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MDMA (3,4-methylenedioxymethamphetamine) nitrate – an atypical salt form or a new trend in the drug market?

Summary

The article presents a case involving an appearance of an atypical 3,4-methylenedioxymethamphetamine (MDMA) in the form of nitrate on the illicit drug market. This compound can be identified only by using such analytical methods as capillary electrophoresis (CE) or scanning electron microscopy (SEM), which are not routinely applied to forensic analyses of this type of substances. Therefore, particular caution should be exercised whenever a gas chromatography-mass spectrometry (GC-MS) method unambiguously identifies a substance, yet infrared spectroscopy fails to confirm this result.

Keywords: MDMA, nitrate, capillary electrophoresis, SEM

Aim of the study

The aim of this study was to draw attention to the appearance of atypical nitric formulations of 3,4-methylenedioxymethamphetamine on the illicit drug market. Although this compound can be successfully identified by a gas chromatography-mass spectrometry method, other methods, such as X-ray diffraction (XRD) and infrared spectroscopy (FT-IR) fail to detect it, due to the absence of nitric MDMA standards in the most popular databases. This can result in a false negative identification error when testing a sample for the presence of MDMA.

Introduction

3,4-methylenedioxymethamphetamine (MDMA, „ecstasy") is a very popular drug, both in Poland and worldwide. According to the report released by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA, 2017), during the past year, in the European Union, 2.7 million people aged 15–64 years, including 2.3 million aged 15–34 years admitted to using MDMA. In total, in the European Union, Turkey and Norway, 9.6 million MDMA tablets have been seized, with a total weight of 212 kg. Since 2005, the seized amounts have been steadily increasing. In recent years, an average MDMA content per tablet has increased from 50 mg to 110 mg. The most popular MDMA forms on the illicit drug market are the tablets with different shapes and logotypes (fig. 1). 3,4-methylenedioxymethamphetamine can be synthesized via different routes from the following precursors: piperonal, 3,4-methylenedioxyphenylpropan-2-one (MDP2P), safrole or isosafrole (Stojanovska, Fu, Tahtouh, Kelly, Beavis, Kirkbridge 2013). The final product is always MDMA (free base) in the form of a colourless or occasionally straw-coloured, oily liquid. Subsequently, the liquid is converted to a crystalline MDMA hydrochloride by passing gaseous hydrogen chloride through a solution of MDMA in an organic solvent, which may contain diethyl ether, toluene or isotropically (Krawczyk, 2005). The final product is aliquoted, mixed with solvents (e.g. lactose) and formed into tablets with imprinted manufacturer's logotype. Due to long lasting presence of MDMA on the drug market, i.e. since the mid-1980s, when it was used as a recreational drug (Freudenmann, Oxler, Bernschneider-Reif 2006), this substance is currently controlled under the 1988 UN Convention (United Nations Convention Against Illicit Traffic in Narcotic Drugs and Psychotropic Substances, 1988).

Materials and Methods

Research material submitted to the Central Forensic Laboratory of the Police (CLKP) consisted of a small

