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On-line identification of 3,4-methylenedioxymethamphetamine in human urine by non-aqueous capillary electrophoresis–fluorescence spectroscopy at 77 K

Yu-Lin Chung[a], Ju-Tsung Liu[b], Cheng-Huang Lin[a,*]

[a]*Department of Chemistry, National Taiwan Normal University, 88 Sec. 4, Tingchow Road, Taipei 116, Taiwan*
[b]*Command of the Army Force of Military Police, Forensic Science Center, Taiwan*

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Abstract

The analytical profiles for 3,4-methylenedioxymethamphetamine (3,4-MDMA) and related amphetamines in urine samples are described for non-aqueous capillary electrophoresis–fluorescence spectroscopy. 3,4-MDMA was detected and identified on-line, using a cryogenic molecular fluorescence technique at 77 K. Under optimized conditions, baseline separation of the selected compounds was achieved in less than 12 min. Precision was evaluated by measuring the repeatability and intermediate precision of the migration times and corrected peak areas. The non-aqueous CE separation conditions and the spectral characteristics of 3,4-MDMA with respect to solvent and temperature effects are also discussed.

Keywords: 3,4-Methylenedioxymethamphetamine

1. Introduction

Methylenedioxylated derivatives of amphetamine, such as methylenedioxyamphetamine (MDA), methylenedioxymethamphetamine (MDMA), benzodioxol-5-yl-2-butylamine (BDB) and *N*-methyl-1-(1,3-benzodioxol-5-yl)-2-butylamine (MBDB) are often referred to as ''designer drugs'' (Fig. 1). They are strong central nervous system stimulants, which are generally considered to be illicit drugs, and are a source of serious social problems in many countries, even more than heroin. Because of the rapid growing abuse of these substances, a simple, economic, fast and consistent method for their determination is necessary, not only for forensic research, but also for clinical analysis. A number of analytical methods have been commercially developed for their identification and include techniques such as fluorescence polarization immunoassay [1], immunochromatographic assay [2], and thin-layer chromatographic analysis [3]. Needless to say, high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS) constitute the most popular and powerful techniques for the analysis of amphetamines and their analogs [4–15]. However, each of the above methods have unique advantages and disadvantages regarding sensitivity, precision and simplicity of use. Capillary electro-

*Corresponding author. Tel.: +886-2-2931-6955; fax: +886-2-2932-4249.

E-mail address: chenglin@cc.ntnu.edu.tw (C.-H. Lin).

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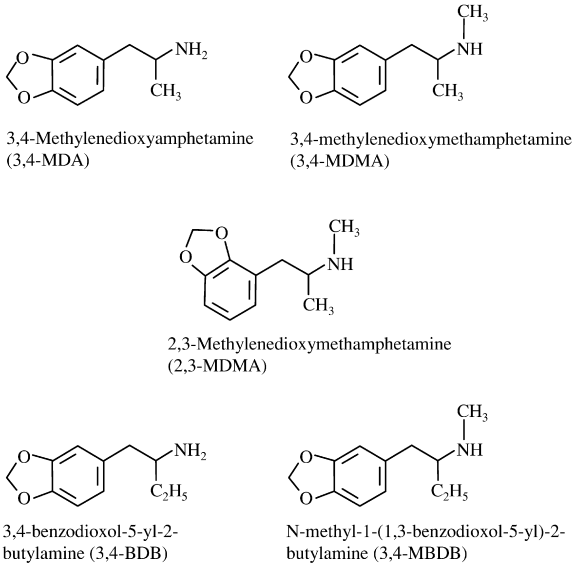

Fig. 1. Molecular structures of amphetamines and abbreviations used.

