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Application Data Sheet

No.139

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of Volatile Toxic Substances Using Headspace GC/MS Part.1 - Paint Thinner and Alcohol -

Forensic toxicologists in the police laboratories and forensic medicine departments of university measure a variety of volatile substances in the course of investigating accidents, crimes, and other incidents.
Blood alcohol (ethanol) is measured to provide evidence in cases of traffic accidents caused by drinking, incidents involving alcohol such as physical assault and injury, and acute alcohol poisoning.
Paint thinner is a solvent with toluene, methanol, and ethyl acetate as its main constituents. Paint thinner also has anesthetic and stimulant properties. Paint thinner abuse by inhalation has become prevalent and laws have been enacted to prevent the harmful effects of its abuse.
Used in industrial applications, cyanide and azide are compounds that are relatively easy to procure. This has resulted in incidents of contamination by these toxic substances. After these incidents, testing regimes for poisons were enhanced in order to determine the cause of such incidents, i.e. crime or suicide.
Blood alcohol and paint thinner can be measured relatively simply using headspace sampler, with measurements performed on a routine basis at police laboratories and in university forensic departments.
There have been reports of the headspace method being used to measure cyanide and azide. These compounds are normally measured by performing PFB derivatization, solvent extraction, and then liquid injection for GC/MS analysis. However, the derivatization and extraction steps of this method are labor-intensive.

This two-part application presents details on the investigation of using headspace GC/MS to measure cyanide and azide, as well as information on optimizing column conditions to allow simultaneous measurement of alcohol and paint thinner. Of these two investigations, results obtained from measuring blood alcohol and paint thinner are presented below. Please see Application Data Sheet No. 140 for part two.

Sample Preparation

Blood Ethanol Analysis

An aqueous solution of 1-propanol (0.5 mg/mL), which was to be added to blood samples as the internal standard, was prepared by dissolving 1-propanol in distilled water. Standards for calibration curve of blood ethanol were prepared by making up samples of hemolyzed equine blood with ethanol concentrations of 0.03, 0.1, 0.3, 1.0, and 2.0 mg/mL, then adding 0.5 mL of each of these samples and 0.5 mL of 1-propanol (0.5 mg/mL) internal standard to a 20 mL headspace vial. Each vial was quickly sealed with a headspace cap and then agitated. To confirm that 2-propanol, which is used for sterilization during blood sampling, is separated from ethanol and 1-propanol on a chromatogram, an aqueous solution of ethanol, 2-propanol, and 1-propanol was also prepared.

Paint Thinner Analysis

Paint thinner (5 μL) was added to a 20 mL headspace vial, which was quickly sealed with a headspace cap.

HS-20 Headspace Sampler + GCMS-QP™2020

Analytical Conditions

Table 1 shows the headspace and GC/MS analytical conditions. Alcohol, cyanide, and azide were all measured using the same headspace and GC/MS conditions, and only paint thinner was measured with different conditions after changing the split ratio and detector voltage. With the HS-20 headspace sampler, even when GC/MS analysis conditions are changed, measurements can be performed within the same batch file by switching methods, as long as the same headspace conditions are used. Changing the split ratio is an effective way of analyzing both cyanides and azides that must be measured at trace quantities, and undiluted thinner solution that contains high-concentration constituents.

For this application, results were collected using the GCMS-TQ™8040 GC-MS/MS device, though the same results can be obtained using the GCMS-QP™2020 single-GC/MS device.

Table 1: Analytical Conditions

HS: HS-20						
GC-MS: GCMS-TQ™8040						
[HS]		[GC]				
Headspace mode: Loop		Column:	Rtx™-BAC2 (length: 30 m, 0.32 mm I.D., df = 1.2 μm, Restek Corporation)			
Oven temp.:	60 °C					
Sample line temp.:	100 °C	Column oven temp.:	40 °C (5 min) → (40 °C /min) → 200 °C (1 min)			
Transfer line temp.:	150 °C	Carrier gas:	Helium			
Vial pressurization gas pressure:	70 kPa	Carrier gas control:	Linear velocity (62.5 cm/sec)			
Vial warming time:	10 min	Injection mode:	Split			
Vial pressurization time:	0.5 min	Split ratio:	10:1 (alcohol, cyanide, azide)			
Loading time:	0.5 min		30:1 (paint thinner)			
Loading equalization time:	0 min	[MS]				
Injection time:	0.5 min	Interface temp.:	230 °C	Ion source temp.:	200 °C	
Needle flush time:	5 min	Solvent elution time:	0.7 min	Data acquisition time:		1 - 10 min
GC cycle time:	18 min	Measurement mode:	Scan	Mass range:	*m/z* 10 - 300	
		Event time:	0.2 sec	Emission current:	60 μA (standard)	

*Note: The detection voltage and other conditions must be optimized since they can differ depending on equipment status.

