

Application Note

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Abstract

With chemists engineering new “designer drugs” everyday, law enforcement and regulatory bodies need testing to quickly and accurately determine the composition of these compounds. This study will present a static headspace method for rapidly determining drug components for use in forensic applications. A Teledyne Tekmar HT3 Headspace Analyzer will be used to examine bath salt samples for the presence of mephedrone (MPD) and methylenedioxypropylvalerone (MPDV or MDPK) by GC/MS.

Introduction

The illegal drug world has evolved over the last couple of centuries. Newly discovered “wonder” drugs such as morphine, heroin and cocaine fueled the first American drug abuse and addiction epidemics in the 19th century. For the most part, these were all derivatives of naturally occurring substances. By the start of the 20th century, this first illegal drug epidemic was virtually forgotten through domestic law enforcement and a worldwide campaign to limit opium and coca crops¹. The drug epidemic resurfaced in the 1960’s when drugs like marijuana, amphetamines and other psychedelics appeared on the market. With the explosion of the drug culture, the U.S. Drug Enforcement Administration (DEA) was formed in 1973 to enforce federal drug laws. Since then, the DEA and legislators has continually been tested by members of society who modify known mind-alternating substances to create new “legal” drugs, typically identified as designer drugs.

The latest designer drug, appearing on the market after the most recent K2 rage, is bath salts. Marketed under names such as Rave On, Loco Motion, Ivory Wave, Bliss, and White Lightning, the salts are absorbed into the body by the typical methods such as snorting, smoking, or ingestion of the powder². Bath salts are marketed as “not for human consumption.” The label typically states “For bathing use only. Never for human consumption. Only 30-50 g recommended per bath.” This label, “Not for Human Consumption”, skirts the US federal Analog Act which is part of the Comprehensive Drug Abuse Prevention and Control Act of 1970³, which makes it illegal to produce, possess, consume and sell substances considered analogs of banned drugs.

The cost of some locally obtained bath salts were \$20 for 0.5 g. At that price, one bath using these salts would cost \$2,000. The labeling gives the seller the apparent legal right to sell the salt, however the bath salts have been found to contain drugs including mephedrone (MPD) and methylenedioxypropylvalerone (MPDV or MDPK). MPD and MDPV are derivatives of methcathinone, which is the oxidation derivative of either ephedrine or pseudoephedrine⁴. The raw sample may also contain other compounds of interest that can assist in the medical care of an overdosed patient or for prosecution of the manufacturer. Static headspace with the Tekmar HT3 can accomplish this. The raw powder is added to the headspace vial and heated to equilibrium. The headspace is then sampled by the static option and injected onto the GC/MS to obtain a fingerprint of any compound that might be present in the sample. Static headspace is a common technique in many labs performing this type of drug analysis for blood alcohols.

For this study, two under-the-counter bath salt samples, Bath Salt 1 and Bath Salt 2, were obtained at a local gas station. Standards of MDPV and MPD were also obtained to determine their headspace GC/MS profile.

Experimental-Instrument Conditions

The HT3TM headspace instrument was connected to Thermo Scientific Focus GC with DSQII Mass Spectrometer for this study. A Thermo TR-5ms SQC column, 15m x 0.25mm x 0.25µm film thickness was used for the characterization of the powders. The instrument parameters are listed in Tables 1 and 2.

HT3 Headspace Instrument Parameters			
Variable	Value	Variable	Value
Constant Heat Time	On	Pressurize	15 psig
GC Cycle Time	55 min	Pressurize Time	2.00 min
Platen/Sample Temp	100°C	Pressurize Equil Time	0.20 min
Valve Oven Temp	200°C	Loop Fill Pressure	10 psig
Transfer Line Temp	200°C	Loop Fill Time	2.00 min
Standby Flow Rate	50mL/min	Inject Time	1.00 min
Sample Equil Time	20.00 min		