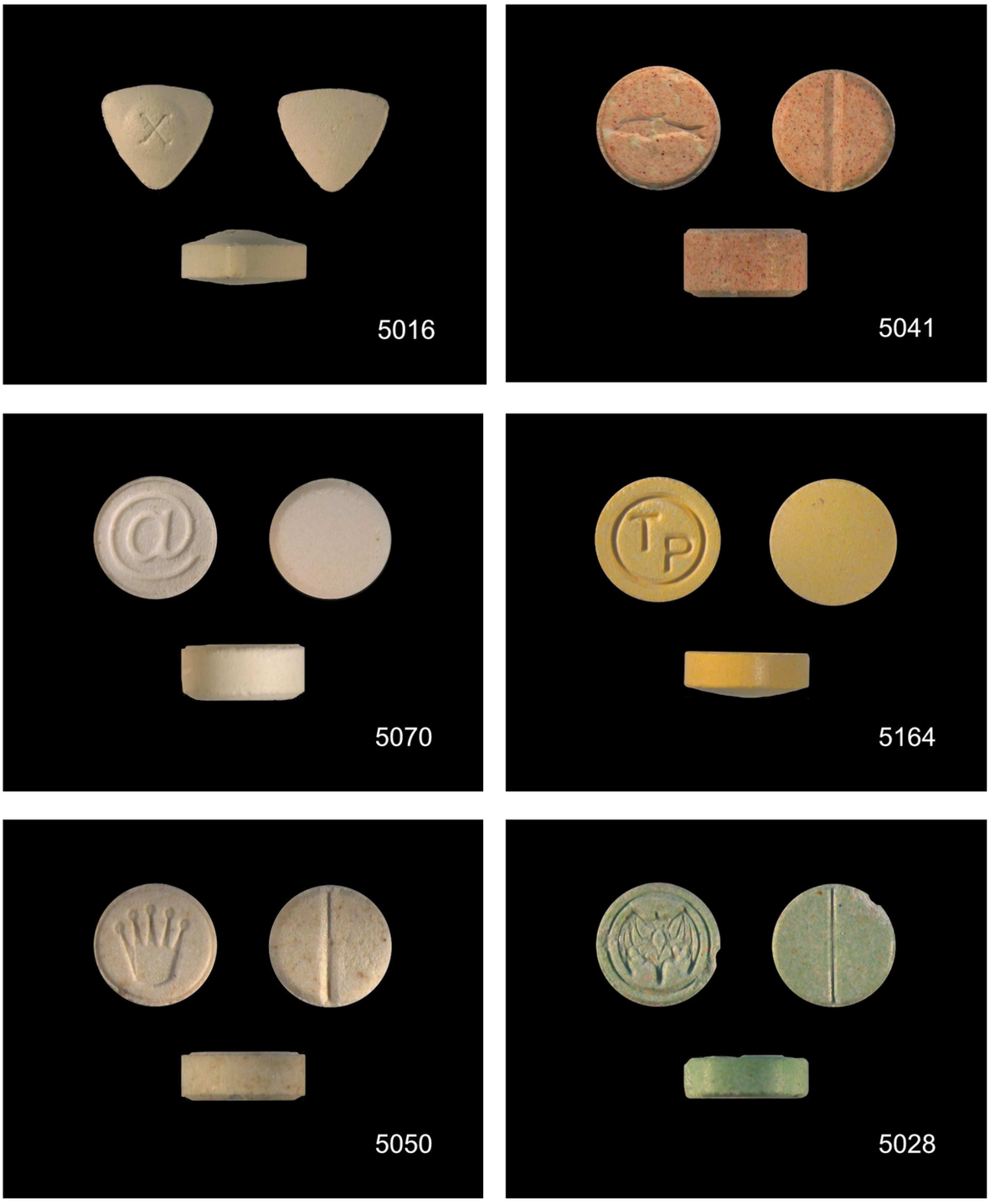


Fig. 1. Examples of MDMA forms available on the illicit drug market.

amount of agglomerated substance in beige colour with a weight of 0.13 g. According to the information received, this sample was part of a larger whole and it was delivered to CLKP in order to confirm the presence of MDMA.

The tests were carried out using the following instrumental methods:

– gas chromatography coupled to mass spectrometry (GC-MS), using a Shimadzu GCMS-QP2010 Plus device equipped with a Zebron ZB-Drug 1 column; length: 30 m; diameter: 0.25 mm; stationary phase film thickness: 0.25 µm; temperature programme: 100°C for 0.50 min, then raised from 100°C to 325°C at