Analytical Results of Blood Ethanol

Fig. 1 shows the total ion current (TIC) chromatogram obtained when analyzing a standard of 0.3 mg/mL ethanol to which 2-propanol had been added—a compound that is used for sterilization during blood collection. The chromatogram shows complete separation of 2-propanol and that quantitative values were not affected by 2-propanol.

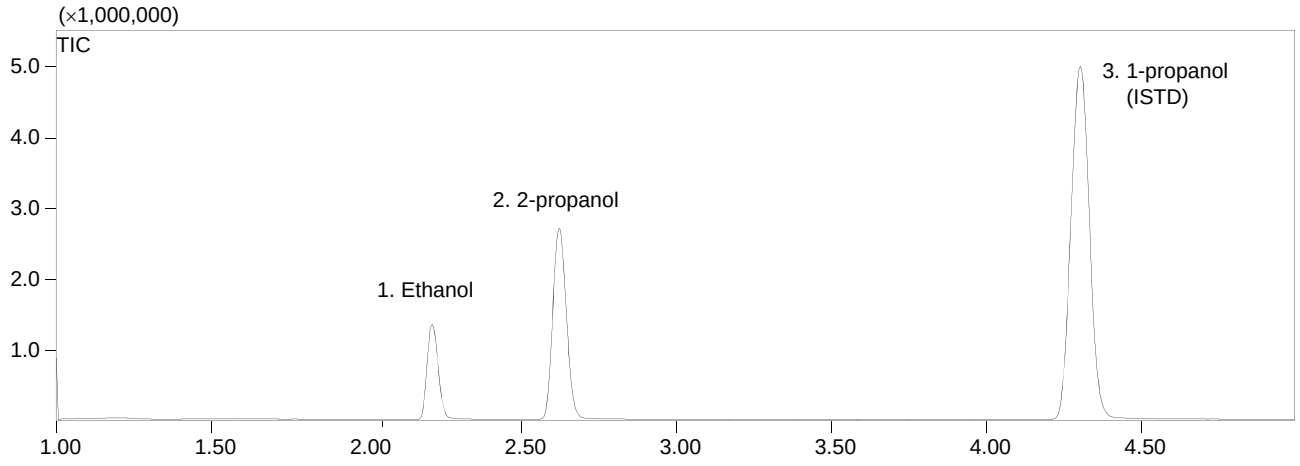

Fig. 1: Total Ion Current Chromatogram of 2-Propanol Added to 0.3 mg/mL Ethanol Standard

The chromatograms obtained when analyzing a blank and a 0.03 mg/mL standard are shown in Fig. 2. The calibration curve (0.03, 0.1, 0.3, 1.0, 2.0 mg/mL) obtained after internal standard correction is shown in Fig. 3. The calibration curve correlation coefficient (R) was 0.9999 or above, showing that linearity was good. Table 2 shows the reproducibility (n = 8) of measuring 0.3 mg/mL, which is the reference concentration used as the basis of the breath test in Japan's Road Traffic Act and Order for Enforcement of the Road Traffic Act. Table 3 shows the reproducibility (n = 8) of measuring 0.03 mg/mL, which is 1/10 the reference concentration. The accuracy of quantitative measurements of the 0.3 mg/mL concentration sample was 100.2 - 100.9 % (average 100.5 %) with a reproducibility relative standard deviation (%RSD) of about 0.2 %. The accuracy of quantitative measurements of the 0.03 mg/mL concentration sample was 89.4 - 97.1 % (average 95.2 %) with a reproducibility relative standard deviation (%RSD) of about 2.8 %.

