Case Report

Death by Paint Thinner

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Abstract

A 38-year-old Caucasian male, reportedly missing for four days, was found dead 40 feet down a steep ravine, apparently after jumping down the cliff. Two rectangular cans of paint thinner, 1-qt and 1-gal sizes, were found in his vehicle at the top of the cliff. The autopsy report indicated that the decedent was normal except for the heart and myocardium, the lung parenchyma, and the gastric and esophageal mucosa. The stomach contents revealed a brownish liquid with a nearly clear, thick, oily film, and the small and large bowels showed oily liquid with a strong odor of a petroleum distillate. Toxicological analysis was negative for ethanol and common drugs of abuse. Valproic acid, diphenhydramine, and norsertraline where found in therapeutic concentrations, and sertraline, diazepam, and nordiazepam were found in subtherapeutic levels. Bupropion metabolites were also detected. Static adsorption-elution, commonly used in fire debris analysis, was used to examine the brain, liver, lung, blood, and urine. A liquid–liquid extraction was performed on the vitreous humor. The stomach contents and samples from the paint thinner cans were diluted with carbon disulfide. All but the blood and vitreous contained a medium petroleum distillate. The stomach content was consistent with the liquid from the one-gallon can. Chromatograms suggest differential metabolism and/or distribution among the different organs.

Introduction

The most common requests received in the forensic toxicology laboratory relates to drugs of abuse (including alcohol), over-the-counter medications and prescription medications, and therefore, all our efforts and facilities focus on their analysis. The case reported in this paper provided the opportunity to join efforts of the Toxicology Section with the Trace Evidence—Fire Debris Analysis Section of our laboratory and use methodology routinely used in suspected arson cases. The decedent had shown depressive symptoms over a recent divorce and had been admitted for suicidal ideations four months previously, with continuous psychiatric consultations after admittance. He reportedly received Haldol®, lithium, Zyprexa®, and Dilantin® for his condition. He was found at the bottom of a cliff with lividity and rigor consistent with his position. An odor of petroleum distillates was noted about his body. Abrasions and rock indentations were noted on the right shoulder, both forearms, and knees. Loose skin was observed on the back and buttocks with no defensive wounds observed. None of these lesions was fatal in nature. The heart was large, and the myocardium was soft and congested. The lung parenchyma reveals congested, atelectatic, edematous, and hemorrhagic lungs with multiple patches of bronchopneumonia and a higher than normal lung weight. Multiple stress ulcers throughout the gastric mucosa were noted with the esophageal mucosa showing discoloration. Stomach contents revealed the presence of brownish liquid with a nearly clear oily thick film. The small and large bowels showed oily liquid with a strong odor of a petroleum distillate. Taking these facts into account, different tissues were analyzed for the presence of petroleum distillate. The analysis was broken into two sections: toxicology and ignitable liquids.

Materials

Toxicological analysis

Alkaline drugs. The alkaline drug analysis was performed on a Hewlett-Packard (HP, Palo Alto, CA) 5980 gas chromatograph (GC) with a nitrogen-phosphorus detector (NPD) and an HP GC with a mass spectrometric detector (MS) 5989B was used for confirmation and identification. Both instruments had an HP 7673A autosampler and a J&W Scientific (Folsom, CA) DB-5 column (30 m × 0.25-mm i.d., 0.25-µm film thickness). Helium at a 1 mL/min flow was used as the carrier. For GC–NPD, a two-step temperature ramp program was used. The initial oven temperature was 150°C for 2 min. The temperature was then increased at a rate of 15°C/min to 250°C and held at 250°C for 2 min. Then, the oven temperature was increased at the same rate (15°C/min) to 300°C and held at 300°C for 18 min for a total run time of 32 min. The injector and the detector temperatures were 260°C and 310°C, respectively. A 1:15 split ratio was used.

The initial GC–MS oven temperature was 150°C. After 2 min, it was increased at a rate of 15°C/min to 300°C where it remained for 6 min for a total run time of 18 min. The injector temperature was at 260°C, and the detector temperature was 280°C.

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The ratio of the detected drugs to the internal standard was compared against the ratio of the same drugs to the internal standard in low and high therapeutic concentration mixes (1).