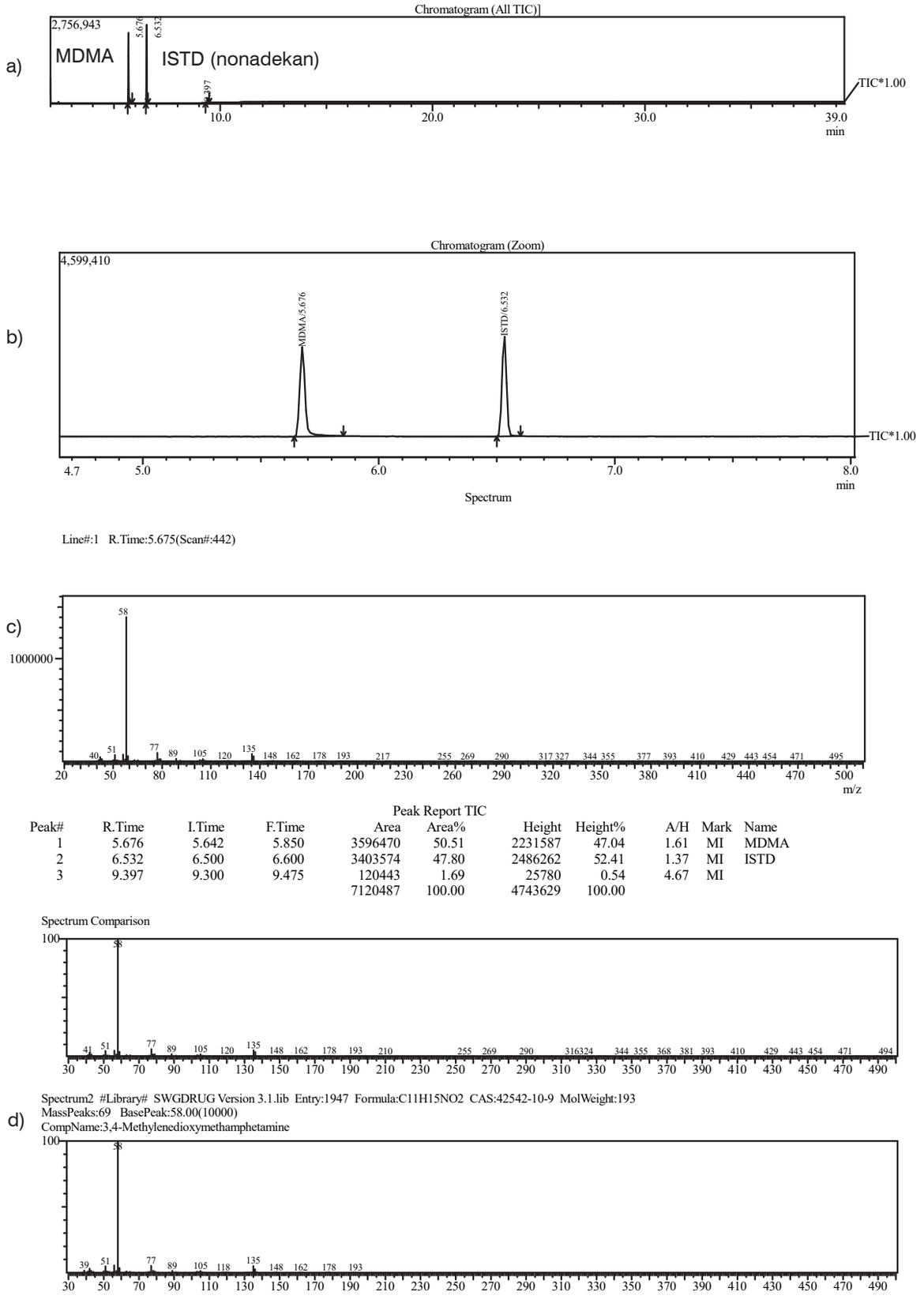


Fig. 2. Result of GC-MS analysis: a) Total ion current (TIC) chromatogram with visible MDMA and ISTD (nonadecane – internal standard) peaks; b) Magnified total ion current (TIC) chromatogram; c) Mass spectrum of a sample containing MDMA; d) Comparison of a mass spectrum obtained, with a SWGDRUG v. 3.1 spectral library.

25°C/min, 325°C for 22 min. The extraction was carried out with the use of a mixture of organic solvents (methanol-toluene) spiked with nonadecane (200 mg/ml) as an internal standard. The same analytical conditions were applied to a certified MDMA standard, in order to verify the retention time (RT);

– attenuated total reflection infrared spectroscopy (FT-IR ATR), using a Thermo Scientific Nicolet iS50 device; measuring range 4000–400 cm^{-1}; number of scans: 32; resolution: 4;
– X-ray diffraction (XRD), using a Seifert FPM XRD-7 device equipped with an X-ray tube with a Cu anode (generator: 30 kV, 20 mA); measuring range of 2-theta angles from 10° to 66° scintillation detector (SC).

The above selection of instrumental methods is sufficient to confirm the presence of MDMA hydrochloride in the sample.

Results

GC-MS analysis yielded a chromatogram with a peak, which retention time RT=5.68 min corresponded to that of a certified MDMA standard (fig. 2).

In addition, in order to confirm the presence of MDMA in the sample and determine the form of salt in which this substance occurs, attenuated total reflection infrared spectroscopy (FT-IR ATR) and X-ray diffraction (XRD) analyses were performed. Both above mentioned analyses failed to yield the results compatible with MDMA hydrochloride standard stored in FT-IR and XRD databases (fig. 3a-b, 4).

Due to the fact that GC-MS analysis confirmed the presence of MDMA in the sample, while other analyses failed to identify a hydrochloride salt form of this compound, the authors decided to apply additional analytical techniques.

The supplementary tests were carried out by using the following techniques:

– ultra-high performance liquid chromatography (UHPLC) coupled to quadrupole time of flight mass spectrometry (Q-TOF); applied device: AB-SCIEX LC100/TripleTOF4600; column: Phenomenex Synergi 4 μ Fusion-RP 80 (50 × 2 mm × 4 µm, packing material C18); measurement conditions for HPLC: phase: (A): water + 0.2% formic acid, B: acetonitrile + 0.2% formic acid; flow rate of 0.2 ml/min in isocratic mode; A:B-50:50, column temperature: 30°C; analysis time: 10 min; spectrometer polarization: positive and negative;
– energy-dispersive micro X-ray fluorescence with polycapillary focusing optics (µ-XRF ED), using an Edax Eagle II XPL spectrometer; measurement conditions: analysis time: 200 s; rhodium lamp; Si/Li semiconductor detector with a resolution of

