TECHNICAL NOTE

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GC Quantitative Determination of Illicit LSD

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ABSTRACT: Several methods are used for the determination of LSD in forensic science casework samples. One of these involving a shift in UV absorption maximum is considered too nonspecific to provide unequivocal confirmation of the presence of LSD. Currently, HPLC methods using fluorescence detectors are recommended for quantification and capillary GC/MS is considered a good technique for the qualitative identification of the drug. In this work we demonstrate the possibility of using capillary GC for the quantitative determination of LSD since this method is equally sensitive but surely more flexible and rapid than the HPLC ones.

KEYWORDS: forensic science, chromatographic analysis, LSD, illicit drugs

One of the most important issues in which we are involved, is the search for a suitable and rapid method for quantitative determination of LSD. Italian legislation, with respect to the control of drugs of abuse, is principally governed by the n.685/1975 Law and by the n.162/1990 Law. These laws report the criteria for the quantitative determination of habitual consumption of drugs of abuse during 24 hours. This concept is called "medium daily dose." In particular there are six tables entitled "Determination of the maximum quantitative limit of drug for the medium daily dose of psychotropic and stupefactive substances." In Table 1 we can find lysergide (LSD) with the indication of 50 μg as medium daily dose.

The high potency of LSD means that illicit preparations contain very small amounts of the drug. Lysergide is rarely encountered in the form of a powdered drug. In fact, the most common forms of presentation are small tablets called "microdots" or little paper sheets called "blotters." Typically, each of these preparations may contain about 50 μg of the drug. A "blotter" may be a simple piece of colored paper or a multi-layered one consisting of a plastic base, a sheet of absorbent paper impregnated with lysergide and a top paper bearing a design (see Fig. 1). There have been some cases in which LSD has been found in postage stamps or small drawings.

"Microdots" are small tablets, sometimes colored, of varying shapes and containing

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TABLE 1—*Substances contained in Table I of n.162/1990 Law with the respective "medium daily dose" expressed in grams, milligrams (*) or micrograms (**).*

Acetildiidrocodeina	0.10	Ossicodone	0.20
Acetorfina	2.5 (*)	Ossimorfone	0.04
Alfacetilmetadolo	0.08	Papavero, paglia	5.0
Alfaprodina	1.0	Petidina	0.20
Alfentanil	0.03	Piminodina	0.20
Anileridina	0.20	Piritramide	0.08
Benzilmorfina	0.02	Propiram	0.15
Benzitramide	0.01	Racemorfano	0.15
Chetobemidone	0.01	Sufentanil	0.7 (*)
Codeina	0.20	Tebacone	5.0 (*)
Destromoramide	0.02	Tebaina	0.05
Diacetilmorfina (Eroina)	0.10	Tilidina	0.40
Difenossilato	0.04	Trimeperidina	0.20
Difenossina	0.06	Cocaina cloridrato	0.15
Diidrocodeina	0.30	Cocaina, base libera (crack)	0.02
Dipipanone	0.80	Amfetamina	0.05
Drotebanolo	0.016	Catina	0.06
Etilmorfina	0.15	Dexamfetamina	0.03
Fenadoxone	0.05	Fenmetrazina	0.08
Fenazocina	0.012	MDA	0.05
Fenoperidina	5.0 (*)	MDMA	0.05
Fentanil	0.5 (*)	Metamfetamina	0.025
Folcodina	0.06	Metilfenidato	0.06
Idrocodone	0.06	DET	0.07
Idromorfone	0.015	Dietilamide dell'acido 1-metillisergico	50 (*)
Idrossipetidina	0.010	DMT	0.06
Levorfanolo	0.010	Lisergide (LSD)	50 (**)
Metadone	0.05	LSD-Acetil-dietilamide	50 (**)
Morfina	0.20	LSD-Monoetilamide	0.2 (*)
Nicocodeina	0.05	Mescalina	0.5
Nicomorfina	0.05	Psilocibina	0.01
Norpipanone	0.02	Psilocina	0.01
Oppio	1.0	Delta-9-THC	0.05
Oppio, alcaloidi totali	0.30	Fenciclidina	0.06

a dose similar in quantity to that of blotters [*1*]. Because of the type of presentations and the very low dosage, the analysis of lysergide is difficult and needs very sensitive methods. In this field, the techniques of HPLC and GC are complementary. In fact HPLC, using ODS-silica columns coupled with fluorescence detector, is recommended for quantification [*2–4*]. On the other hand, capillary GC using fused silica bonded phase columns is said to be the best technique for the identification of LSD and other ergot alkaloids [*5*]. This is principally because most ergot alkaloids are thermally unstable or photo-labile and so packed column gas chromatography has not been very successful. The introduction of modern capillary column gas chromatography has surely been an important step forward because of the inertness of the system and the possibility of obtaining a large number of theoretical plates quickly in a short column. Another important factor involved in the successful use of this technique in the analysis of such labile compounds by GC is the use of a very inert fused silica injection port liner [*6*].

