

## Technical Note

# Instrumental Separation of 3,4-Methylenedioxyamphetamine (MDA) from 1-(3,4-Methylenedioxyphenyl)-2-propanol, a Co-Eluting Compound

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**ABSTRACT:** Analysis of a set of mixed-component Ecstasy tablets by GC/MS indicated an apparent mixture of 3,4-methylenedioxymethamphetamine (MDMA) and 3,4-methylenedioxyamphetamine (MDA); however, the mass spectrum for the MDA did not exactly match an MDA standard. Additional work confirmed that the presumed MDA was actually a co-eluting mixture of MDA and 1-(3,4-methylenedioxyphenyl)-2-propanol. The latter alcohol has a mass spectrum that is highly similar to MDA, but displays a molecular weight peak of 180 (versus 179 for MDA). Varying the temperature programming of the normal GC/MS run separated the alcohol.

**KEYWORDS:** 3,4-Methylenedioxymethamphetamine, MDMA, 3,4-Methylenedioxyamphetamine, MDA, 1-(3,4-Methylenedioxyphenyl)-2-propanol, Ecstasy, GC/MS, Co-Elution

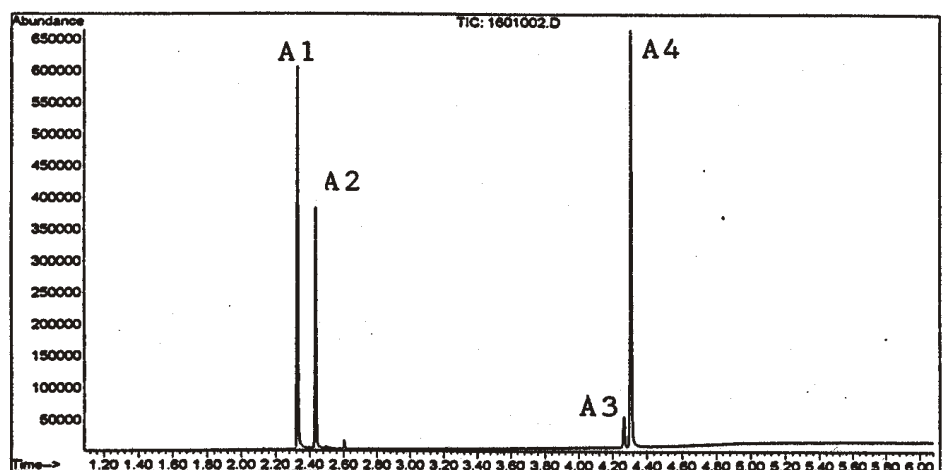
### Introduction

Over the past few years, so-called “Ecstasy” tablets have undergone a dramatic transition in their composition. Five years ago, most Ecstasy tablets contained either 3,4-methylenedioxymethamphetamine (MDMA), 3,4-methylenedioxyamphetamine (MDA), or (less commonly), a mixture of MDMA and MDA. More recently, however, Ecstasy tablets have often contained complex mixtures of controlled substances, control substance analogues, alternate abused substances, adulterants, diluents, and manufacturing impurities and byproducts. These mixed component tablets can offer unusual analytical challenges.