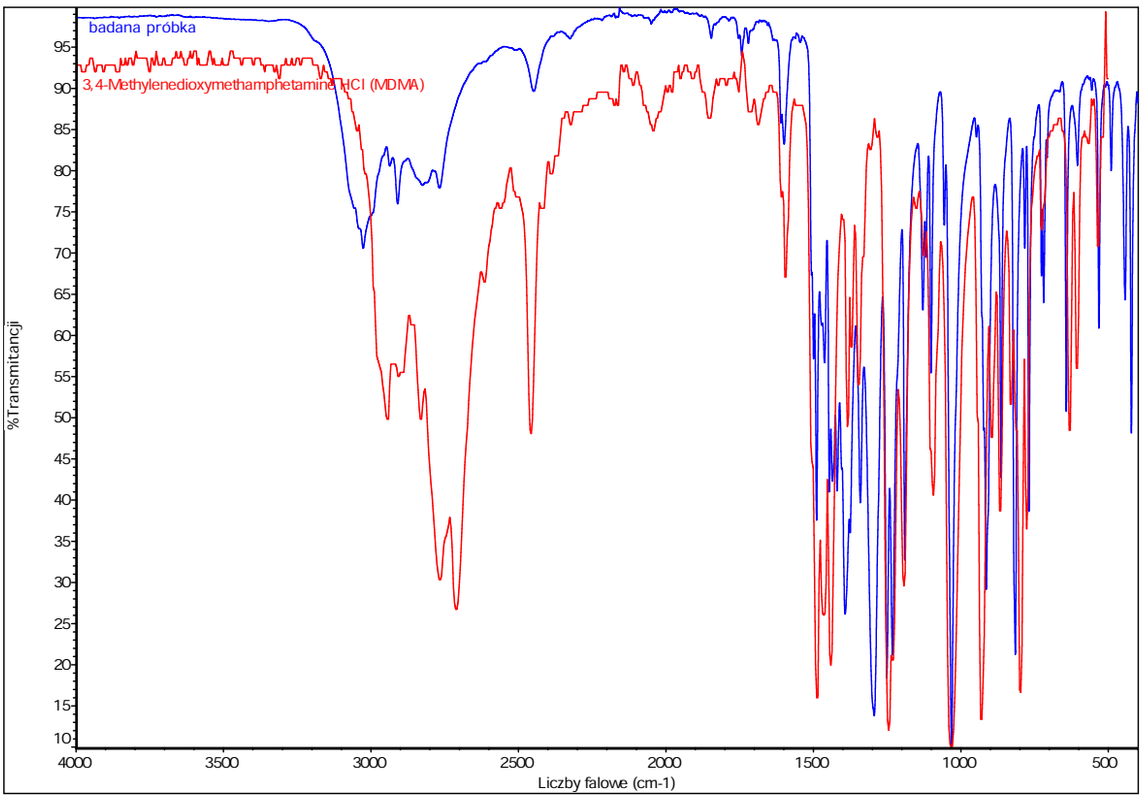
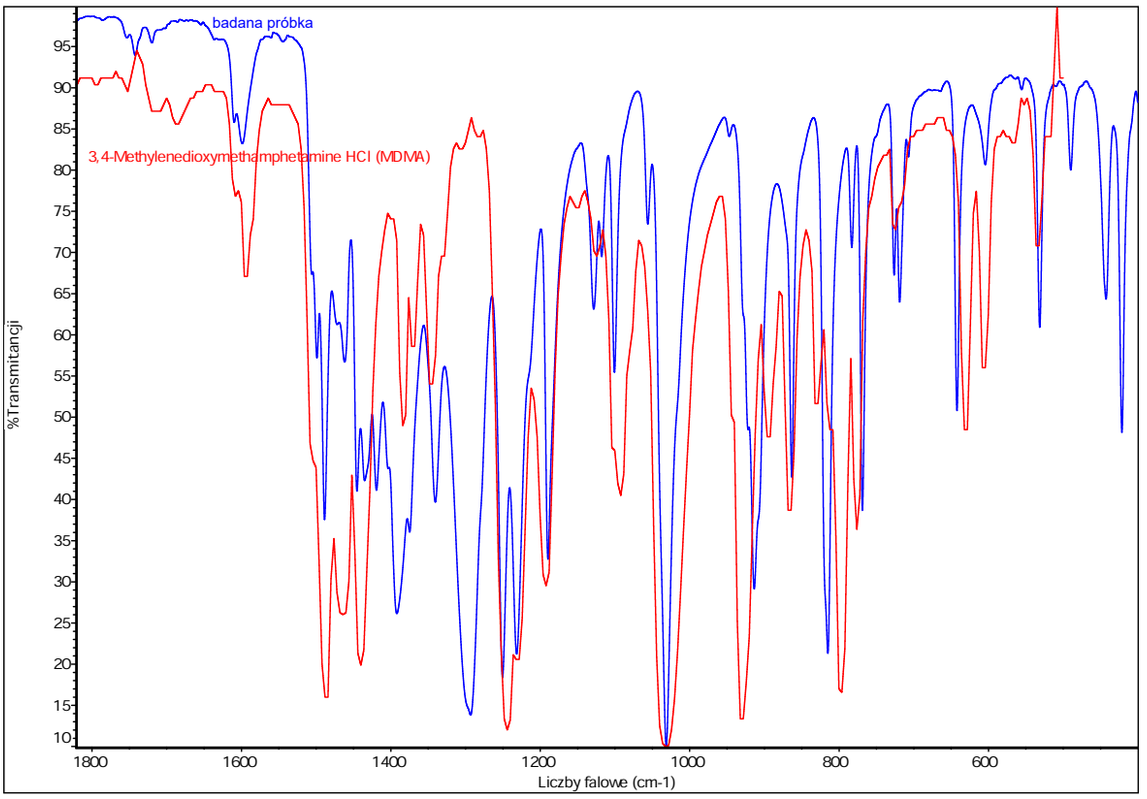


Fig. 3a. Result of FT-IR ATR analysis of a sample containing MDMA – no database match.



Ryc. 3b. Result of FT-IR ATR analysis of a sample containing MDMA – no database match.