Weak acidic drugs. The acidic and neutral drug analysis was performed on a Shimadzu GC14A GC with a flame ionization detector (FID). An HP GC with a 5989B MS was used for confirmation and identification. The GC–FID had an AOC1400 autosampler and a J&W Scientific DB-5 column (15 m × 0.53-mm i.d., 1.2-µm film thickness). Helium at a 1 mL/min flow was used as the carrier gas. The GC–FID used a three-step temperature ramp program. The initial oven temperature was 90°C for 1 min. The temperature was then increased at a rate of 15°C/min to 195°C. Then, the oven temperature was increased at 5°C/min to 240°C. Finally, the oven temperature was increased at 20°C/min to 300°C and held at 300°C for 3 min for a total run time of 23 min. The injector temperature was 200°C A splitless injection was used.

The GC–MS initial oven temperature was 90°C for 1 min. The temperature was then increased at a rate of 15°C/min to 195°C. Then, the oven temperature was increased at 5°C/min to 240°C. Finally, the oven temperature was increased at 20°C/min to 300°C and held at 300°C for 5 min for a total run time of 25 min. The injector and the detector temperature were 280°C.

The ratio of the detected drugs to the internal standard was compared against the ratio of the same drugs to the internal standard in low and high therapeutic concentration mixes.

Ignitable liquid analysis

Activated charcoal strips (ACS) from Albrayco (Albrayco Laboratories, Inc., Cromwell, CT) were used for adsorption of volatile compounds from various tissues. Carbon disulfide (CS2), (J.T. Baker, Ultra Resi-analyzed E350-01, Philipsburg, NJ) was used for eluting the ACS, a blank between samples, diluting the liquid samples, and washing the syringe between injections. Lined, clean 1-qt metal friction lid cans (MFLC), commonly known as paint cans, were from the US Can Corp. (Lombard, IL). The screw-cap analysis vials (SCAV), Teflon-lined septum screw-cap clear glass containers, and clear glass 100-µL conical inserts were manufactured by Sun International (Wilmington, NC). An HP 5890 series II GC with an HP 6890 series automated liquid sampler (ALS) with a flame ionization detector (FID) was used for analysis. Also used was an HP 5890 series II GC having a 7673 ALS and a 5970 mass selective detector (MS) running ChemStation G1034C software. The GCs (GC–FID, GC–MS) contained the same column type (e.g., DB-1, 15 m × 0.25-mm i.d., 0.25-µm film thickness, J&W Scientific). Helium was used as the carrier gas.

The *n*-alkane standard was created from each of the following alkanes from Matheson Curtis and Bell (MCB) (EM Science, Gibbstown, NJ): heptane (C7), octane (C8), nonane (C9), decane (C10), dodecane (C12), tridecane (C13), tetradecane (C14), and hexadecane (C16). One milliliter of each of these alkanes were mixed together with 0.5 mL of undecane (C11) as the stock solution standard. The reduced volume of C11 acts as a reference point in the chromatogram. One drop of the *n*-alkane standard stock solution was diluted with 40 drops of carbon disulfide for the working standard.

Samples

The sample organs from the decedent included the liver, lung, and brain. Additionally submitted were blood, urine, vitreous humor and stomach contents. One-quart and 1-gal rectangular metal screw-cap cans commercially labeled as paint thinner were reportedly found in the decedent's car.

Methods

Toxicology

Alkaline drugs extraction. To a 2-mL aliquot of blood or of drug standard were added 1.0 µg of promazine, 2.5 mL of saturated sodium borate, and 7 mL of chlorobutane. A few drops of saturated sodium hydroxide, diluted 1:10, were added to assure alkalinity. The organic layer was separated after centrifugation and extracted with 3.5 mL of 0.5M sulfuric acid. After centrifugation, the acid layer was separated then alkalinized with concentrated sodium hydroxide, and extracted with 6 mL of chlorobutane. The organic layer was separated after centrifugation, and a drop of 1% hydrochloric acid in methanol was added. The mixture was evaporated and reconstituted in 4–5 drops of ethanol before being transferred to GC crimp-cap analysis vials.

Weak acidic drugs extraction. The weak acidic drugs were extracted by solid-phase extraction (SPE, United Chemical Technology ZSTHC020 200 mg C8 and Amynopropyl mixed bed SPE columns with 10-mL reservoir). A 1-mg/mL solution of α-methyl-α-propylsuccinimide and 7-(β-chloroethyl)theophylline was used as the internal standard. The samples were applied to the preconditioned columns. The columns were solvent washed with 0.1M phosphate buffer (pH 7), then a strong vacuum (10–15 Hg mm) was applied for 20–25 min. The columns were washed with hexane and a gentle vacuum was applied briefly. Finally the samples were eluted with ethyl acetate/hexane (75:25) and the eluants were evaporated to dryness. The samples were reconstituted with ethyl acetate.