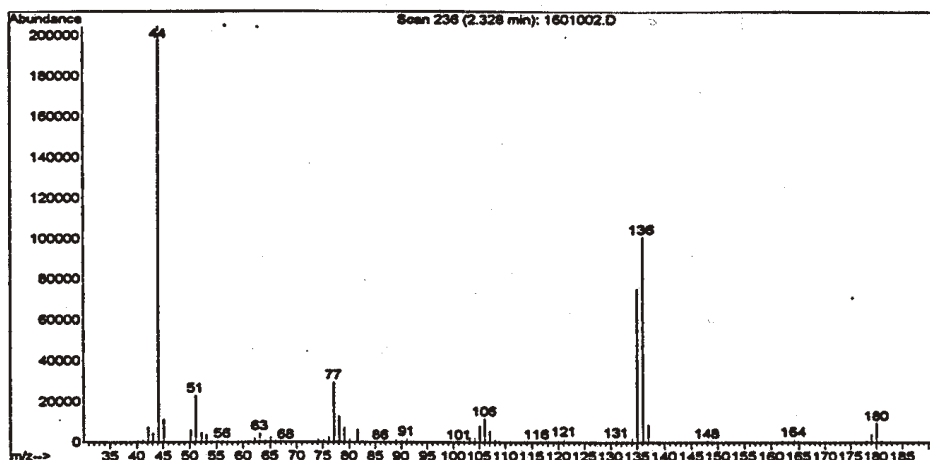
In late 2001, this laboratory received an exhibit consisting of 11 white tablets with a three-point crown imprint on one side and unmarked on the other side (photo not available), total net mass 3.3 grams. The exhibit was seized just north of Tampa, Florida, but had no other associated source information. Analysis was conducted by color testing (Marquis, cobalt thiocyanate, and Dille-Koppanyi), thin layer chromatography (TLC) (Clarke’s TB developer, visualized with acidified iodoplatinate), and gas chromatography/mass spectrometry (GC/MS). The color test results were consistent with typical (MDMA) type preparations. The Marquis test showed the usual purple, blue, and green colors, and the cobalt thiocyanate gave a slight blue reaction. After elution, spraying, and development, the TLC showed two spots consistent in both color and  $R_f$  to MDMA and MDA; however, a third spot was also noted. The first GC/MS run revealed four peaks, one with a retention time and mass spectrum corresponding to MDMA, a second with a retention time and mass spectrum very similar to MDA but with an apparent molecular ion at 180 instead of the expected 179 (for MDA), and two unknowns that did not correspond to any known controlled substances and were therefore not further analyzed. Closer examination of the “MDA” mass spectrum indicated that the fragment ion ratios at 135 relative to 136, and at 106 relative to 105, both appeared to be slightly higher than normally expected for MDA. The sample was then injected on a second GC/MS to determine if the anomalous results were an instrumental variation or a glitch of some type in the run. The second GC/MS run again revealed the same four peaks (see Figure 1, next page); the first compound (designated “A1” on Figure 1) had a retention time and mass spectrum very similar to MDA but still with the

apparent molecular ion at 180 instead of the expected 179. The second peak (designated "A2" on Figure 1) had a retention time and mass spectrum corresponding to MDMA. The two additional peaks ("A3" and "A4" on Figure 1) were also still present, but were not identified. The mass spectra of A1 through A4 are shown in Figures 2 - 5.

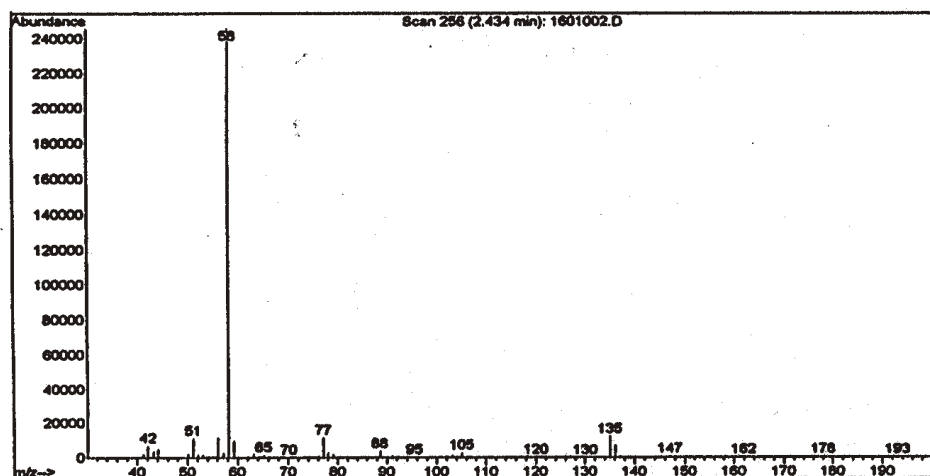
**Figure 1.**  
**Total Ion Chromatogram**