phoresis (CE) has been proven to be a powerful tool in many fields. In particular, CE has advantages in terms of higher resolution, greater sensitivity and a smaller injection volume than HPLC or GC. However, in the case of chromatographic separation, the migration time and spiking methods are normally used to identify sample constituents. It must also be noted that dependence on the migration time can cause problems because of the time scale shifts, and that spiking occasionally requires difficult and expensive standards, especially for identification in complicated matrices, i.e., in vitro and in vivo samples. To solve such problems, CE has also been coupled to MS and nuclear magnetic resonance (NMR) in attempts to more efficiently characterize analytes online [16–21]. Although both methods yield interesting results and do not require standards during analysis, CE–MS has drawbacks, in terms of distinguishing isomers and CE–NMR problems still exist in its implementation. Of very considerable importance in future research with CE is its combination with spectroscopic detection methods, that are capable of providing spectral information on molecular analytes. However, with detection at ambient temperature this method provides only very limited spectral resolution due to the large vibronic fluorescence bandwidths. Low-temperature fluorescence spectroscopy is much more appropriate for the identification of analytes, compared to the ambient temperature spectra [22–26]. The combination of two analytical methods, CE and low-temperature fluorescence spectroscopy, provides separation and on-line high-resolution spectroscopic identification of CE-separated analyzes via the fingerprint structure of vibrationally resolved fluorescence spectra at low temperature [27–29]. Recently, we described a non-aqueous CE method coupled with fluorescence detection for the determination of 2,3- and 3,4-MDMA at 77 K [30]. In this study, five structure similar amphetamines were selected as the samples and optimum conditions for their separation were investigated by non-aqueous CE. On-line identification of 3,4-MDMA (ecstasy) in a sample of a suspect's urine was achieved. Several electrophoretic parameters, spectral properties of 3,4-MDMA, such as temperature and solvent effect, and the sensitivity and precision of the method are also discussed.

2. Materials and methods

2.1. Chemicals

3,4-MDMA was acquired from Radian International (catalog No. M-013, 99%; 1 mg/1 ml methanol). Sodium cholate ($C_{24}H_{39}O_5Na$), acetonitrile (ACN) and methanol (99.8%) were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Dioctyl sulfosccinate (DOSS) and sodium dodecyl sulfate (SDS) were obtained from Acros (Belgium). Ethanol (99.8%) and ammonium acetate (CH_3COONH_4) were purchased from Riedel-de Haen (RdH Laborchemikalien). Liquid nitrogen and nitrogen gas were supplied from Echo (Taiwan). 3,4-MDA, 2,3-MDMA, 3,4-BDB and 3,4-MBDB were synthesized and generously donated by the Command of the Army Force of Military Police, Forensic Science Center, Taiwan.

2.2. CE apparatus

The CE set-up (Fig. 2) fabricated in the laboratory is the same as that described previously [30]. Briefly,