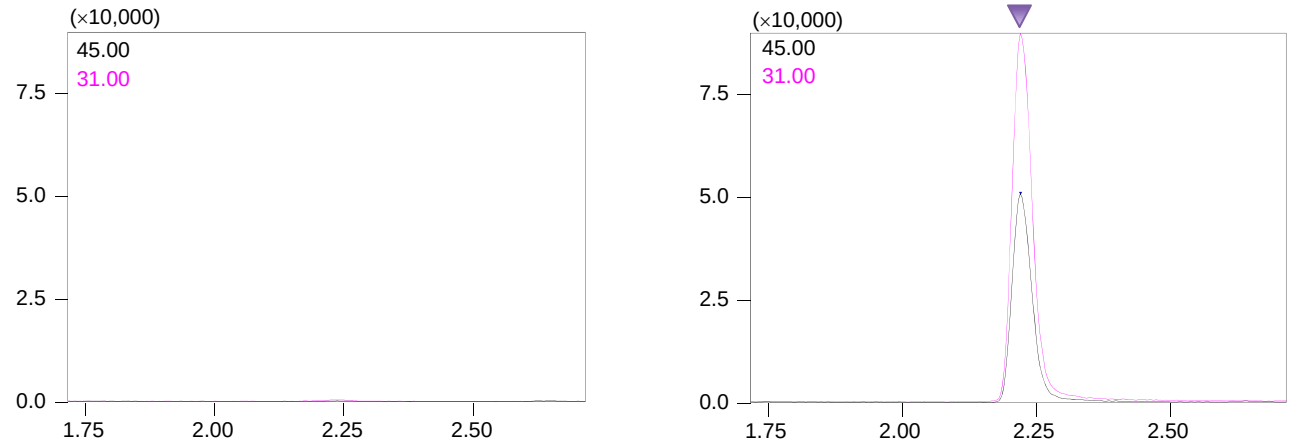

Fig. 2: Mass Chromatograms of Ethanol when Analyzing a Blank Sample and a 0.03 mg/mL Standard Sample
Left: Blank, Right: 0.03 mg/mL Standard

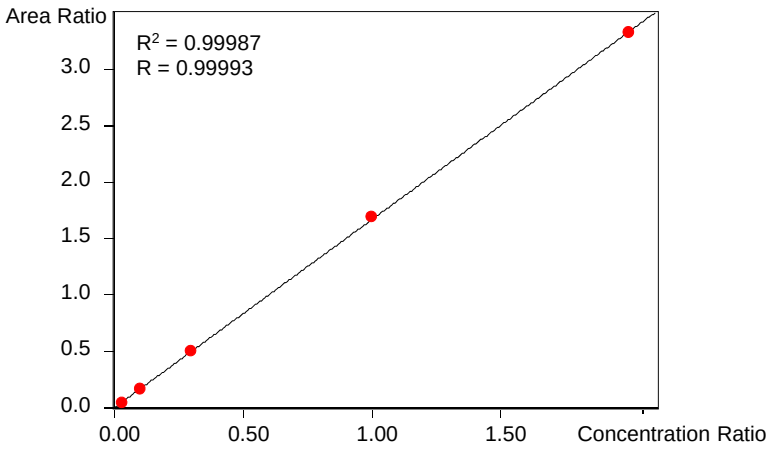

Fig. 3: Ethanol Calibration Curve (Concentration: 0.03 - 2.0 mg/mL)

Table 2: Reproducibility for 0.3 mg/mL (n = 8)

	Area Ratio	Concentration (mg/mL)	Accuracy (%)
1st	0.502	0.302	100.5
2nd	0.501	0.301	100.4
3rd	0.500	0.301	100.2
4th	0.504	0.302	100.8
5th	0.504	0.303	100.9
6th	0.503	0.302	100.7
7th	0.502	0.301	100.4
8th	0.502	0.301	100.5
Average	0.502	0.302	100.5
Standard Deviation (SD)	0.001	0.001	0.227
%RSD	0.226	0.226	0.226

Table 3: Reproducibility for 0.03 mg/mL (n = 8)

	Area Ratio	Concentration (mg/mL)	Accuracy (%)
1st	0.130	0.029	96.1
2nd	0.131	0.029	96.8
3rd	0.131	0.029	96.8
4th	0.129	0.029	95.5
5th	0.131	0.029	97.1
6th	0.131	0.029	97.1
7th	0.121	0.027	89.4
8th	0.126	0.028	92.9
Average	0.129	0.029	95.2
Standard Deviation (SD)	0.004	0.001	2.716
%RSD	2.849	2.853	2.853

Analytical Results of Paint Thinner

The total ion current chromatogram obtained after analyzing commercially available paint thinner is shown in Fig. 4. The mass spectra of each constituent of paint thinner (methanol, ethyl acetate, and toluene) are shown in Fig. 5. The analysis conditions used in this investigation allowed for separation of the three main constituents of paint thinner (methanol, ethyl acetate, and toluene) in 10 minutes.