In this work we demonstrate the possibility of using capillary GC for quantitative determination of LSD, this method being equally sensitive but surely more flexible and rapid than the HPLC ones. In fact, we successfully applied this method for quantification of LSD to four illicit street samples.

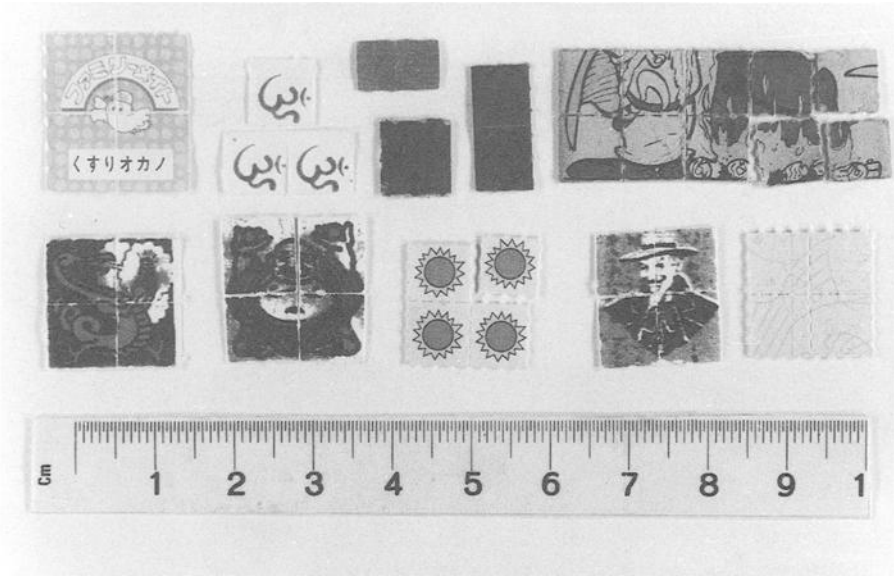

FIG. 1—*Typical lysergide paper presentation ("blotters").*

Experimental Procedures

Materials

All the chemicals (methanol, methyl-terbutyl-ether, distilled water, ammonia) were RPE grade from Carlo Erba Reagenti and Lychrosolv grade from Merck. The LSD used for preparing the standard solution was obtained from Sigma. Alkane Triacontane was from Merck.