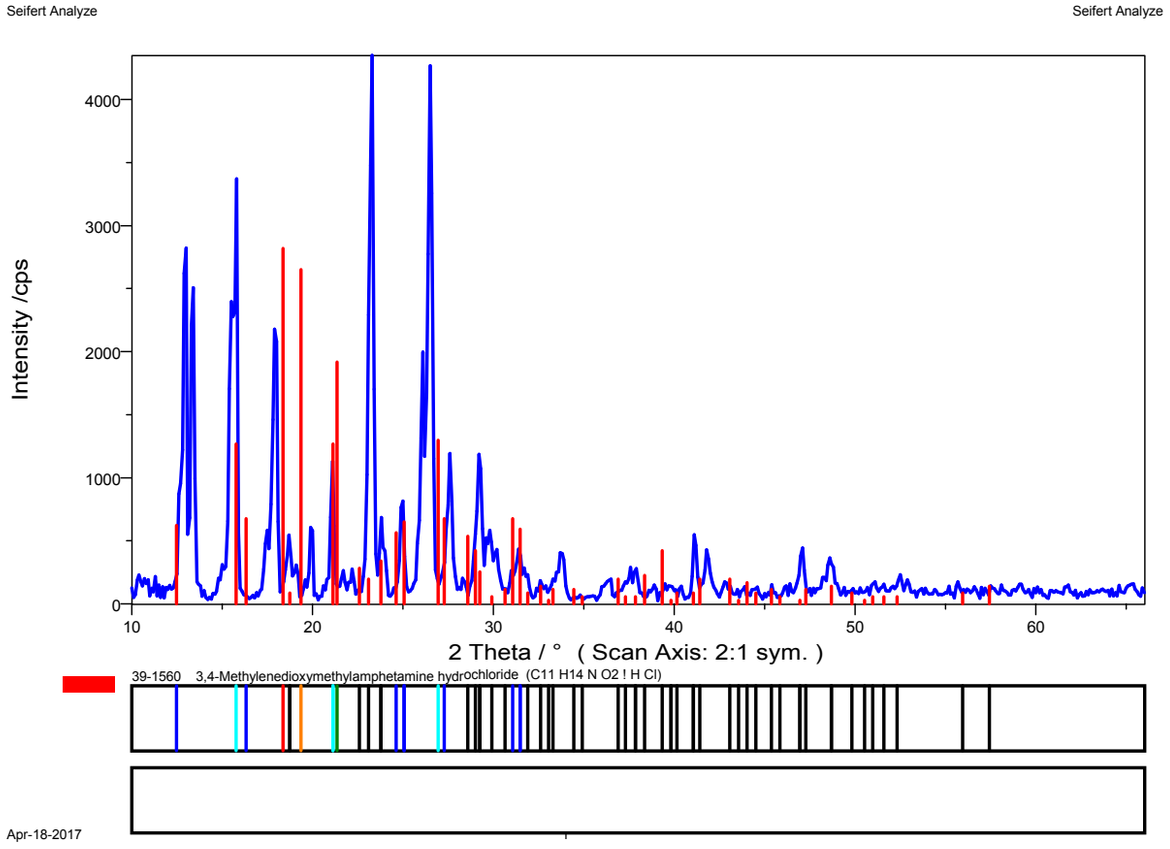


Fig. 4. Result of XRD analysis of a sample containing MDMA – no database match.

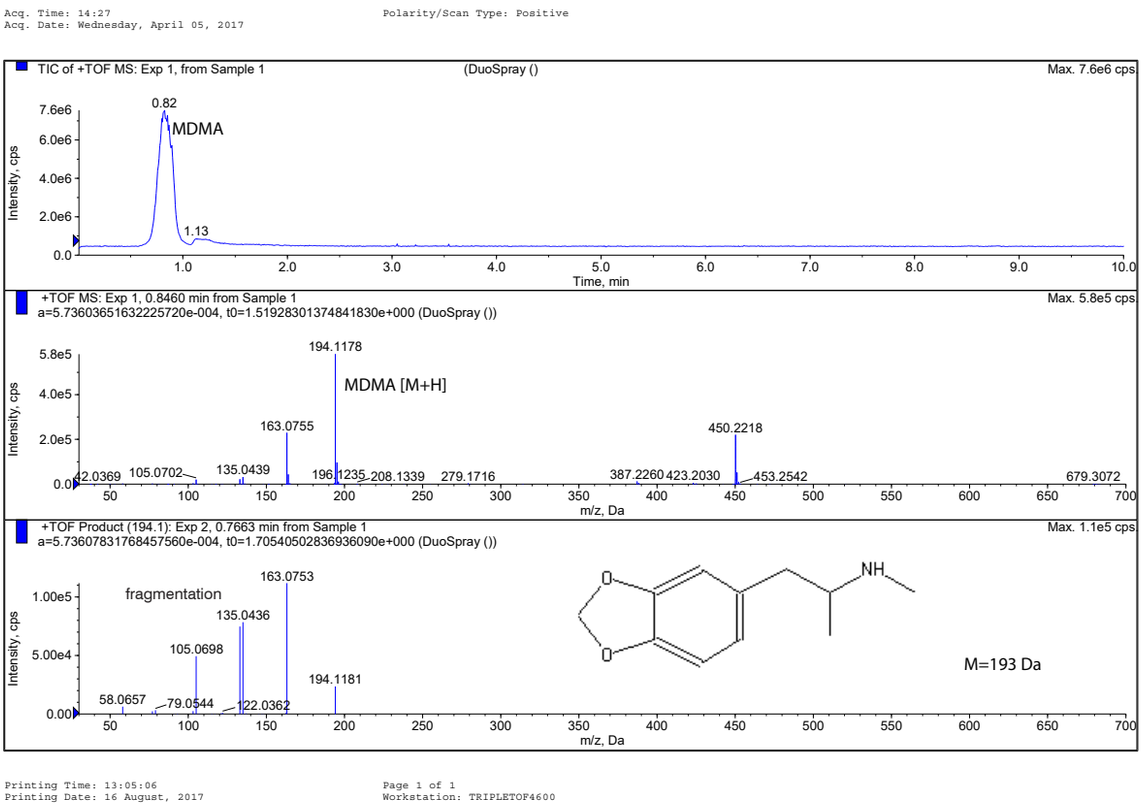


Fig. 5. Result of UHPLC-Q-TOF analysis (positive polarity) of a sample containing MDMA – visible total ion current (TIC) spectrum and fragmented spectrum confirming the presence of MDMA in the sample.