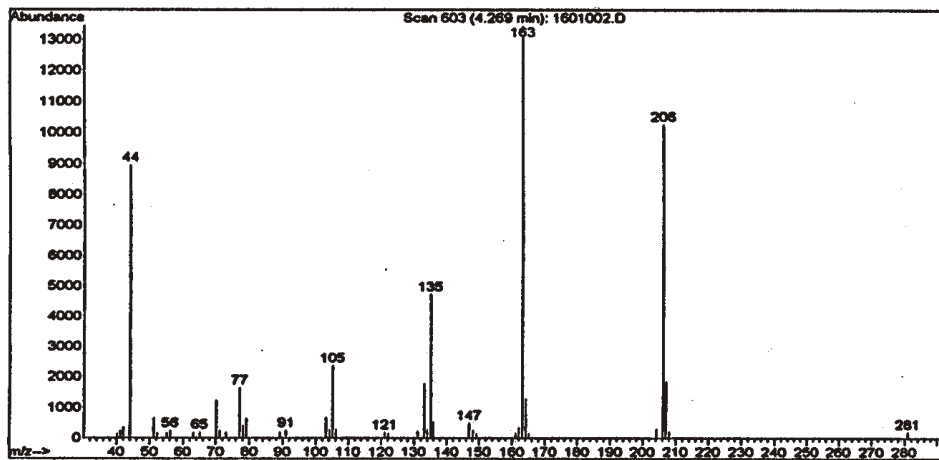
**Figure 2.**  
**Mass Spectrum of Compound A1 (Anomalous MDA).**



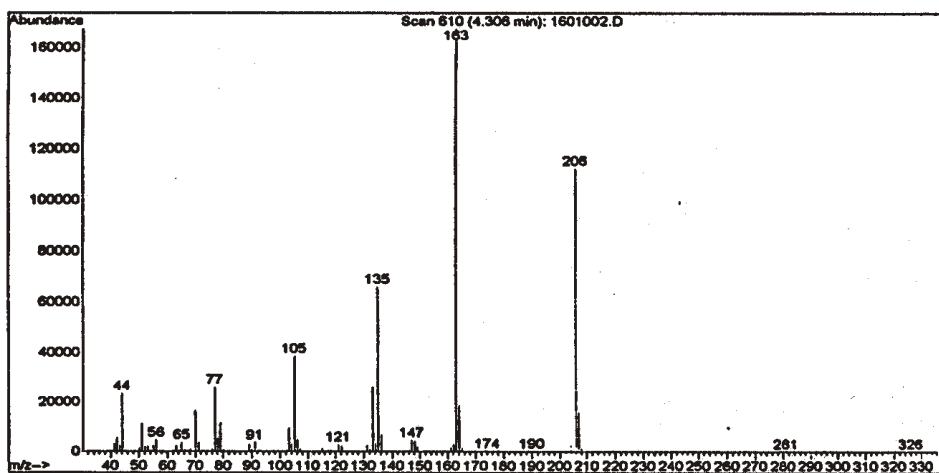
**Figure 3.**  
**Mass Spectrum of Compound A2 (MDMA)**



**Figure 4.**  
**Mass Spectrum of**  
**Compound A3 (Unknown)**

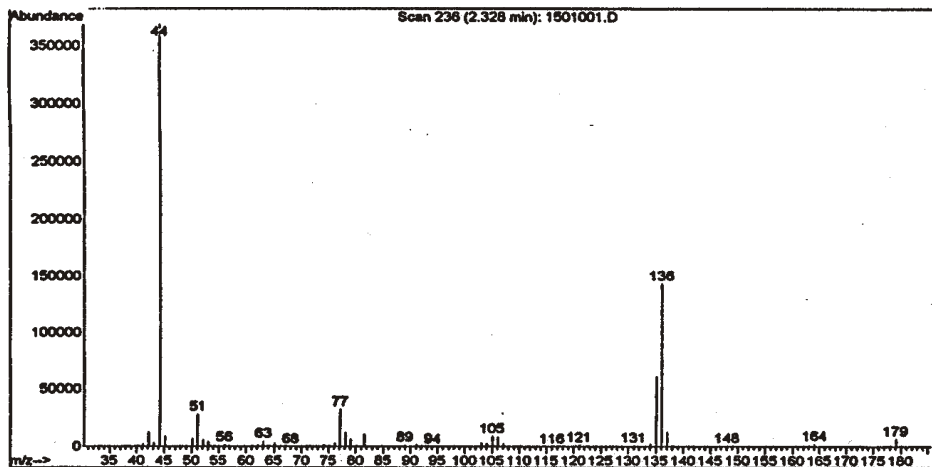


**Figure 5.**  
**Mass Spectrum of**  
**Compound A4 (Unknown;**  
**expanded to display possible**  
**molecular ion at m/z = 326)**



A standard of MDA was then run on the second GC/MS, and the resulting spectra was found to be normal (i.e., displaying a typical MDA spectrum with a “proper” 179 molecular ion (See Figure 6). Since the mass spectrum of standard MDA run on the same instruments in the same time frame did not match the unknown, it was clear

**Figure 6.**  
**Mass Spectrum of**  
**MDA Standard Under**  
**Identical Conditions**



that this could not be a simple instrumental variation of the MDA spectrum. A literature search of mass spectra found no matches. The question then arose: Was the second component actually an unknown substance, or was the anomalous spectrum the result of a compound co-eluting with MDA? The presence of a third compound by TLC analysis suggested the possibility of a co-eluter.