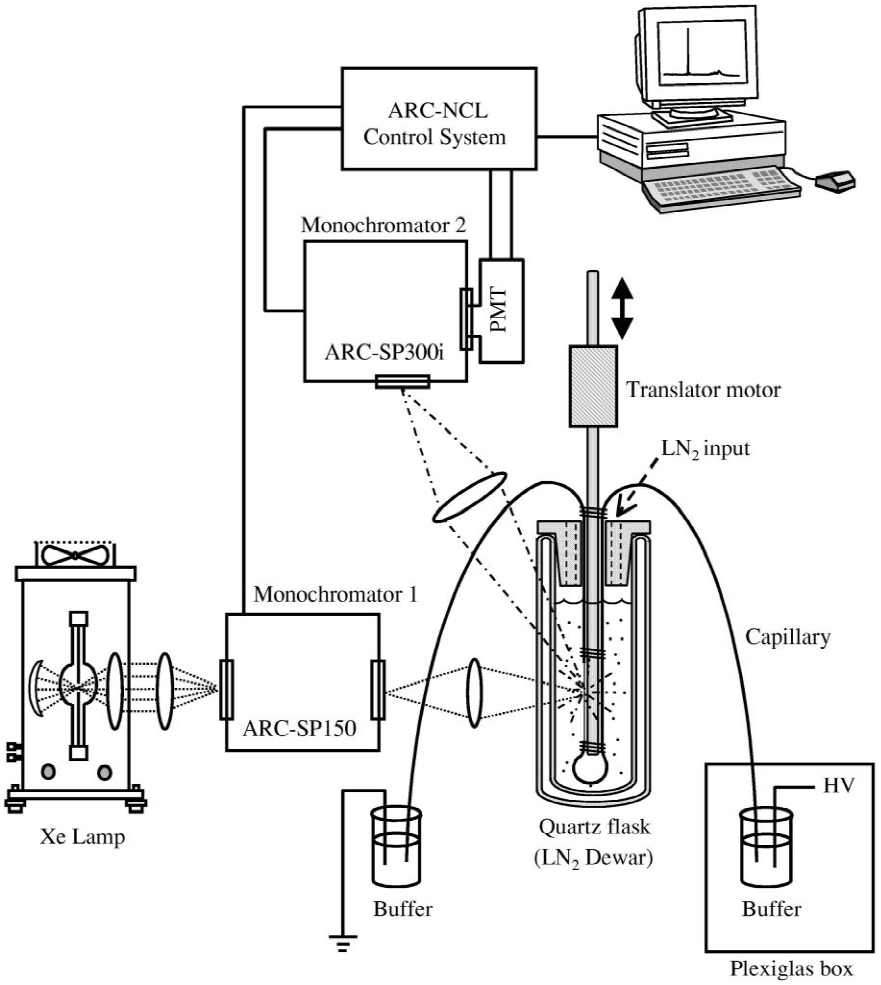

Fig. 2. A schematic apparatus of the CE–fluorescence spectroscopy system used for the low-temperature spectral fingerprint identification of CE-separated analytes.

a high-voltage power supply (Model RR30-2R, 0–30 kV, 0–2 mA, reversible, Gamma, FL, USA) was used to drive the electrophoresis and a 75-μm I.D. fused-silica capillary (J&W Scientific, CA, USA) was used for the separation. The excitation source was selected by a monochromator (ARC, Acton Research; Model SP-150, 1200 grooves/mm grating) connected to an Xe lamp (Muller Elektronik Optik, SVX/LAX 1450, 500 W) which provides an output power in excess of ~6 W. Fluorescence data were collected at a right angle to the light source and dispersed by another monochromator (ARC Model SP-300i, 2400 grooves/mm grating), followed by detection by a photomultiplier tube (ARC Model P2-R928, for 190–900 nm). Electropherograms were collected at a speed of 200 ms/point with a data acquisition system (ARC's Spectra-Sense NCL package), connected to a personal computer. For off-line experiments, samples were placed in quartz tubes (1.5 cm×2 mm I.D.), sealed with rubber septa (Aldrich; catalog No. Z10071-4) and brought to 77 K for low-temperature fluorescence measurements. Solvent purity was verified by recording absorption and fluorescence spectra under conditions of high sensitivity.

2.3. Methods

A locally designed capillary-Dewar (CD) was custom made by Genchen Glass (Taiwan) which consists of a double-walled quartz flask for introducing liquid nitrogen. The diameter of the CD was 38 mm, the inner portion was 22 mm×120 mm in height, and it was evacuated to ~10^{-5} Torr (1 Torr=133.322 Pa). The capillary was bent into a hoop, secured to a glass rod (5 mm O.D.) and positioned in the central region of the CD. The CE detection window, formed by removing the coating of the capillary was 3 cm. The progress of the separation was observed on a computer monitor. Once the CE-separated analytes appeared on the screen, the HV power supply was immediately turn off and liquid nitrogen poured directly into the CD. Once frozen, arbitrary detection times can be used to completely characterize the separated analytes by low-temperature spectroscopy. The capillary inside the CD can be moved up and down by a translator or manually in order to locate the exact position of the next CE-separated analyte. For 30-min low-temperature experiments, the consumption of liquid nitrogen was 40~60 ml. Condensation on the Dewar can easily be removed with a fan.

2.4. Liquid–liquid extraction procedure

A 1-ml volume of a urine sample was made alkaline by the addition of excess K_2CO_3. The free bases were then extracted into 2 ml of a hexane–CH_2Cl_2 (3:1, v/v) solution by stirring for 1 h. After centrifugation for 5 min at 5000 rpm, the upper layer organic phase was collected and evaporated to dryness. The residue was dissolved in 10 μl of MeOH for the subsequent CE separation.