Table 1: Static HT3™ Parameters

Thermo Focus DSQ II GC/MS Parameters	
Column	Thermo TR-5ms SQC, 15 m x 0.25mm ID x 0.25 µm Film Thickness, Helium Carrier Gas, Constant Flow 1.5 mL/min
Inlet	Split Flow 15mL/min
Oven Program	35°C for 2 min; 12°C/min to 320°C, hold for 10 min
MS Source Temp	230°C, Transfer Line 230°C
Mass Range Parameters	Full Scan 35.0 to 500.0, Scan Rate 1492.11, Chrom Filter Width 2.5 Sec
FID	320°C, Hydrogen Flow 35.0mL/min, Air Flow -400.0mL/min, Constant Column and Makeup Flow – 30mL/min

Table 2: GC/MS Parameters

Standard Sample Preparation

3,4-Methylenedioxypropylvaleron HCL (MDPV) and mephedrone (MPD) were obtained from Cerrilliant as 1mg/mL solutions as the free base. 5µl was added to a 22mL headspace vial and sealed. Caffeine powder was obtained from Aldrich Chemical Company and a small amount of the dry powder was added to a headspace vial as a reference. 50 mg of each bath salt powders were added to separate 22mL headspace vials and sealed.

Results and Conclusions

Both bath salt samples showed numerous peaks of interest. The individual bath salts were compared to the three available standards. Figure 1 shows the comparison of the total ion current of the MDPV, caffeine and Bath Salt 1. Bath Salt 1 was found to have MDPV (13.87, 17.12 and 17.46 min RTs), caffeine (14.72 min) and two unidentified compounds (13.68 and 14.89 min RTs). The mass spectra of the 3 peaks observed in the MDPV standard were consistent with the three peaks in the sample, as was the caffeine. Figure 2 and 3 show the spectra of the two unidentified compounds. The MDPV was confirmed to be about 26% of the sample concentration using LC/MS/MS.

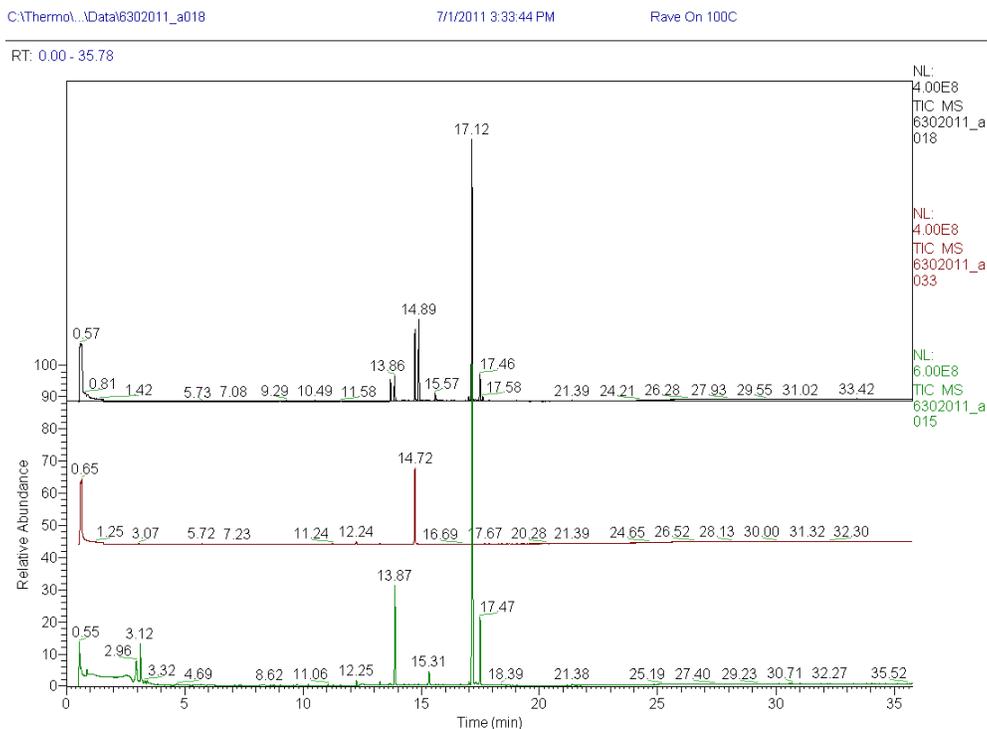


Figure 1: TIC Comparison of MDPV (green), Caffeine (red), and Bath Salt 1 (black).

