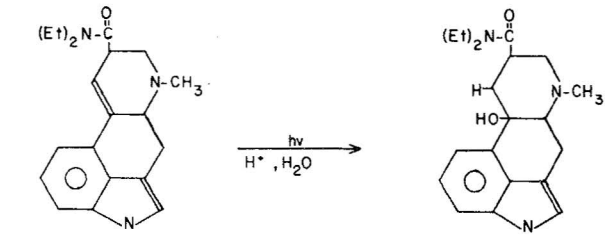


Figure 3. Photochemical hydration of LSD

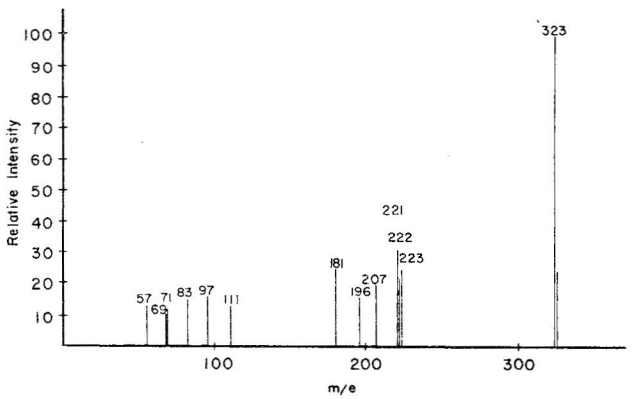


Figure 4. Mass spectrum of LSD extract (residue A)

Table I. Percent Ion Intensities *vs.* Probe Temperature for LSD m/e Peaks

m/e	75–85 °C	110–120 °C	140–150 °C	180–195 °C	210–220 °C
323	...	...	0.82	9.94	1.92
223	1.74	0.63	0.24	1.89	0.91
222	...	...	0.24	2.04	1.01
221	0.68	...	0.33	3.58	1.55
207	0.44	...	0.22	2.19	1.08
196	0.56	...	0.72	1.59	0.72
181	0.44	...	0.41	2.54	1.08
111	2.06	2.01	1.05	1.21	0.70
97	2.49	2.89	1.67	1.64	1.03
83	2.37	2.58	1.65	1.69	1.06
71	3.49	4.15	1.89	1.84	2.03
69	2.06	2.77	1.26	1.49	1.04
57	4.36	7.92	6.24	2.29	1.62

mostly due to impurities and not from LSD fragmentation. Table I summarizes the findings for only the characteristic LSD m/e peaks. These findings suggest that the optimum probe temperature for observing the most intense molecular ion peak for LSD at m/e = 323 is between 180–195 °C. Figure 4 depicts the observed mass spectrum of the LSD extract. The molecular ion, m/e = 323, also is the base peak and is assigned a relative intensity of 100. Peaks with relative intensities less than 10% of the base peak are not presented in this portrayal.

We have found reasonable agreement between the spectrum recorded at a probe temperature of 180–195 °C and previously reported spectra. Table II describes this comparison. The differences can be attributed to different instrument parameters resulting in slightly different fragmentation pathways. The fragmentation pathways leading to these m/e peaks have previously been reported (*9, 11*).

The analytical sequence for the confirmation of LSD in illicit preparations is completed with identification of the

Table II. Comparison of LSD Mass Spectra

LSD, 180–195°C	LSD[a]	LSD[b]
323 (100%)	323 (100%)	323
...	...	251
...	...	235
223 (26%)	223 (28%)	...
222 (24%)	222 (39%)	...
221 (32%)	221 (70%)	221
207 (22%)	207 (40%)	207
196 (16%)	196 (20%)	196
181 (26%)	181 (38%)	181
...	167 (15%)	167
...	154 (12%)	154
...	...	139
...	...	127
111 (12%)	...	111
...	...	100
97 (15%)	...	...
83 (15%)	...	83
71 (12%)	...	...
69 (10%)	...	...
...	...	62
...	...	60
57 (14%)	...	...
...	...	42

[a] From the data of Nigam and Holmes (*9*). Relative intensities determined from published spectrum. Only m/e peaks greater than 140 were presented. [b] From the data of Finkle, Foltz, and Taylor (*15*). Relative intensity data not available.

acid catalyzed photochemical hydration product. Mass spectral analyses confirm the hypothesized hydration reaction of Stoll and Schlientz. Observation of a molecular ion at m/e = 341 (42.4%) confirms the addition of H_2O (mol wt = 18) to LSD (mol wt = 323). Figure 5 depicts the mass spectrum of the irradiated product. The base peak is observed at m/e = 323. Alcohols are known to exhibit base peaks of mass M − 18 arising from loss of the neutral molecule H_2O (*16*). The loss of H_2O can occur both before or after ionization. The loss before ionization occurs through thermal modes. It is apparent that the peak at m/e = 323 arises from the hydrated product and not from residual LSD in the reaction mixture. The ultraviolet spectrum of

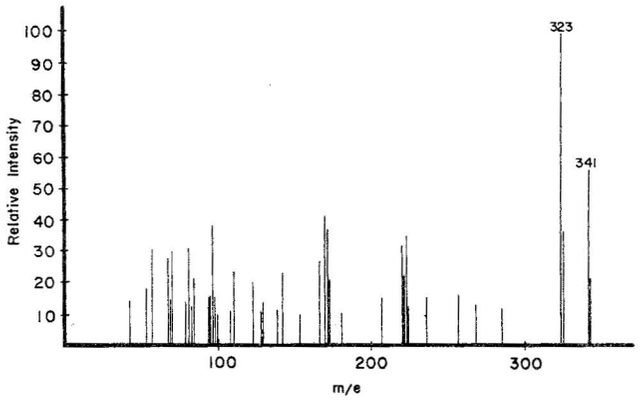


Figure 5. Mass spectrum of irradiated LSD extract (residue B)

the irradiated product shows no appreciable absorption at 313 nm, the characteristic absorption maximum for LSD, hence indicating that the hydration reaction was complete.

These findings, *i.e.*, ultraviolet and mass spectral analyses of both LSD and the acid catalyzed photochemically induced hydration product of LSD, provide unequivocal confirmation of the presence of lysergic acid diethylamide in illicit preparations.

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Microdetermination of Nitrogen by Means of a Thermal Conductivity Detector. Application to the Determination of Nitrogen in Tin–Nitrogen and Germanium–Nitrogen Compounds

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Research in our laboratory relating to metal–nitrogen compounds prepared in the form of thin films by reactive cathodic sputtering (*1*) has involved the determination of nitrogen in such compounds. A comparative study carried out by Healy and Parker (*2*) showed that conventional methods of nitrogen determination on metallic nitrides (Kjeldahl method, alkaline fusion...) are only efficient when this element is at oxidation state −3. Surveys (*3–6*) have established, however, that the hydrolysis of some nitrides will produce ammonia, hydrazine, and even molecular nitrogen, suggesting that nitrogen, in these compounds, is not entirely at its oxidation state −3. The Dumas method