3. Results and discussion

3.1. Separation of amphetamine standards by non-aqueous CE buffer

Some of the merits of non-aqueous CE include a higher number of theoretical plates, a much wider range of analytes and enhanced fluorescence properties for many organic compounds [31–33]. The use of sodium cholate (SC), a bile salt, a naturally occurring compound, has been used to extend the scope of the separations. SC has a steroidal structure and forms helical micelles in water. The critical micelle concentration (CMC) is reported to be 13–15 m*M* at 25°C [34]. Although it has been reported that such bile salts form reversed micelles in organic solvents [35–37], the data in this paper are insufficient to show this value of CMC* under our working conditions. Fig. 3 shows typical fluorescence CE chromatograms of the five amphetamines (Fig. 1) separated by non-aqueous CE in the pres-

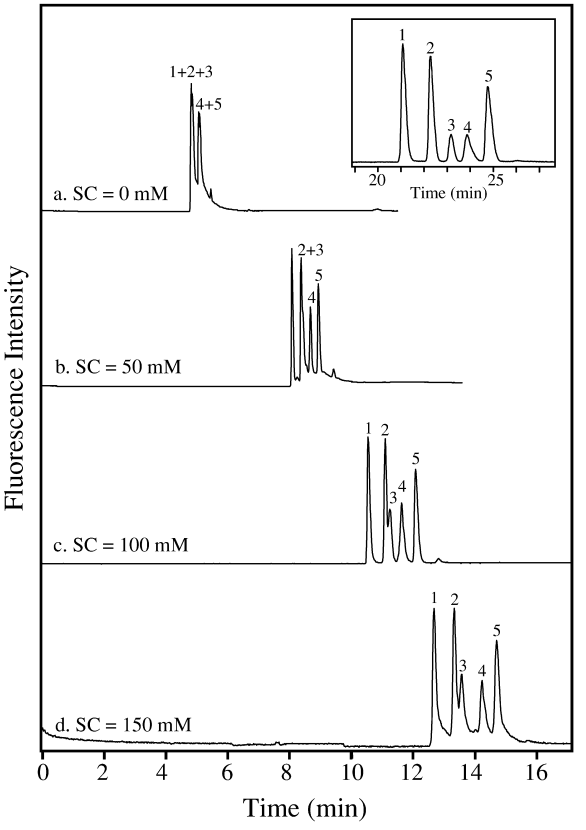

Fig. 3. Electropherogram of five amphetamine standards with fluorescence detection by non-aqueous CE. Sample concentration was 100 ppm in each case. CE conditions: capillary, 50 cm (40 cm to detector); pumping and detection wavelengths, λ_{ex}=280 nm/λ_{em}=320 nm; temperature, 22°C; running buffer, 0–150 m*M* SC (chromatograms: a to d), 20 m*M* ammonium acetate (CH_3COONH_4) in the formamide–methanol–ethanol (30:20:50, v/v) solution; applied voltage: 20 kV; currents: ~9, 17, 23 and 30 μA. Peaks: 1=3,4-MDA; 2=3,4-MDMA; 3=2,3-MDMA; 4=3,4-BDB; 5=3,4-MBDB.

ence of different concentrations of SC. In addition to SC, the non-aqueous CE buffer was a mixture solution of formamide–methanol–ethanol (30:20:50, v/v), and contained 20 m*M* ammonium acetate. As shown in chromatogram a of Fig. 3 (SC=0 m*M*), the separation was performed using non-aqueous capillary zone electrophoresis (CZE). When the SC was added, as shown chromatogram b (SC=50 m*M*), the separation was improved due to interactions of the analytes with SC. Even though in the case of the non-aqueous CE, where our knowledge concerning its acid–base chemistry in organic solution is very limited, we found that the separation was not complete until the SC concentration was in excess of ~100 m*M*, especially for the separation of positional isomers of 3,4- and 2,3-MDMA (chromatogram c, peaks 2 and 3). A higher concentration of SC (150 m*M*) resulted in an even more improved separation (chromatogram d). Inset shows the best separation of the five amphetamines when a longer capillary was used. The migration order was: 3,4-MDA<3,4-MDMA < 2,3-MDMA < 3,4-BDB < 3,4-MBDB. It should be noted that the order of molecular mass: 3,4-MDA<3,4-MDMA=2,3-MDMA=3,4-BDB<3,4-MBDB. The compounds basically migrated in the order of mass per charge. In order to investigate the effects of organic solvents, a methanol–hexane (7:3, v/v) solution containing 100 m*M* SC and 20 m*M* of ammonium acetate was examined. Under this condition the migration order was observed to be: 3,4-MDA<3,4-MBDB<2,3-MDMA<3,4-BDB<3,4-MDMA, i.e., some changes in the order of elution had occurred. Furthermore, we found that the concentration of SC was not the only parameter that affected for the separation. Under exactly the same experimental conditions, we used a single organic solvent, e.g., formamide or methanol, instead of a mixed solvent, and found that the separation degraded. Thus, by a simple variation of organic solvents a significant change in selectivity can be achieved. Such a modification had no significant effect on sensitivity. The concentration of ammonium acetate (5~20 m*M*) would be expected to enhance the efficiency of separation. The use of 20 m*M* of ammonium acetate provided best separation in this study. Other types of surfactants were also tested, such as SDS and DOSS, but no separation of the five amphetamines was detected.