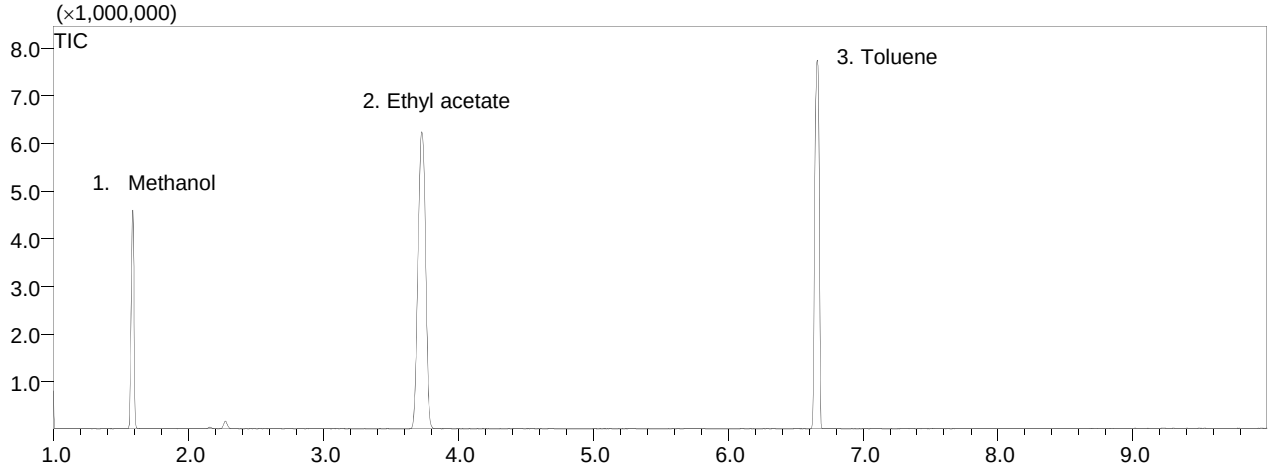

Fig. 4: Total Ion Current Chromatogram Obtained after Analysis of Undiluted Paint Thinner

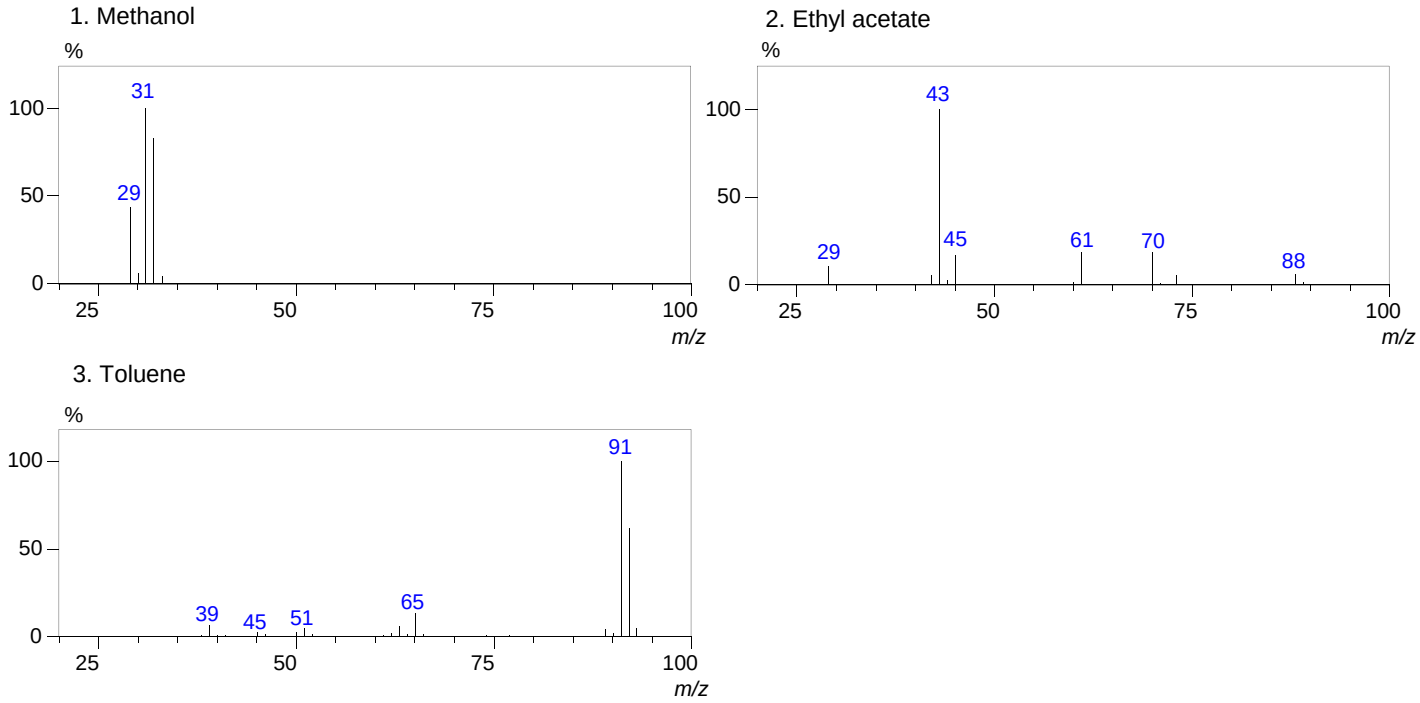

Fig. 5: Mass Spectra of Main Constituents Obtained after Analysis of Paint Thinner

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