J Forensic Sci, Nov. 2004, Vol. 49, No. 6
Paper ID JFS2004200
Available online at: www.astm.org

CASE REPORT

Joseph Avella,[1] *M.S. and Michael Lehrer,*[2] *Ph.D.*

Fatality Due to Methyl Acetylene-Propadiene (MAPP) Inhalation

ABSTRACT: A 33-year-old man died after intentionally inhaling a gaseous mix of methyl acetylene (propyne) and propadiene (allene) commonly known as MAPP, which is used for soldering and welding. He was found with a plastic bag securely placed over his head and a cylinder of MAPP alongside his head. The cylinder had been vented into the bag using a flexible hose. A comprehensive toxicological analysis revealed only a trace of diphenhydramine in the liver and 0.02 mg/L of morphine in the urine. Analysis of blood by headspace gas chromatography (HS-GC) detected two unknown peaks. These were determined to be the components of MAPP gas. MAPP was quantitated in femoral blood (59.6 mg/L) and brain (43.6 mg/kg) using a HS-GC method. The cause of death was attributed to acute MAPP intoxication, and the manner was determined to be suicide. A discussion on the analytical and interpretive considerations commonly encountered when analyzing volatile compounds is also presented.

KEYWORDS: forensic science, forensic toxicology, methyl acetylene, propadiene, MAPP, volatile abuse

Misuse of volatile compounds leading to death has been reported periodically in the literature. Many reports have detailed accidental deaths that resulted from the abuse of inhalants ("huffing") for their euphoric effects (1–10). In such cases, the use of surgical anesthetics and halogenated hydrocarbons is common, as is abuse of solvents. Reported use of volatiles to facilitate suicide has included propane and helium (11–13). Here we report what we believe to be the first documented case of suicide by intentional exposure to methyl acetylene-propadiene (MAPP) gas. MAPP is an isomeric mixture of methyl acetylene (propyne) and propadiene (allene) with the chemical formula C_3H_4 and weighing 40.07 amu (14). These flammable gases are used for soldering and welding. Like other gases, inhalation is the primary route of exposure, though dermal absorption is possible. Once absorbed via the lungs, distribution is rapid. Elimination is accomplished primarily by pulmonary excretion. MAPP can act as a simple anesthetic and in high concentrations will asphyxiate by displacement of oxygen rather than by blocking the action of hemoglobin or cytochrome oxidase (11,15,16). The NIOSH time weighted exposure limit is given as 1000 ppm (1800 mg/m^3) (17). A literature search using PubMed found no reports of the use of MAPP as an abused inhalant or as a vehicle for suicide. If any previous inappropriate use of MAPP has led to death, it appears to have gone unreported or undetected. MAPP is readily available to the public. The authors were able to purchase it during a visit to the local home center store where it is sold for home plumbing projects.

[1] Toxicologist, Department of Forensic Toxicology, Suffolk County Office of the Medical Examiner, Hauppauge, NY.
[2] Chief Toxicologist, Department of Forensic Toxicology, Suffolk County Office of the Medical Examiner, Hauppauge, NY.
Received 8 May 2004; and in revised form 25 June 2004; accepted 25 June 2004; published 5 Oct. 2004.

Case History

The decedent was a 33-year-old male with a history of depression and recent suicidal ideations. He was living with his mother for the last couple of months after losing his job and was not receiving treatment for his depression. On the date of his death, the decedent's mother received a call that he had not picked up his school-aged son. After picking up the child, the mother returned home and found a note on the door stating "Don't enter there is propane gas call 911." The deceased was found dead with a plastic bag over his head along with a 16 oz. cylinder of MAPP gas manufactured by Bernz-O-matic®. A small hose attached to the valve had been used to vent the contents of the cylinder into the bag. A suicide note was found at the scene. The postmortem examination was unremarkable. Tissues were collected and submitted for toxicologic analysis. These included blood, brain, liver, urine, vitreous fluid and gastric content. Separate samples of blood, brain, lung, kidney, and adipose were immediately sealed in 10 mL headspace vials and stored at −20°C.