3.2. Determination of 3,4-MDMA in urine with CE–fluorescence detection

In Fig. 4, electropherograms a and b show typical electropherograms of a normal human urine extract (electropherogram a), an extract of normal human urine spiked with the five standards (electropherogram b) and the urine extract from suspect I (electropherogram c). Herein, the UV excitation and fluorescence emission wavelengths were 280±8 nm and 320±2 nm, respectively. Only one major peak at ~24 min was detected in the normal human urine sample. Thus, it is clear that in typical human urine samples, only a few native fluorescent compounds are present which illuminate in the wavelength range of 320±2 nm. With this fluorescence detection, the electropherogram was much simpler than with UV

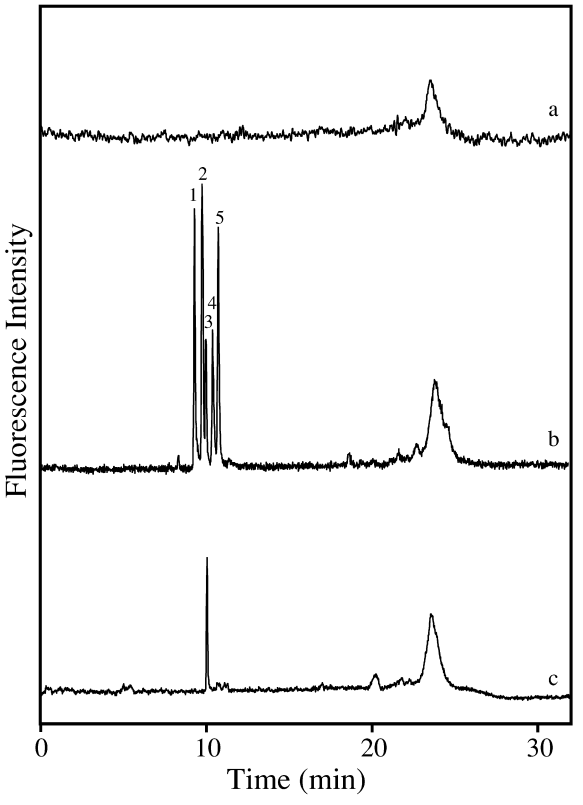

Fig. 4. Electropherograms of (a) a normal urine sample, (b) a normal urine sample spiked with five amphetamine standards (each 10 ppm), and (c) a urine sample from suspect I, after liquid–liquid extraction. CE conditions as stated in Fig. 3 (chromatogram c).

detection due to the UV-absorption of numerous organic compounds in urine sample. This approach also provides a simple way to observe non-natural compounds in urine, such as MDMAs. Electropherogram b shows that the spiked five standards (10 ppm each) were extracted and detected. For the extracts of urine sample from suspect I, 3,4-MDMA was clearly detected at a 10.5 min migration time (electropherogram c), at a concentration of 3.4 ppm. Several samples were tested by this method and one is shown in Fig. 6 (suspect II). In addition to several minor peaks, 3,4-MDMA was clearly observed and the concentration was determined to be 12.3 ppm. Using the liquid–liquid extraction method described here and sample concentration, it is possible to have an acceptable signal-to-noise ratio for detecting 3,4-MDMA in urine of ~50 ppb. However, as mentioned earlier, only the dependence on migration time can lead to an ambiguous assignment owing to the time scale shifts, particularly when the separation is inadequate. The on-line identification of a CE-separated analyte is described in Section 3.4.