Fire debris analysis

GC method. The GC method incorporated on both GC–FID and GC–MS are identical for fire debris analysis. The oven temperature began at 40°C, was held for 2 min then increased in temperature at 25°C/min to 300°C and held for 2 min. The injector was set at 250°C with an approximate 80:1 split with the detector temperature maintained at 300°C. For GC–MS, the mass spectral detector was turned on at injection, turned off for the CS2 solvent peak, then turned on after the solvent front passed through the detector.

Protocol. Before proceeding with the analysis for ignitable liquids, an ACS was checked for contamination by dividing into smaller pieces (approximately 2 × 2 mm) then eluting with 11 drops of CS2 in a SCAV and transferring the eluate to a conical insert in a separate SCAV. A 1-µL injection of the ACS eluate was analyzed on the ALS-GC–FID using the GC method described. After showing there was no contamination, the ACS were used for adsorption of the samples.

The method used by fire debris analysts for capturing ig-

nitable liquids from fire debris, known as static adsorption-elution (2–8), was used on the organs, urine, and blood from the decedent. Portions of the liver, lung, and brain were placed directly into separate 1-qt MFLC. Approximately 10 mL of the urine and approximately 3 mL of the blood sample were placed into separate 50-mL Pyrex® beakers, and each beaker was placed into a separate MFLC. A clean, empty MFLC was used as a can blank and followed the sample cans through the procedure. To each MFLC, one ACS was punctured by a bent paper clip then suspended above the sample. The paper clip was held against the interior lid of the container by using a strong magnet on the exterior surface. The sample and blank MFLCs were placed into a 65°C oven for 1.5 h, after which time they were removed and allowed to cool to ambient temperature. Individually, the ACS from each can was removed, divided into smaller pieces (approximately 2 mm × 2 mm), placed into a SCAV, and eluted with 11 drops of carbon disulfide; the eluate was transferred to a conical insert in a separate SCAV. One drop of the liquid from each of the commercially labeled "paint thinner" cans, reportedly found in the decedent's vehicle, was diluted separately with 40 drops of CS2 in a SCAV. One drop of the unfrozen liquid found with the frozen stomach contents was diluted with 40 drops of CS2 in a SCAV. Approximately 0.5 mL of vitreous humor was liquid–liquid extracted with approximately 10 drops of CS2. Aliquots of the diluted and extracted samples were separately transferred to their respective conical insert in a SCAV. A blank of CS2 was run before each sample or standard. The *n*-alkane sample was analyzed to characterize the locations of the *n*-alkanes. After analyzing all samples on the GC–FID, a decision was made to re-analyze certain samples on the GC–MS for specific peak identification.

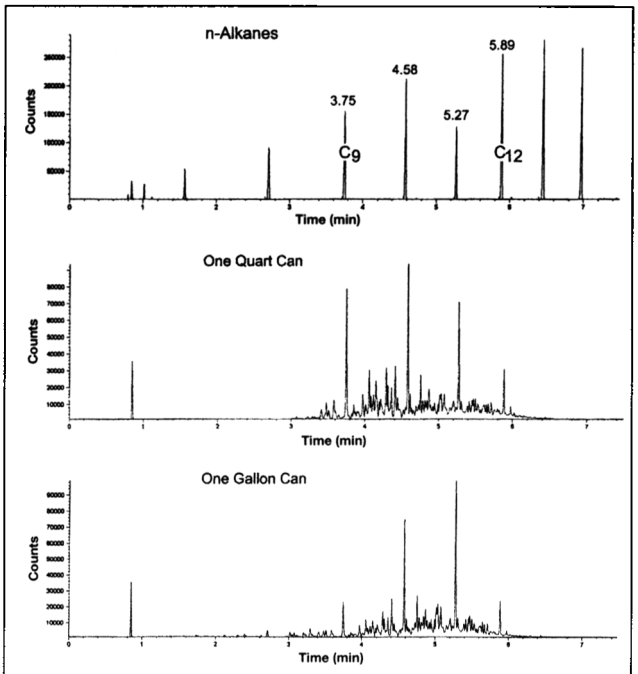

Figure 1. *n*-Alkane standard GC–FID chromatogram (top) and GC–FID chromatogram of the contents of the 1-qt (middle) and the gallon (bottom) paint thinner cans found in the trunk of the decedent's car.