Experimental

Toxicological Analysis

A general unknown toxicological analysis was performed. Toxicological analyses included immunoassay of urine using EMIT® for drugs of abuse. The liver was prepared using liquid/liquid extraction and submitted to gas chromatography/mass spectrometry (GC/MS) for basic drug analysis. Aortic blood was extracted and analyzed by GC/MS for weak acids and neutrals. In addition, femoral blood was analyzed using a capillary gas chromatograph with flame ionization detector (GC/FID) equipped with a headspace autosampler for common volatiles.

MAPP Analysis

Autopsy tissues collected in 10 mL headspace vials were sealed with Teflon caps, and the vials were stored at –20°C until analysis.

Specimens were analyzed using a GC/FID method. Blood calibrators and controls were prepared by first sealing 2 mL of negative blood in four 10 mL headspace vials. A gas tight cylinder was purged with MAPP gas obtained from Bernz-O-matic®, allowed to come to equilibrium, and sealed (purchase of individual pure standards was cost prohibitive). According to Charles' law, one mole of gas will occupy 24.45 L at 25°C. Using 40.07 g/mole (the molar weight of the MAPP gases), the resulting relationship is 1.638 g/L. With a gas tight syringe 50, 100, and 200 μL of MAPP from the gas tight cylinder was added to the headspace vials containing 2 mL of negative blood, creating calibrators containing 0.0, 40.9, 81.9, and 163.8 mg/L of MAPP. After a separate preparation of MAPP in a gas tight cylinder, a positive control containing 61.4 mg/L was prepared by adding 75 μL to another sealed vial containing 2 mL of negative blood. A negative control was also prepared. The calibrators and controls were frozen at −20°C until analysis.

To determine the amount of the autopsy samples received, an electronic balance was tared with a clean headspace vial/cap, and then the selected autopsy samples were weighed. The samples contained 4.2 mL of femoral blood and 2.4 g of brain.

All specimens were analyzed using a Hewlett Packard 5890 gas chromatograph with flame ionization detector and equipped with a 7694 headspace autosampler. The samples were equilibrated at 40°C for 15 min prior to the injection using a 1 mL sample loop. The vial parameters in minutes were as follows: pressurization 0.15, loop fill 0.15, and sample inject 0.25. The GC column was a 30 m, 0.53 mm, ID Restek RTX-BAC1®. The GC oven temperature was 40°C (isothermal) with injector and detector temperatures set at 200°C and 225°C, respectively.

Methyl acetylene and propadiene were analyzed simultaneously. Each injection produced two peaks, corresponding to methyl acetylene and propadiene (reported as MAPP). For each calibrator, the area under the curve (AUC) of both peaks was summed and plotted against the concentration. The resulting linear regression had a correlation coefficient of 0.9998. The targeted value of the positive control was 61.4 mg/L. The calculated value was 59.5 mg/L. Analysis of the MAPP free control was negative. The concentration of MAPP in the other unknowns was then calculated by plotting the AUC and correcting for volume and sample weight.

Results and Discussion

Urine immunoassay results were elevated for opiates. The laboratory defines elevated results as those whose change in absorbance is above the negative control but below the cutoff calibrator. Subsequent quantitative GC/MS analysis for codeine, hydrocodone, hydromorphone, morphine, and 6-monoacetylmorphine in blood and urine detected only 0.02 mg/L of free morphine in the urine. A trace amount of diphenhydramine was detected in liver, which was not quantitated. The GC/MS analysis for weak acids and neutrals in pulmonary artery blood was negative. Volatile analysis did not detect any ethanol, methanol, isopropanol, or acetone, but did detect two unidentified peaks in femoral blood. These were later identified as the two-component mixture of MAPP that was quantitated by GC/FID.

To quantify MAPP we employed a method in agreement with those described by Wagner et al. and Foerster et al. (18,19). The use of blood based calibrators and controls was beneficial in minimizing potential error due to partitioning. MAPP was quantified in femoral blood (59.6 mg/L) and brain (43.6 mg/kg).

No comparable reports on MAPP were found in the literature, so results cannot be correlated to other findings. However, the circumstances surrounding the scene are highly suggestive of suicide, including recent verbal ideation and the presence of a suicide note. The postmortem examination was unremarkable. A moderate amount of slightly frothy hemorrhagic fluid was noted in the lungs and bronchi, consistent with volatile inhalation (20). Based upon the investigation and toxicological findings, the cause of death was attributed to acute MAPP intoxication, and the manner was ruled a suicide.