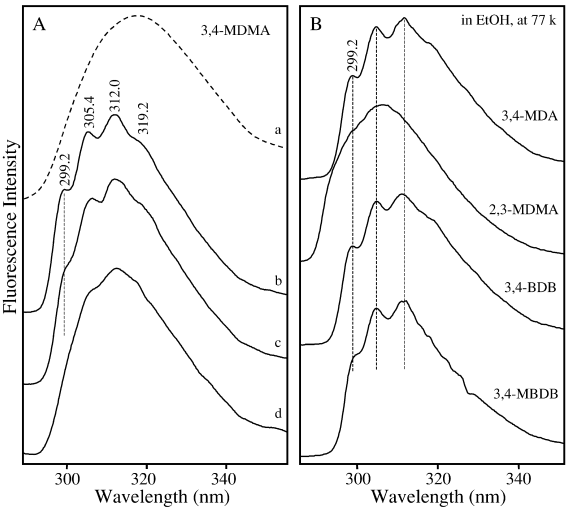

Fig. 5. Spectral properties of 3,4-MDMA: temperature and solvent effect. Spectrum a, room temperature (in EtOH); spectrum b, 77 K (in EtOH); spectrum c, 77 K (in non-aqueous CE buffer); spectrum d, 77 K (in water–acetonitrile, 7:3, v/v solution). The concentrations of samples were 100 ppm.

3.3. Spectral properties of 3,4-MDMA: temperature and solvent effect

The principal advantage of the use of Shopl'skii effect is that spectral sharpening occurs both in absorption and emission. The most interesting point for the use of a non-aqueous capillary buffer is that the organic solvent would be able to form a glass matrix at 77 K, which permits the acquisition of highly resolved (quasiline) spectra. Our results suggest that 3,4-MDMA provides enhanced fluorescence intensity at 77 K in the order of 2~3-fold, in either EtOH or the non-aqueous CE buffer used. This is the benefit of obtaining the low-temperature spectra with high sensitivity and spectral resolution. Using a high resolution (2400 grooves/mm grating and 0.2 mm entrance slit) monochromator, Fig. 5A (spectra a–d) shows the spectra of 3,4-MDMA at different temperature in various solutions. At room temperature, 3,4-MDMA (in EtOH) only provides a broad band spectrum with a maximum at ~320 nm (spectrum a); whereas sharp spectral bands were observed when the temperature was reduced to 77 K (spectrum b). The (0,0) origin band of 3,4-MDMA was observed at 299.2 nm. The other bands are labeled with their wavelength and are important parameters for use in spectral fingerprinting. The other matrix dependent (off-line) studies of 3,4-MDMA at 77 K were performed in non-aqueous CE buffer and acetonitrile–water (30:70, v/v) in order to determine the matrix effect, as shown in spectra c and d. As a result, the non-aqueous CE buffer provided a higher spectral resolution than did the aqueous CE buffer. 3,4-MDA, 3,4-MBDB and 3,4-BDB show similar fluorescence spectra at 77 K, as shown in Fig. 5B. To distinguish these, a further low temperature, e.g., 4.2 K, is necessary because at such low temperature, the (0,0) origin band would divide to mutliplet structures when the sample was excited with lasers, the so-called fluorescence line-narrowing spectroscopy (FLNS) [22–28]. Herein, the experiments were done at 77 K and such fine structures could not be observed. However, the origin of the fluorescence is the 3,4-dioxolane, which is totally different from other amphetamines, such as 2,3-dioxolane, brolamphetamine and methylamphetamine at 77 K.

3.4. On-line identification of 3,4-MDMA in a urine sample

Using the same experimental conditions, the urine extract from suspect II was separated and the electropherogram is shown in Fig. 6. Because of the identical migration time, the peak at 10.5 min was identified with 3,4-MDMA. As mentioned before, a dependence on the migration time could lead to misjudgemensts because of time scale shifts. In our laboratory, the CE method coupled with 77 K fluorescence spectroscopy was developed and validated for the on-line identification of isomers [30]. The low-temperature spectrum was measured when the CE-separated analyte reached the CE detection window and was then cooled to a temperature of 77 K. The inset spectra a and b, show the on-line 77 K spectra of a 3,4-MDMA standard and the CE-separated analyte, respectively. The (0,0) origin band was observed at 299.2 nm and were easily recognized. Thus, we concluded that the 3,4-MDMA could be absolutely identified using this approach.