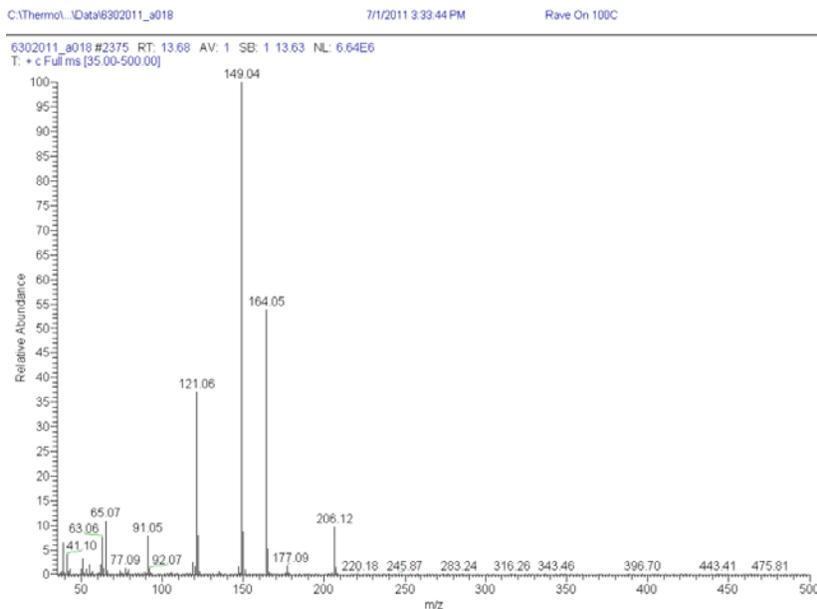


Figure 2: Mass Spectrum of Unidentified Compound in Bath Salt 1.

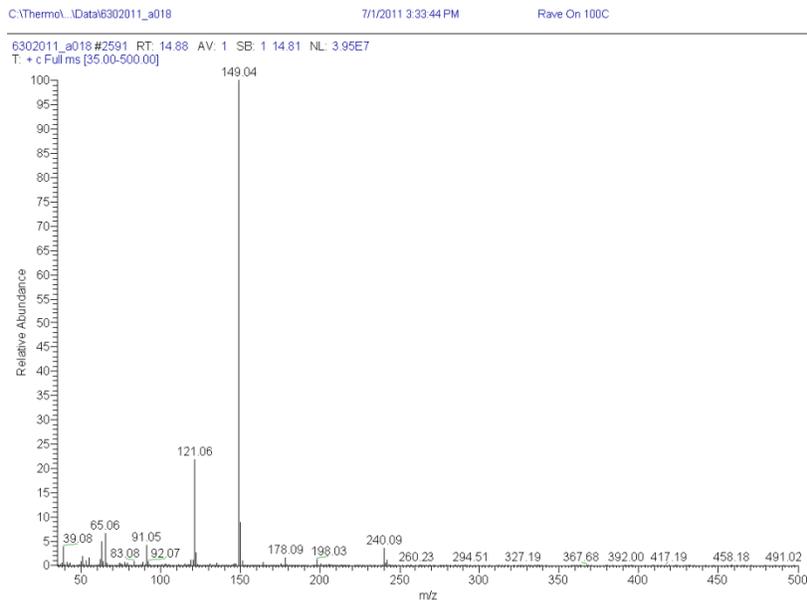


Figure 3: Mass Spectrum of Unidentified Compound in Bath Salt 1.

Figure 4 shows the comparison of the total ion current chromatograms of Bath Salt 2, the MDPV, MPD, and caffeine standards. The sample was found to contain MDPV (13.85 and 17.11 min RTs) and caffeine (14.71 min) and confirmed by MS spectra match. The mass spectrum of MDPV in the bath salt can be found in Figure 5. MDPV was confirmed to be approximately 8% of the sample using LC/MS/MS analysis.