145 eV; voltage: 40 kV; current: 450 μA; beam diameter: 50 μm;

- scanning electron microscopy (SEM), using a Tescan Mira 3 LMU electron microscope coupled with energy dispersive X-ray spectrometer (Oxford Instruments X-ManN Silicon Drift De-tector – SDD); measurement conditions: voltage: 20kV; energy 20 keV; magnification: 246 ×; analysis type: BSE;
- capillary electrophoresis (CE), using a SCIEX P/ACE MDQ ™ plus device equipped with an autosampler and a photodiode array (PDA) detector enabling spectral registration within the range of 190–600 nm. A deuterium lamp was used as the light source. The results of analyses were registered and processed using 32 Karat software. The following parameters were used: fused-silica capillary 60 cm/75 μm; separation voltage: – 20 kV; indirect detection; PDA: 190–500 nm; hydrodynamic injection: 0.8 psi, 8 s; electrolyte: borate buffer (pH = 7.8) + diethylenetriamine + $K_2Cr_2O_7$.

UHPLC-Q-TOF analysis carried out in positive polarity mode confirmed the presence of 3,4-methylenedioxymetamphetamine (MDMA) in the sample by means of identification and fragmentation of precursor ion at m/z = 194 (the molecular weight of MDMA is 193 Da, Q-TOF analysis in positive polarity increases this weight by the mass of a single proton, i.e. 1.0079 Da) (fig. 5). In addition, several measurements were taken in negative polarity, yielding the main peak at m/z = 61.0441 (fig. 6). which suggested the presence of an anion with a mass of 62 Da in the sample.

μ-XRF ED analysis did not reveal the presence of Cl^- ions, thus confirming earlier assumptions that the sample may contain MDMA in form of a salt other than hydrochloride salt (fig. 7).

Electron microscopy (SEM) analysis revealed the presence of approx. 17% nitrogen, 6% chlorine and 2% sodium in the sample (fig. 8).

The presence of nitrogen was additionally confirmed by capillary electrophoresis (CE) analysis wherein the migration time of an analyte corresponded to that of a nitrate anion (fig. 9).

Conclusions

Without doubt, the sample of agglomerated substance in beige color submitted for analysis contained 3,4-methylenedioxymethamphetamine (MDMA) in the form of nitrate. The presence of the nitrate ion was confirmed by a Q-TOF method (carried out in negative polarity), yielding a peak at m/z = 61.044, which corresponded to the weight of this anion. An additional confirmation was obtained by using

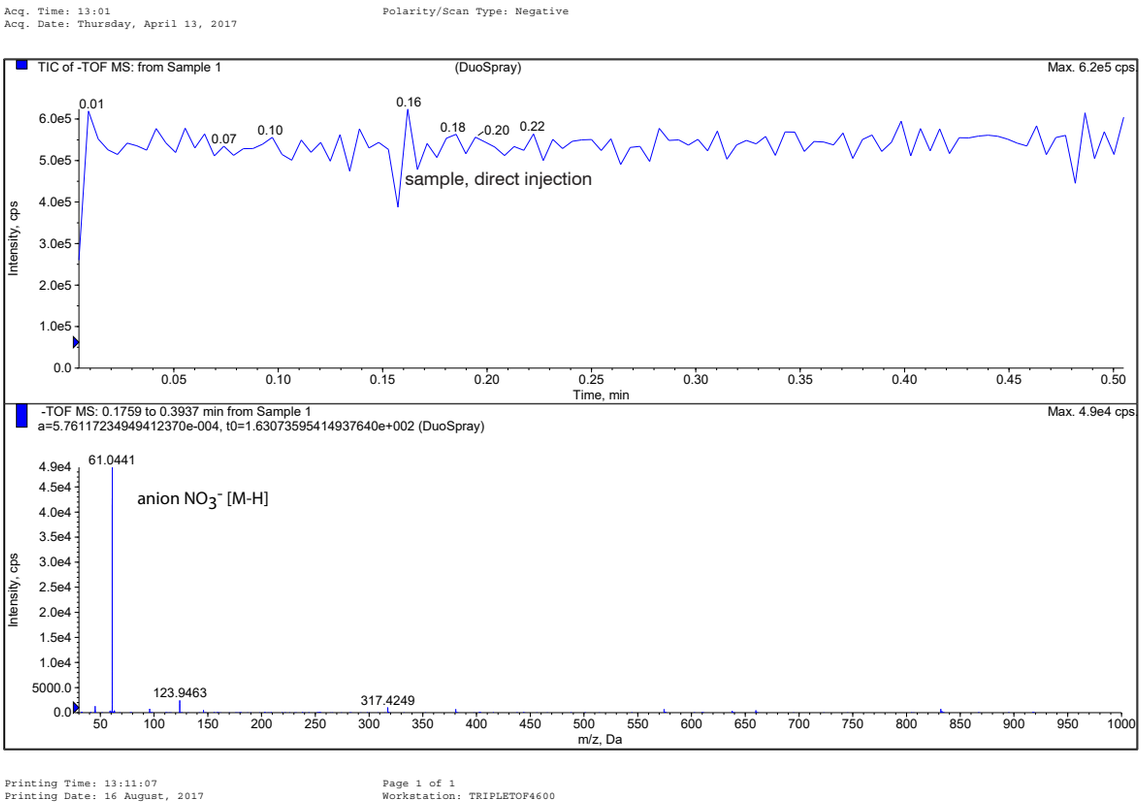


Fig. 6. Result of Q-TOF analysis (negative polarity, direct injection with bypassing UHPLC) of a sample containing MDMA – visible ion at m/z = 62 corresponds to the nitrate anion.