Table I. Identification Table of the *n*-Alkane Peaks from the GC–MS Chromatogram

Retention Time (min)	GC–MS Peak Identification
3.47*	**Nonane**
3.80	2,6-Dimethyl Octane
4.04	Ethyl Methyl Benzene
4.16	1,2,4-Trimethyl Benzene
4.35	**Decane**
4.54	4-Methyl Decane
4.81	Ethyl Dimethyl Benzene
4.88	3-Methyl Decane
5.08	**Undecane**
5.71	**Dodecane**

* Bold = *n*-alkane series.

Results and Discussion

Toxicology

A sample of the postmortem blood was screened for barbitu-

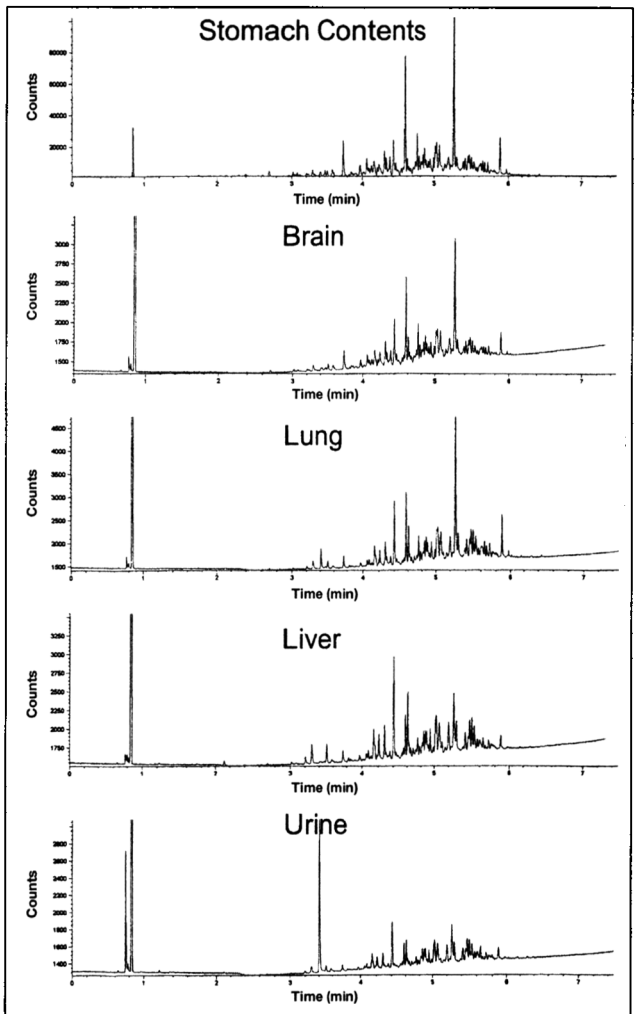

Figure 2. GC–FID chromatograms of the stomach contents, brain, lung, liver, and urine.

rates, cocaine and benzoylecgonine, opiates, and methamphetamine (and related compounds) by ELISA using Immunalysis® in a Tecan Minilyzer Instrument. The results were negative for all these drugs. A sample of the blood was analyzed for occasionally consumed low boiling point alcohols (methanol, ethanol, propanol, and iso-propanol) and ketones (acetone, methyl ethyl ketone) with an HP GC–FID. None were detected.

Valproic acid, diphenhydramine, and norsertraline were detected in concentrations consistent with concentrations reported as therapeutic. The sertraline, diazepam, and nordiazepam concentrations found in this case are consistent with concentrations reported as subtherapeutic to low therapeutic. Bupropion metabolites, but not the parent drug, were also detected.