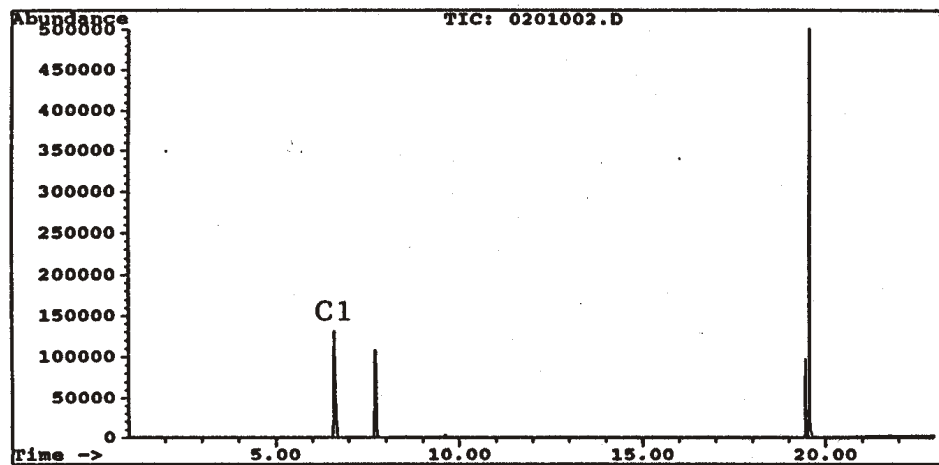
### Experimental

Two GC/MS instruments were utilized in the study. The first was an Agilent 5973 Mass Spectrometer interfaced with an Agilent 6890 Gas Chromatograph equipped with a 12 meter capillary column of 0.20 mm i.d. and having a 0.33  $\mu\text{m}$  film thickness of methyl silicone. The temperature program was 100°C held for one minute, then ramped at 75°C per minute to 200°C, then ramped at 50°C per minute to 325°C, held for one minute. The second was a Hewlett Packard 5971A Mass Spectrometer interfaced with a Hewlett Packard 5890 Gas Chromatograph also equipped with a 12 meter capillary column of 0.20 mm i.d. and having a 0.33  $\mu\text{m}$  film thickness of methyl silicone. The temperature program was 100°C with no hold, ramped at 5°C per minute to 200°C, then ramped at 25°C per minute to 325°C, held for two minutes.