Numerous other unidentified peaks were also observed in this sample. Their spectra are listed in Figures 6-10. These spectra are presented to demonstrate the HT3's ability to uncover other synthetic drugs in bath salts that may or may not yet be identified.

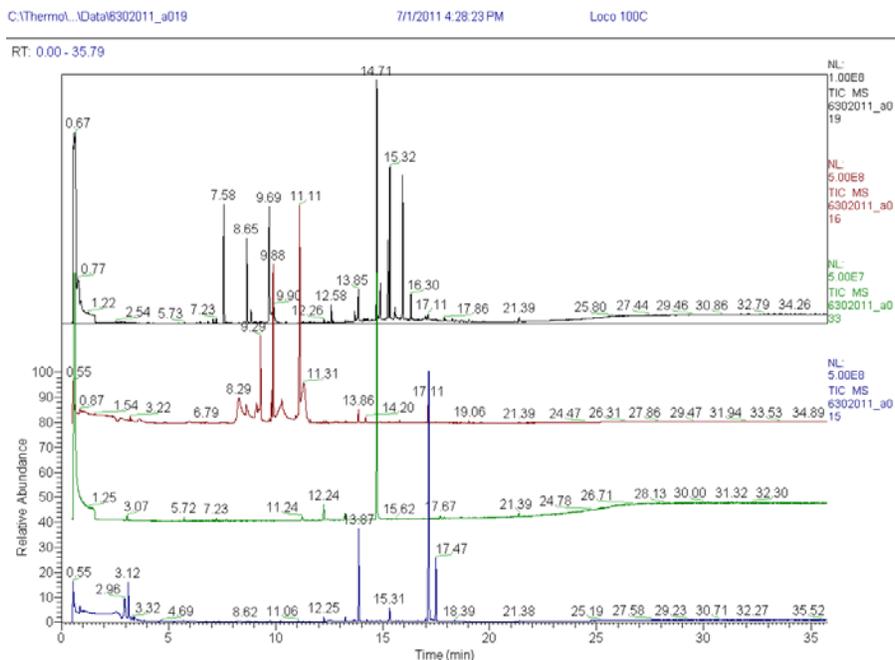


Figure 4: TIC Comparison of MPD (red), Caffeine (green), MDPV (blue), and Bath Salt 2 (black).

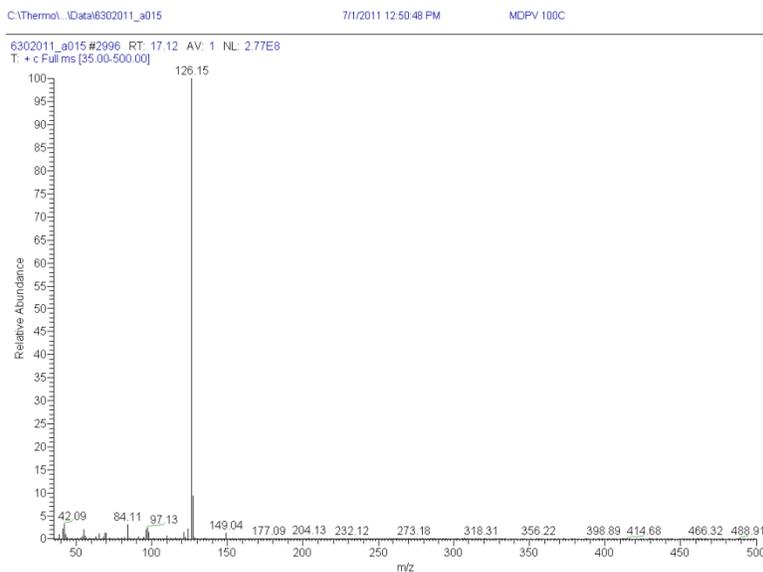


Figure 5: Mass Spectrum of MDPV found in Bath Salt 2.