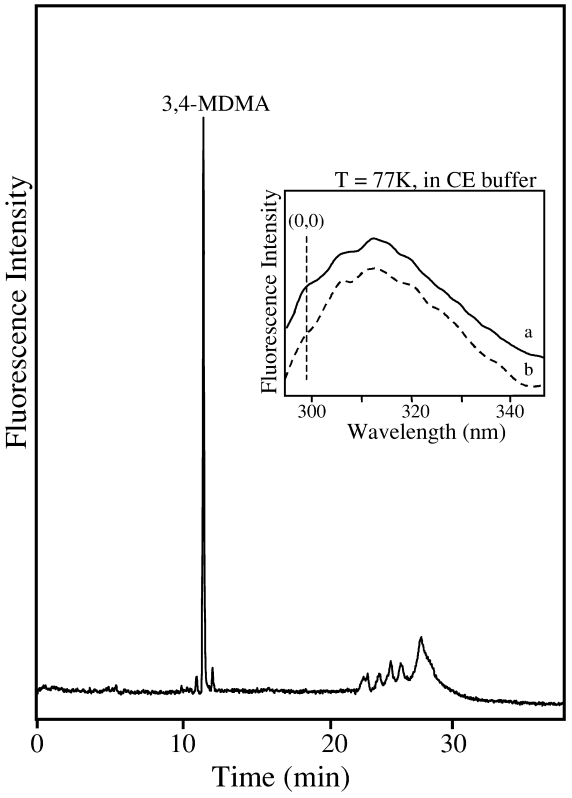

Fig. 6. CE-separated chromatogram of the urine extraction from suspect II. Inset, on-line 77 K fluorescence spectra for the CE-separated peak (spectrum a) and 3,4-MDMA standard (spectrum b).

3.5. Method sensitivity and precision

3,4-MDMA is naturally fluorescent, so derivatization is not necessary. A calibration curve was prepared for 3,4-MDMA at concentrations between 5 and 100 ppm in MeOH (5, 10, 25, 50, 100 ppm). A linear relationship over the 5~100 ppm range of 3,4-MDMA standards was observed. There was a 3:1 signal-to-noise ratio for ~1 ppm of 3,4-MDMA with 2400 grooves/mm grating–3 mm slit entrance of the monochromator. After liquid–liquid extraction, the sample can be condensed by ~20-fold and a detection limit of 3,4-MDMA in urine of ~50 ppb ($S/N=3$) can be achieved. Using a 300 grooves/mm grating, the detection limits could be further improved by a factor of 10-fold. However, this provides lower spectral resolution and is not suitable for 77 K on-line spectral identification. In Taiwan, if the concentration of amphetamines or its related metabolite exceeds 0.5 ppm, then the suspect is judged guilty. Other types of abuse drugs such as cocaine, opium have more strict limitations as 0.3 ppm. The limitation for cannabis is 0.05 ppm. The proposed method here provides sufficient sensitivity to permits the identification such low levels of MDMAs.

4. Conclusions

We demonstrated here that a non-aqueous CE–fluorescence spectroscopy method can be successfully used for the separation and on-line spectral identification of 3,4-MDMA in urine samples of suspects, via low-temperature fluorescence spectroscopy at 77 K. The proposed method allows for the excellent separation of 3,4-MDMA and related compounds from urine samples and their presence can be unambiguously assigned. Moreover, the method proposed here can provide the results in less than 12

min without any pre-treatments and provided a ~1 ppm detected limit for 3,4-MDMA; whereas GC–MS requires a derivatization and additional sample handling for similar results. Using a simple liquid–liquid extraction developed in this study, the detection limit could be improved to ~50 ppb ($S/N=3$). We conclude that the combining of CE and low-temperature fluorescence spectroscopy provides a sensitive, accurate, rapid, simple, and economic methodology for on-line identification, along with the possibility for structural assignments by spectral fingerprinting.

Acknowledgements

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