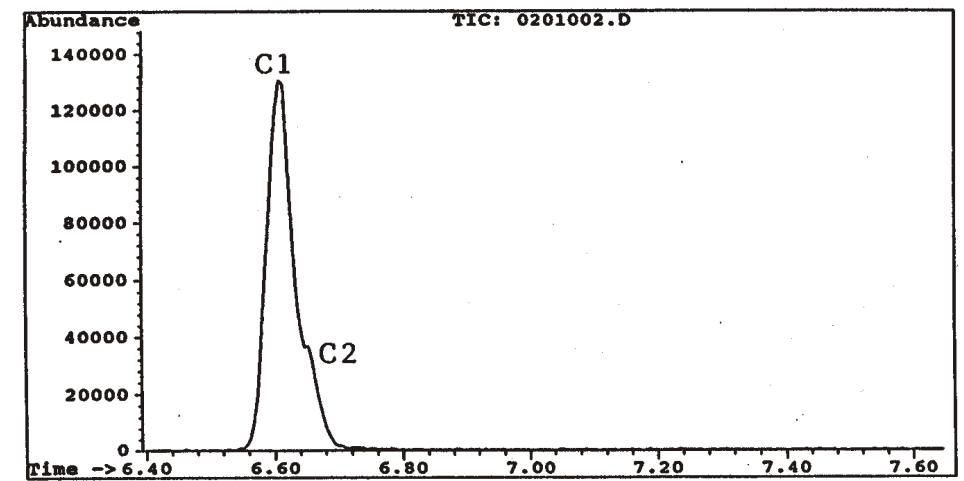
### Results and Discussion

The color testing, TLC, and GC/MS results excluded common manufacturing byproducts or “mistakes” such as N-hydroxy-3,4-methylenedioxyamphetamine or 1-(3,4-methylenedioxyphenyl)-2-propanone-oxime. However, an unusual impurity 1-(3,4-methylenedioxyphenyl)-2-propanol had been identified in another recent case seen in this laboratory. This compound can result from reduction of excess 1-(3,4-methylenedioxyphenyl)-2-propanone in botched clandestine syntheses. 1-(3,4-Methylenedioxyphenyl)-2-propanol has a molecular weight of 180, and a base peak of 135. The mass units for the remaining peaks are nearly identical to MDA, though their abundances vary. To determine if the MDA mass spectrum anomaly was in fact the result of a co-elution with 1-(3,4-methylenedioxyphenyl)-2-propanol, the sample was injected onto the Hewlett Packard 5971A mass spectrometer with a much slower temperature programming (i.e., 5°C per minute from 100 to 200°C, then ramped at 25°C per minute to 325°C, held for two minutes). There still appeared to be a single peak for the MDA area on the ion chromatogram (see Figure 7), but the mass spectrum of the suspected MDA (taken at the peak) was now normal. However, by expanding the peak on the computer screen, a shoulder became visible (see Figure 8). The mass spectrum of this shoulder (Figure 9) was that of 1-(3,4-methylenedioxyphenyl)-2-propanol, confirmed by comparison to a spectrum copy obtained from Drug Enforcement Administration’s Southeast Laboratory (Miami, Florida). Though the peaks did not fully resolve even using the slower temperature programming, they were separated enough to obtain identifiable mass spectra for both MDA and 1-(3,4-methylenedioxyphenyl)-2-

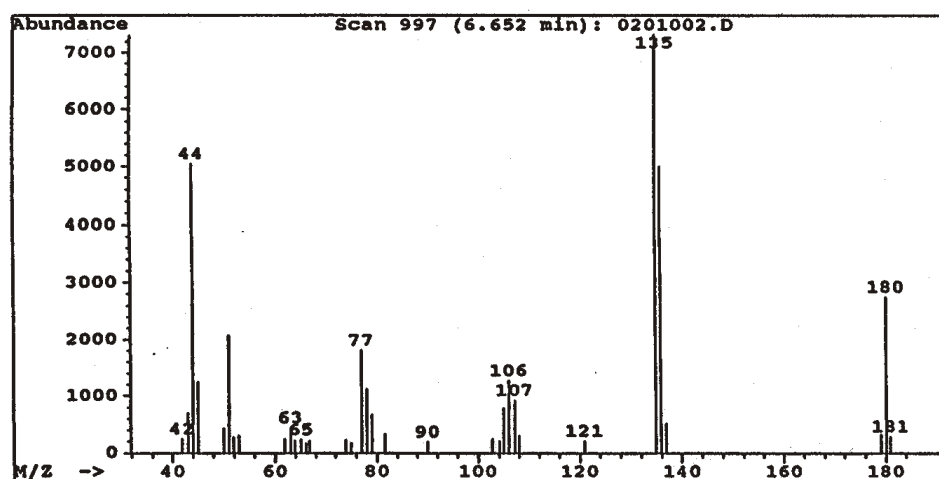
**Figure 7.**  
**Total Ion Chromatogram**  
**at Slow Temperature**  
**Programming**



**Figure 8.**  
Expanded Total Ion  
Chromatogram at  
at Slow Temperature  
Programming



**Figure 9.**  
Mass Spectrum of  
1-(3,4-methylenedioxy-  
phenyl)-2-propanol



propanol, allowing for a positive identification of the controlled substance. Since the alcohol is not controlled, further analyses (e.g., acid/base shakeouts or derivatization studies) were not required; however, such procedures could be useful for other laboratories who encounter similar mixtures or who wish to more formally isolate and identify 1-(3,4-methylenedioxyphenyl)-2-propanol.

Based on the peak heights as measured by the Agilent 5973 (total ion chromatogram), the extracted components in the mixture were approximately 22% MDMA, 35% MDA, and 3% 1-(3,4-methylenedioxyphenyl)-2-propanol, and 40% other, unidentified components (there may also have been other components which did not extract). To date no other samples of this particular mixture have been encountered at this laboratory.

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