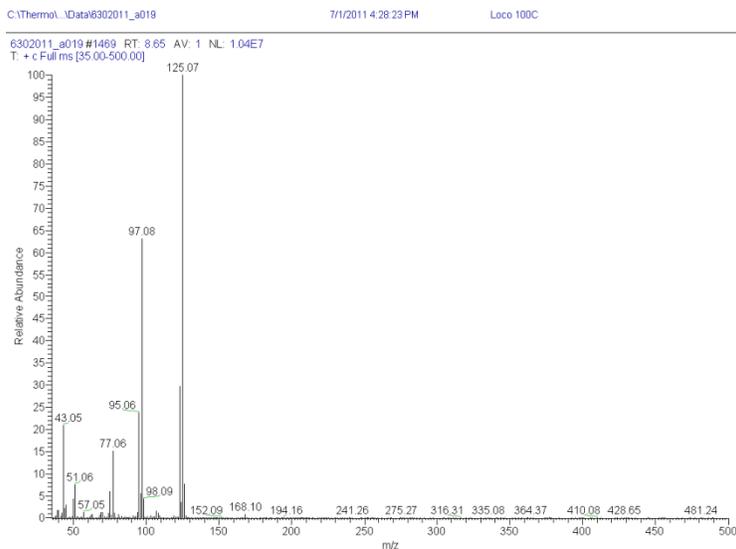


Figure 6: Mass Spectrum of Unidentified Compound in Bath Salt 2.

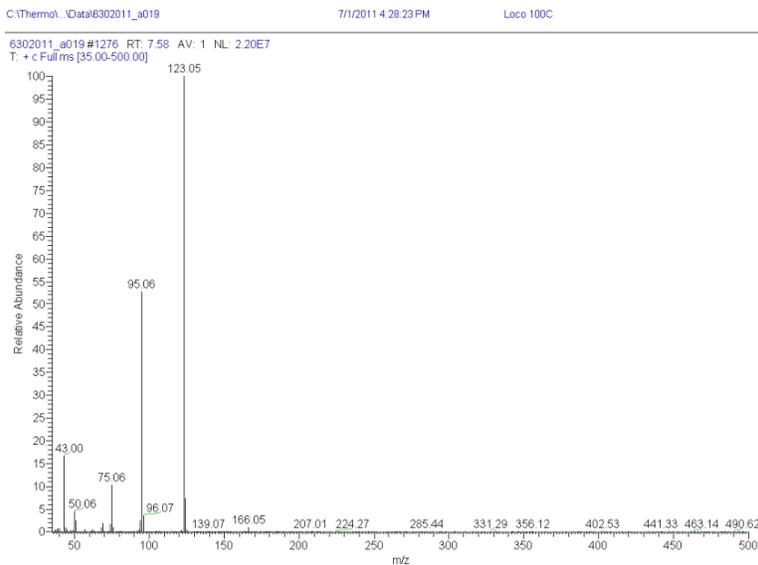


Figure 7: Mass Spectrum of Unidentified Compound in Bath Salt 2.

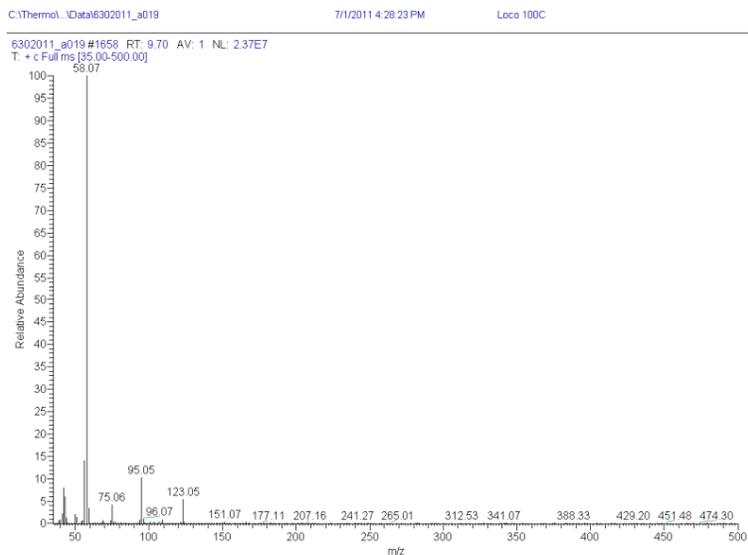


Figure 8: Mass Spectrum of Unidentified Compound in Bath Salt 2.