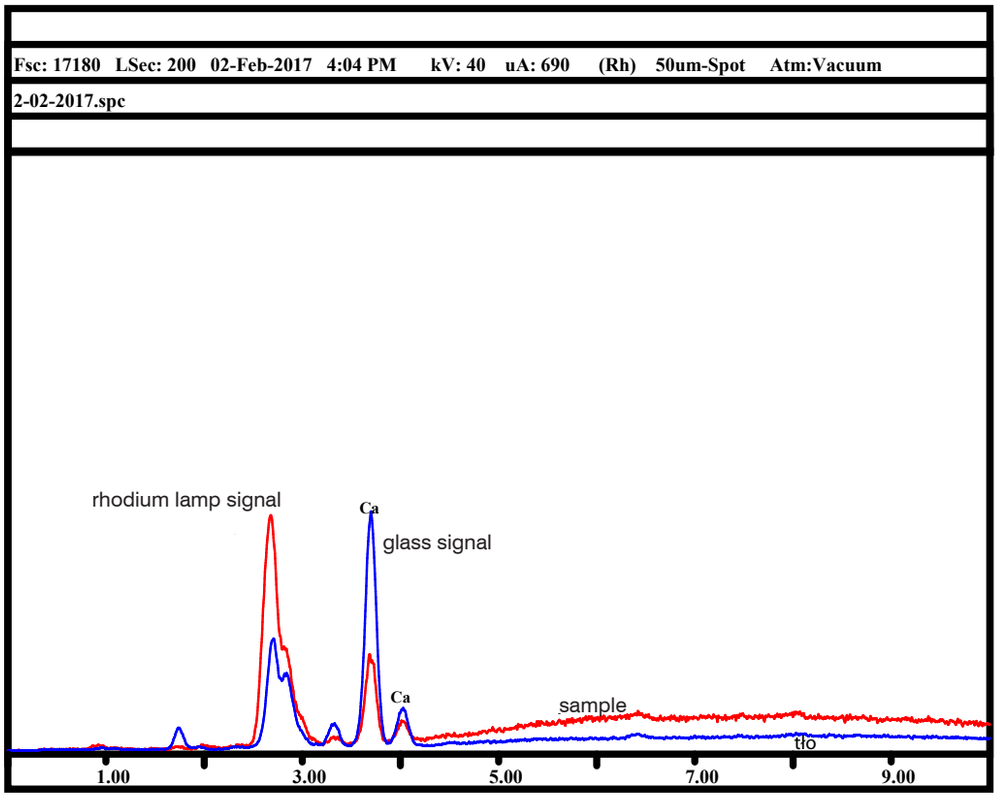


Fig. 7. Result of μXRF analysis – absence of chloride anion signals rules out the presence of a hydrochloride salt in the sample.