Fire debris analysis

The *n*-alkane series (Figure 1) provides nine alkane peaks in the GC–FID chromatogram for classification of ignitable liquids. The GC–MS provides relative retention times for known straight chain alkanes for comparison and identification of the samples. No significant peaks were observed in the vitreous humor and the blood sample. The blood and vitreous humor resulted in no detectable quantities of an ignitable liquid (e.g., paint thinner). The liquid in the 1-qt (Figure 1) and 1-gal (Figure 1) container each fall into the medium petroleum distillate (MPD) class for ignitable liquids (8) with the *n*-alkane, undecane (C11), the most prominent peak. Some paint thinners are representative members of the MPD class. The 1-gal paint thinner can be chromatographically distinguished from the 1-qt paint thinner particularly around the nonane (C9) region. Consistent features were observed in the GC–MS total ion chromatograms (TIC). The GC–MS peak identification is shown in Table I. The liquid present with the frozen stomach contents (Figures 2 and 3) falls into the MPD class and was chromatographically indistinguishable from the paint thinner in the 1-gal container. Based on the chromatograms, the liquid in the frozen stomach contents was probably from the 1-gal can of paint thinner. The brain sample (Figure 2) falls into the MPD class and is consistent with the liquid from the 1-gal container. In the chromatogram from the recovered lung sample (Figures 2 and 3), a MPD class ignitable liquid consistent with the 1-gal can contents was observed with the C11 peak remaining the prominent peak, but with a noted decline of C9 and C10 peaks with specific other peaks becoming more prominent. In both the GC–FID (Figure 2) and GC–MS (Figure 3) chromatograms, the lung sample exhibited a decrease in the lower boiling point compounds as noticed in the significant drop of nonane and decane (Table II) and showing a pattern that may be a combination of typical evaporation of the "light" ends of the paint thinner, through normal respiration, with some possible differential metabolism occurring. The lung chromatogram was otherwise consistent with paint thinner.

The liver chromatogram showed considerable alteration from the contents of the 1-gal can and stomach contents. In the liver chromatograms (Figures 2 and 3), the *n*-alkane peaks C9