The analysis of MAPP illustrates some of the analytical and interpretive considerations common to all volatile compounds. Volatile inhalant analyses are improved when specialized sample collection and storage techniques are used (21). A primary reason for concern is the low boiling points (bp) of these compounds. For example, the bps of methyl acetylene and propadiene are –23.3 and –34.0°C, respectively (14). Therefore losses can be expected to occur at temperatures above their bps, unless the samples are stored in containers designed to retain gases. In fact for some volatiles (i.e., fluorocarbons), losses due to inappropriate storage can be greater than from an intact body (22).

If volatile exposure is suspected at the time of autopsy, the immediate collection of samples in sealed vials will improve the chance of detection by stopping any further losses from occurring. If investigators learn of volatile exposure after the autopsy, detection is still possible. The halogenated hydrocarbon 1,1-difluoroethane, bp –24.7°C, was detected in postmortem blood after 6 months of storage in plastic screw top containers that had been first refrigerated at 4°C for several weeks then frozen at –20°C prior to the analysis (4). In such cases, the samples are even less likely to reflect the concentration at the time of death. The analysis of sealed samples should be done with care since analyte is removed during analysis (19), permanently altering the original sample.

Another factor that affects volatiles found in biological samples is the blood or tissue/gas partition coefficient. The retention and therefore detection of volatiles in blood is likely to be due in part to the blood/gas partition coefficient (1). Greater retention in blood is expected of anesthetic gases, such as halothane, diethyl ether, and methoxyflurane, which have higher blood/gas partition coefficients (2.35, 12.1, and 12.1, respectively) relative to those with smaller blood/gas coefficients like nitrous oxide (0.47) (23) that are more likely to be subject to loss due to volatilization. If the blood/gas partition coefficient favors losses, alternate tissues can be used for detection. For example, the blood/gas partition coefficient of cyclopropane is 0.42, but the fat/gas coefficient is 21 (23). If dose or volatile losses are such that cyclopropane is undetectable in blood, detection may still be possible in fat.

Besides the effect on concentration and detection, the partition coefficient is also important during analysis. Quantitative methods analyzing compounds that have different partition coefficients in various tissues are likely to be biased unless reference material is matrix matched. An investigation of the effect of partitioning on a headspace method used to quantitate aliphatic alcohols demonstrated both positive (methanol as much as +13.6%) and negative (n-butanol as much as –8.0%) bias when these alcohols were measured from brain using aqueous calibrators (24). The error was due to partition variation of both the analyte and the internal standard, the selection of which should therefore be made to minimize error. The method we used to quantitate MAPP employed blood calibrators. The blood/gas partition coefficient of MAPP was unknown but was assumed to be low like other low molecular weight hydrocarbons (ethylene 0.14, cyclopropane 0.42) (23), the result being that most of the gas was in the headspace at 40°C. If analytical error due to partitioning was responsible for the lesser amounts of MAPP detected in brain is unknown but possible.

Data interpretation is problematic when confronted with infrequently encountered compounds like MAPP. The toxicokinetic parameters of highly volatile compounds may be complex. Biphasic or multiphasic elimination can occur when, after exposure is discontinued, tissues begin to release any volatile compounds (25). The time between death and autopsy and the conditions that the body is subject to prior to sample collection will affect the concentrations of volatile compounds in tissue. Thus blood concentrations from autopsy samples should not be assumed to correlate with concentrations at the time of death (3). Other investigators have commented on the difficulty in interpreting volatile concentrations in uncontrolled conditions and without knowledge of the time and amount of exposure, especially in the absence of toxicokinetic data (5,8). Interpretation is also more difficult when, as in the case of MAPP, no postmortem data is available in the literature for comparison. The detection of the volatile gas combined with solid investigation may need to suffice in these cases when determining cause and manner of death.