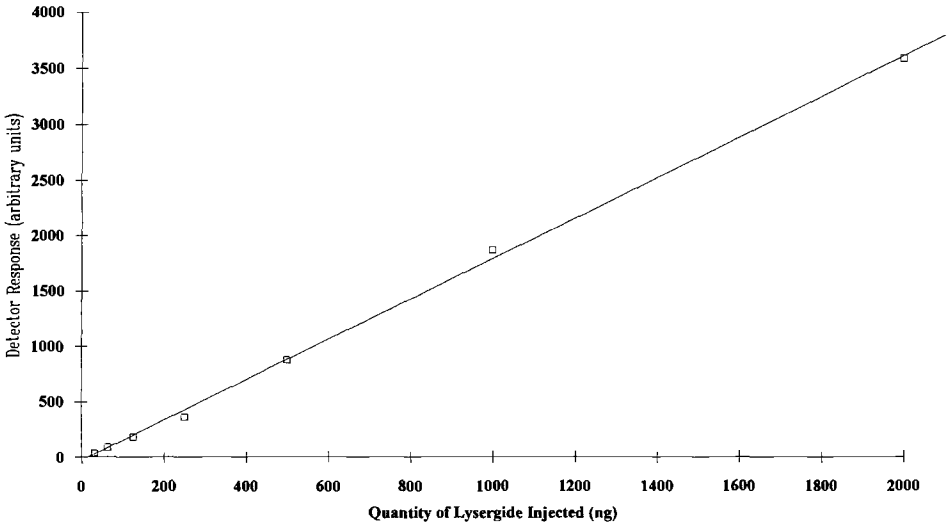

FIG. 2—*Linearity of flame ionization detector with respect to lysergide.*

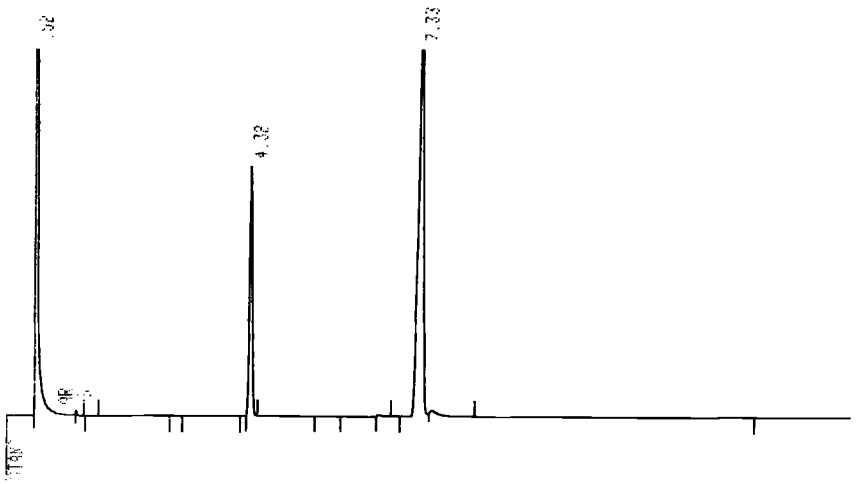

FIG. 3—*Chromatogram of LSD street sample.*

Capillary Gas Chromatography

Chromatography was performed with a Hewlett Packard Model 5890 gas chromatograph with capillary injector in the split mode at a split ratio of 20:1. An important specification is the use of a packed, tapered, deactivated liner from HP having the following configuration: 4 mm id, nominal volume 900 μL, borosilicate glass (deactivated), silanized glass wool plug (deactivated). The packing using silica Kieselgel 60 from Merck may be self-made. The oven was operated isothermally at 275°C with an injector temperature of 280°C and a detector temperature of 280°C.

Helium was used as the carrier gas at a flow rate of 105 mL per min. The detector was a flame ionization detector (FID). The column was a 15 m fused silica capillary column with crosslinked methyl silicone as stationary phase, 0.20 mm inner diameter (ID) with a film thickness of 0.33 microns (Hewlett-Packard, U.S.A.). One microliter samples of LSD in chloroform, at different specified concentrations, were injected into the column to obtain the calibration curve. The same quantities of solution were injected to run the analysis of street samples. In order to obtain maximum reproducibility, the instrument was connected with a HP 7673 A Automatic Injector and Sampler.

Extraction of Illicit LSD Samples

Extracts for analysis by capillary GC were obtained from 4 types of paper squares ("blotters") encountered as casework. We applied the method proposed by Japp et al.: the paper squares have been cut into small pieces and then 500 microliters of methanol/water (50:50 v/v) were added and the sample vortex mixed for 30 s [*5*]. Concentrated ammonia (about two drops) and 1 ml of methyl-tert-butyl ether were then added and the mixture placed in an ultrasonic bath for 20 min. in the dark. The ether layer was removed and evaporated to dryness under a stream of nitrogen gas and then added with a known volume of chloroform containing triacontane as internal standard at 0.5 mg/ml concentration. A 1 microliter sample of this fraction was analyzed by capillary GC.

Results and Discussion

The separation between LSD and lysergic acid methylpropylamide (LAMPA) by capillary gas chromatography has been demonstrated in several publications [*6,7*]. Using a

methyl silicone phase, separations have been achieved under many instrumental conditions (both isothermal or temperature programmed) and using either split or on-column injection. In this way we eliminated the possibility of an interference of LAMPA with the quantitative determination of LSD. We prepared seven different solutions of LSD with a concentration of 2 - 1 - 0.5 - 0.25 - 0.125 - 0.0625 - 0.03125 mg/mL and injected 1 μL of these solutions in order to obtain a calibration curve (see Fig. 2).

We confirmed the linearity of the detector over the range of lysergide concentrations encountered in illicit preparations.

The regression line was: $y = 1842x - 38$.

The percentile value for the chi-square distribution was: 95.

Eleven illicit samples ("blotters") known to contain lysergide were analyzed. We obtained a quantity of LSD that ranged from a minimum of 35 μg to a maximum of 77 μg for each blotter.

In order to minimize the instrumental error in the LSD peaks' integration during quantitative analysis we introduced an internal standard into the solutions obtained from these materials. Hydrocarbon, triacontane, was chosen with a concentration of 0.5 mg/mL. In this way we could quantify LSD by comparing the chromatogram of the street sample having triacontane added with that of LSD at known concentration containing the same internal standard at the same concentration. This comparison was made by using the peak areas of the previous two substances.

Another important factor involved in using triacontane as an internal standard can be found in the chemical inertness of this compound. It can allow us to verify the eventual degradation of standard solutions containing LSD at known concentrations previously prepared and used for analysis.

In the end, although the HPLC coupled with fluorimetry represents a very good method to quantify LSD especially for its sensitivity [*1*], capillary GC/FID can be easily used in the quantitative analysis of the drug, this method being equally sensitive (detection limit of about 10 nanograms) but surely more flexible and rapid than the HPLC ones. In addition this method is to be considered reliable because of the strong linear relationship between LSD and known concentrations. It can also allow us to carry out a complete quantitative analysis in less than ten minutes. See Fig. 3.

Acknowledgment

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