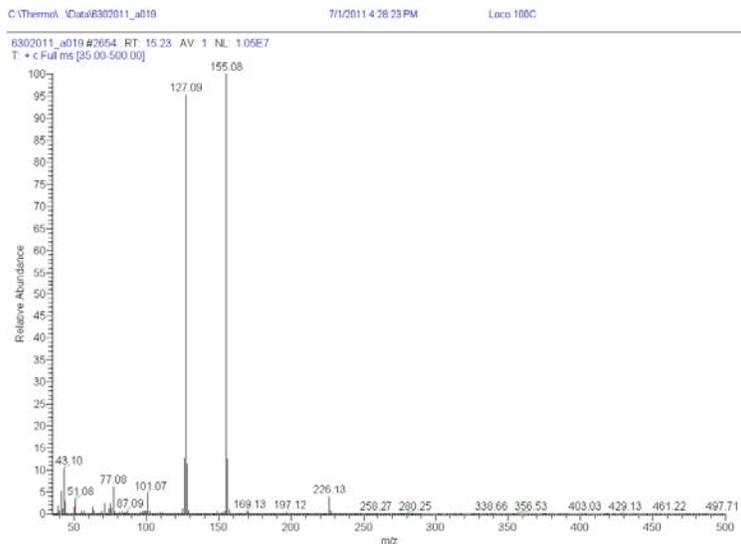


Figure 9: Mass Spectrum of Unidentified Compound in Bath Salt 2.

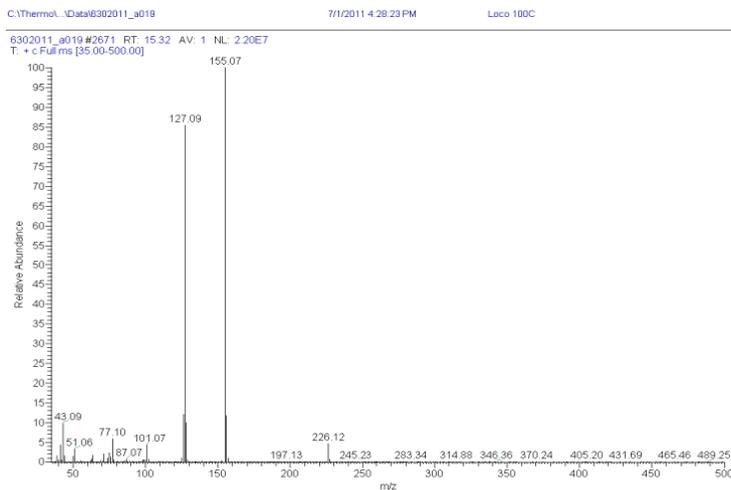


Figure 10: Mass Spectrum of Unidentified Compound in Bath Salt 2.

With the drug formulations constantly changing, very little toxicological or pharmacological testing has been done on these designer drugs. Determining the composition of these drugs could be a matter of life and death. The characterization of the components of bath salts can assist in the treatment of overdosed patients and as well as the determination of the manufacturing sites that produce these mixtures. The dry headspace samples allow excellent detection of MDPV, and potentially other designer drug components, in the sample. This technique has implications as a screening procedure for law enforcement and regulatory bodies. Using Teledyne Tekmar's HT3 Headspace Analyzer, bath salts and other designer drugs can be characterized rapidly and without interferences associated with these potentially difficult matrices.

References

- 1) "Illegal Drugs in America: A Modern History", United States Drug Enforcement Administration, http://www.deamuseum.org/museum_ida.html.
- 2) "Bath Salts' A Growing Drug Problem, Officials Say", Byrd, Sheila, Huffington Post Health, Jan. 22, 2011.
- 3) "Controlled Substances Act", Title 21, Chapter 13, United States Drug Enforcement Administration, 2010.
- 4) "Bath Salts Hit Bangor, or why you should care about 3,4-methylenedioxypropylvalerone (MDPV) and 4-methylmethcathinone (mephedrone)", Busko, Jonnathan, MD, 2011, <http://www.northeastems.org/blog>