References

1. Kulman JJ, Magliuilo J, Levine B, Smith ML. Two deaths involving isoflurane abuse. J Forensic Sci 1993;38(4):968–71. [PubMed]
2. Burrows DL, Nicolaides A, Stephens GC, Ferslew KE. The distribution of sevoflurane in a sevoflurane induced death. J Forensic Sci 2004;49(2):394–7. [PubMed]
3. Jacob B, Heller C, Daldrup T, Burrig KF, Barz J, Bonte W. Fatal accidental enflurane intoxication. J Forensic Sci 1989;34(6):1408–12. [PubMed]
4. Xiong Z, Avella J, Wetli CV. Sudden death caused by 1,1, difluoroethane inhalation. J Forensic Sci 2004;49(3):627–9. [PubMed]
5. Fitzgerald RL, Fishel CE, Bush LLE. Fatality due to recreational use of chlorodifluromethane and chloropentafluroethane. J Forensic Sci 1993;38(2):476–82.
6. Groppi A, Polettini A, Lunetta P, Achille G, Montagna M. A fatal case of trichlorofluoromethane (Freon 11) poisoning. Tissue distribution study by gas chromatography-mass spectrometry. J Forensic Sci 1994;39(3):871–6.
7. McGee MB, Meyer RF, Jejurikar SG. A death resulting from trichlorotrifluroethane poisoning. J Forensic Sci 1990;35(6):1453–60. [PubMed]
8. Broussard LA, Brustowicz T, Pittman T, Atkins KD, Presley L. Two traffic fatalities related to the use of difluoroethane. J Forensic Sci;42(6):1186–7. [PubMed]
9. Broussard LA, Broussard AK, Pittman TS, Lirette DK. Death due to inhalation of ethyl chloride. J Forensic Sci 2000;45(1):223–5. [PubMed]
10. Isenschmid DS, Cassin BJ, Hepler BR, Kanluen SK. Tetrachloroethylene intoxication in an autoerotic fatality. J Forensic Sci 1998;43(1):231–4. [PubMed]
11. Avis SP, Archibald T. Asphyxial suicide by propane inhalation and plastic bag suffocation. J Forensic Sci 1994;39(1):253–6. [PubMed]
12. Fonseca CA, Auerbach BA, Suarez RV. The forensic investigation of propane gas asphyxiation. Am J Forensic Med Path 2002;23(2):167–9.
13. Gilson T, Parks BO, Porterfield CM. Suicide with inert gases. Addendum to final exit. Am J Forensic Med Path 2003;24(3):306–8.
14. Sax NI, Lewis RJ. Dangerous properties of industrial materials. 7th ed. Vol III. New York: Van Nostrand-Reinhold, 1989;2913,2125.
15. ACGIH: Documentation of the threshold limit values and biological exposure indices. 5th ed. Cincinnati, OH: Am Conference of Govt Ind Hyg, Inc, 1986.
16. Weiss SM, Lakshminarayan S. Acute inhalation injury. Clinics Chest Med 1994;15:103–16.
17. NIOSH pocket guide to chemical hazards. Washington, DC: U.S. Dept. of Health and Human Services, 1990.
18. Wagner SA, Clark MA, Wesche DL, Doedens DJ, Lloyd AW. Asphyxial deaths from the recreational use of nitrous oxide. J Forensic Sci 1992;37(4)1008–15. [PubMed]
19. Foerster EH, Garriott JC. Analysis of volatile compounds in biological samples. J Anal Tox 1981;5:241–4.
20. McBride P, Busuttil A. A new trend in solvent abuse deaths? Med Sci Law 1990;30:207–213. [PubMed]
21. Imani RH, Kemal M. Propane asphyxiation. Am J Forensic Med Path 1986;7:76–7.
22. RC Baselt. Disposition of toxic drugs and chemicals in man. 6th ed. Foster City, CA: Biomedical Publications, 2002;449–50.
23. Goodman LS, Gilman A, Eds. The pharmacological basis of therapeutics. 4th ed. New York: Collier-MacMillan, 1970;60–70.
24. Avella J, Briglia EJ, Manning T, Modesto R. Partition characteristics of aliphatic alcohols as measured from biological samples using headspace gas chromatography. Proceedings of the Annual Meeting of the Society of Forensic Toxicologists; 2001 Sep 29–Oct 5; New Orleans (LA). New Orleans (LA): SOFT, 2001;34.
25. Levine B, Ed. Principles of forensic toxicology. USA: American Association for Clinical Chemistry, 1999;346.

Additional information and reprint requests:
Joseph Avella, M.S.
Suffolk County Office of the Medical Examiner, Toxicology
P.O. Box 6100
North County Complex, Building 487
Veterans Memorial Highway
Hauppauge, NY 11788-0099
Phone: 631-853-5572
E-mail: joseph.avella@suffolkcountyny.gov