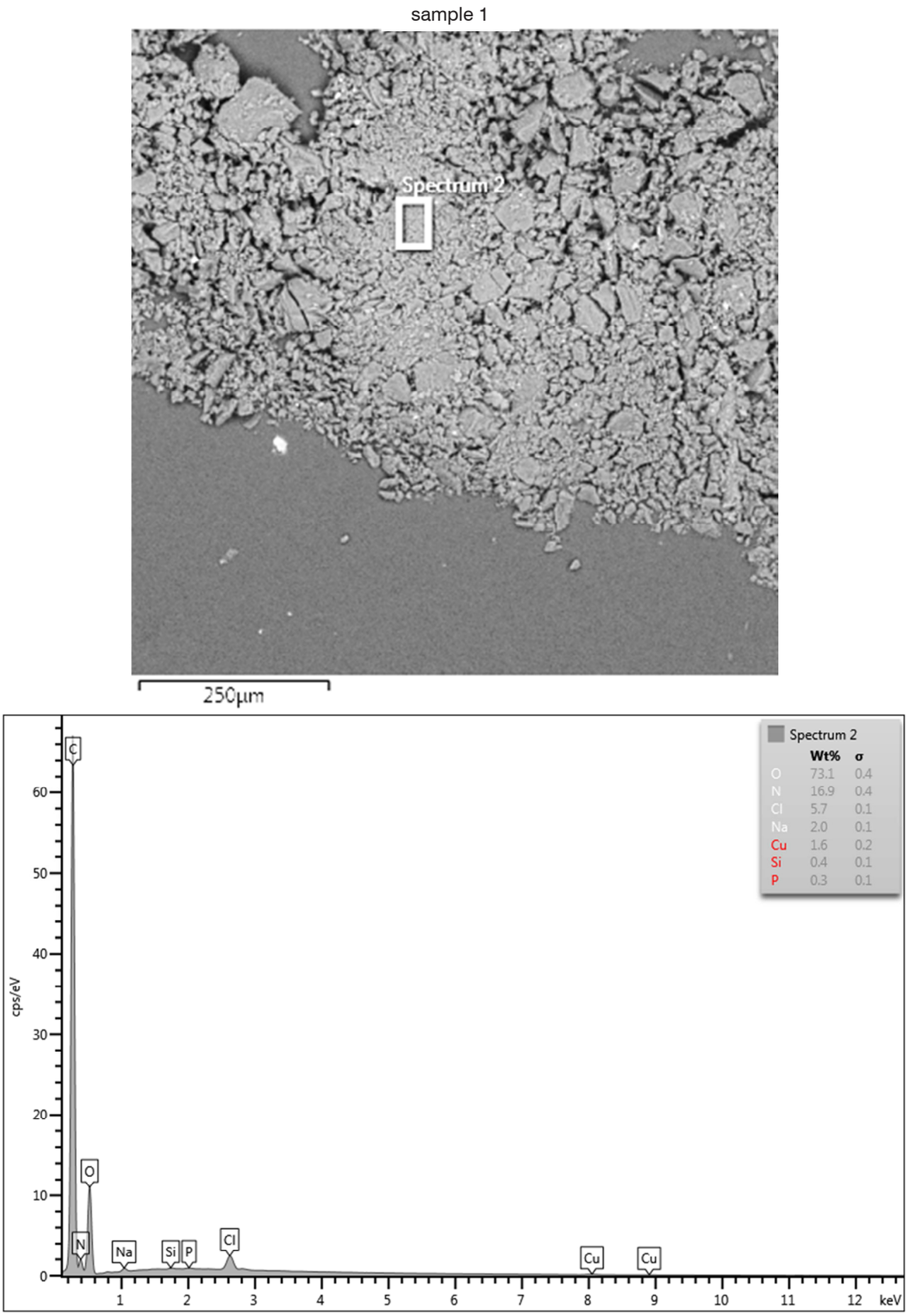


Fig. 8. Result of SEM analysis of a sample containing MDMA – visible nitrogen signals.

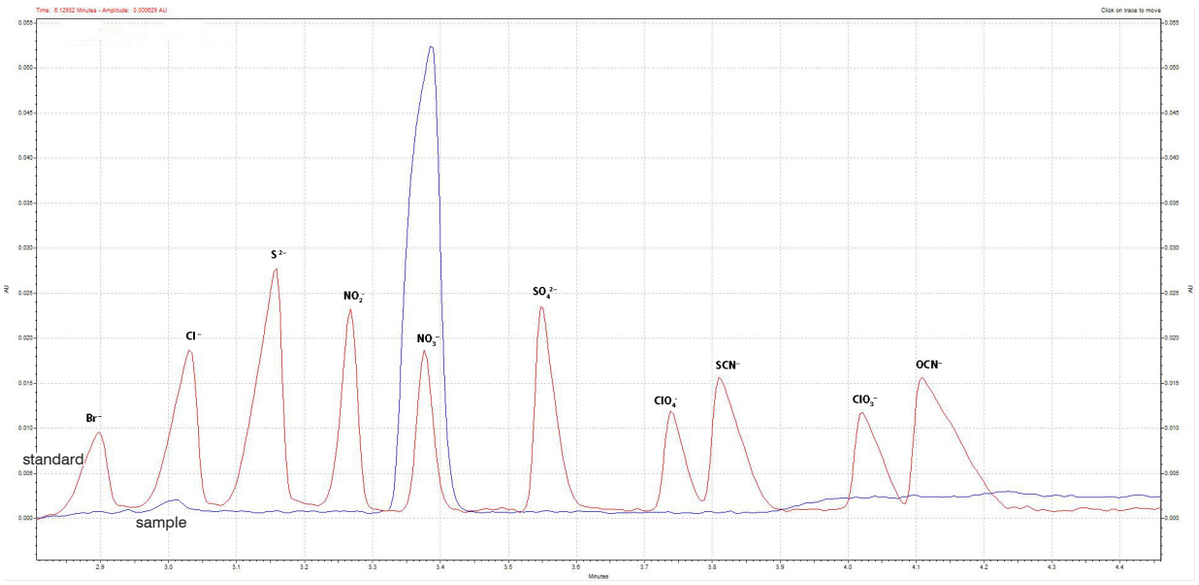


Fig. 9. Result of CE analysis – unambiguous identification of the nitrate anion.

capillary electrophoresis (CE) and scanning electron microscopy (SEM/EDX) techniques. The standard analytical procedures for this type of substance do not provide for so numerous tests. Usually, the analysis is carried out by GC-MS and, additionally, FT-IR method, and it is aimed at confirming the presence of salt. However, as regards the case presented herein, the lack of confirmation by a FT-IR (and XRD) method could have led to a false assumption that the sample contained a different substance (in spite of positive GC-MS identification). In such a situation, the results should be interpreted with caution and, preferably, further test should be carried out by using other instrumental methods.

With respect to the synthetic method used to obtain nitric form of MDMA, it should be concluded that the origin of this compound is uncertain, since none of the known methods lead to this kind of the final product. It is possible that the synthesis occurred by accident and it will never be repeated. However, it could also be a completely new formula of 3,4-methylenedioxymethamphetamine that will make more frequent appearances on the drug market. In the latter scenario, great caution should be exercised, as positive GC-MS identification with the concurrent negative FT-IR identification do not rule out the presence of nitric MDMA in the sample.

Sources of figures:

Figure 1: CLKP
Figures 2–9: authors

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