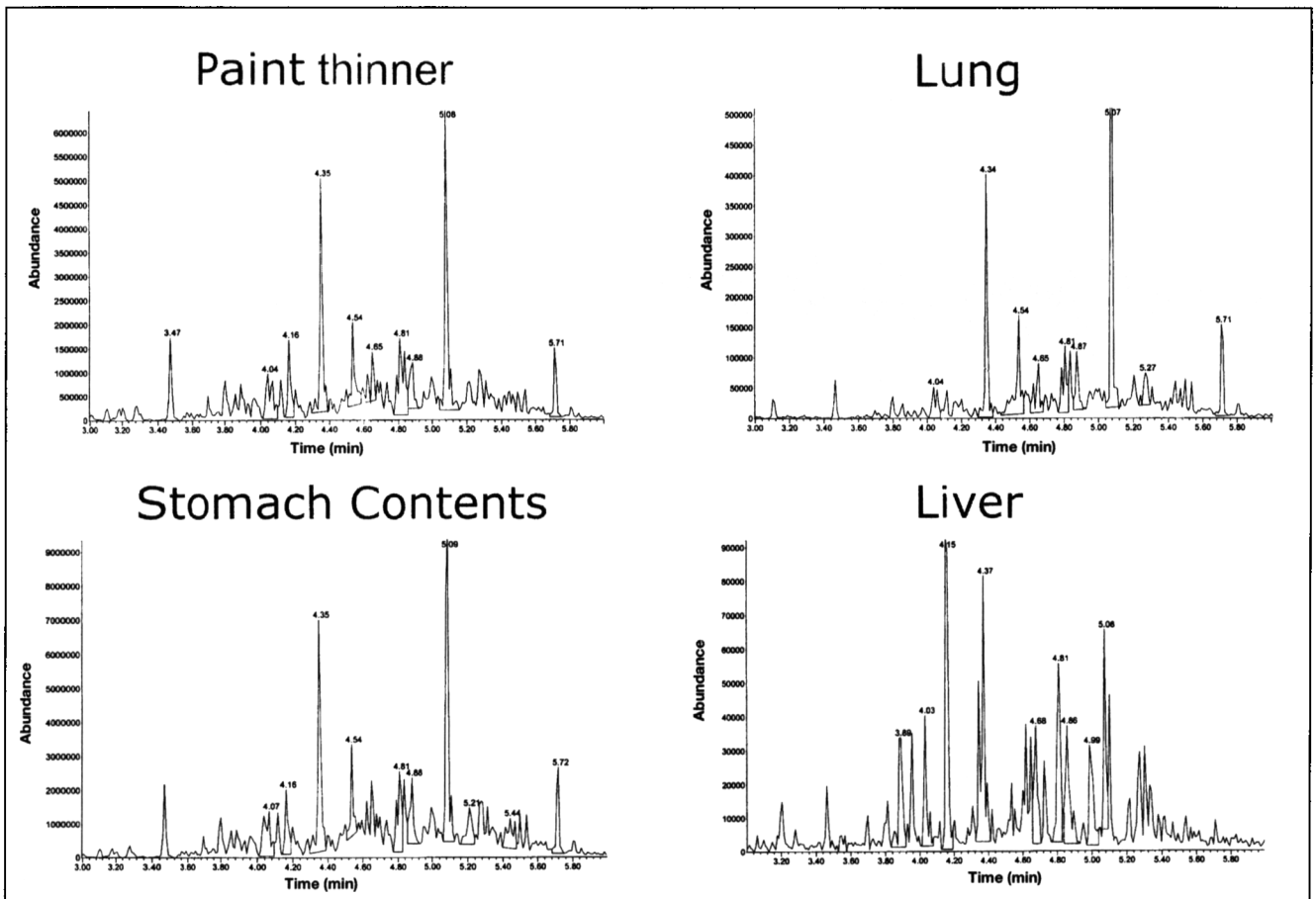

Figure 3. GC–MS chromatograms of the paint thinner (from the gallon container), lung, stomach contents, and liver.

through C12 were present but altered in abundance relative to other peaks, which had become more prominent (Table III). Nonane increased slightly while decane decreased significantly relative to other peaks in the liver chromatogram using undecane as 100%. Additionally, the chromatogram exhibited the absence of some peaks and ratio changes between peaks altered the chromatogram significantly from the paint thinner and stomach contents chromatograms. Several peaks significantly increased (3.80, 4.04, 4.16, 4.81, 4.88, and 5.27), while several peaks (4.35, 4.54, and 5.71) significantly decreased to the point of absence relative to the C11 peak in the liver chromatogram when compared to the 1-gal paint thinner. Additionally, ratio changes were observed between peaks in the chromatogram which were significantly different from the chromatograms of paint thinner and stomach contents.

The chromatogram for the urine sample (Figure 2) showed the presence of n-alkanes in the region for MPD but significantly reduced relative to other peaks. On close inspection, the urine chromatogram was consistent with the liver chromatogram. The liver and urine GC–MS TIC when compared were consistent in the region from 4 to 6 min but there were differences in some relative peak ratios, possibly indicating differential metabolism of some petroleum products over others and possible creation of new species in the pathway to elimination.

Table II. Ratio % of *n*-Alkanes in GC–MS Chromatogram from the Contents of the Gallon Container, Lung, Stomach Contents, and Liver

Ratio % Based on C-11	Paint Thinner	Stomach Contents	Lungs	Liver
Nonane	27.6	20.6	10.0	31.5
Decane	86.1	73.6	52.9	60.0
Undecane	100.0	100.0	100.0	100.0
Dodecane	23.0	23.8	26.0	< 1.0

Table III. Ratio % of Specific GC–MS Peaks Corresponding to Contents of the Paint Thinner Gallon Container and the Liver

		Ratio %	
Retention Time	Peak Identification	Gallon P.T.	Liver
3.47*	**Nonane**	27.6	31.5
3.80	2,6-Dimethyl Octane	0.0	32.3
4.04	Ethyl Methyl Benzene	21.0	62.7
4.16	1,2,4-Trimethyl Benzene	31.9	182.2
4.35	**Decane**	86.1	60.0
4.54	4-Methyl Decane	27.6	0.0
4.81	Ethyl Dimethyl Benzene	19.9	124.5
4.88	3-Methyl Decane	26.3	69.4
5.08	**Undecane**	100.0	100.0
5.27	Not identified	20.0	65.0
5.71	**Dodecane**	23.0	< 1.0

* Bold *n*-alkane series.

Conclusions

The lack of detection of hydrocarbons from paint thinner in the blood and vitreous may be the result of insufficient sample size for the sensitivity of the methods used for analysis. An alternative explanation for the inability to detect paint thinner in these two samples maybe the lower solubility of the hydrocarbons in aqueous samples. In addition, it is possible that a combination of these two theories accounts for the inability to detect paint thinner in these samples. In support of the last theory, the presence of apparently metabolized paint thinner in the larger urine sample and the distribution in the tissues appears to indicate detectable levels should have been present in the blood had a larger sample size been available. The results of the lung sample showed potential respiratory evaporation of the "light" ends of the paint thinner. The data from liver and urine both suggested the possibility of differential metabolism of the various compounds present in the paint thinner. The prescription drugs, though present, were not considered contributing factors.

The cause of death was ruled ingestion of paint thinner, and the mode of death was ruled to be suicide.

References

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