

Gas Chromatography

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Analysis of Trimethylamine in Exhaust Gas of Station Pollution Source by HS-GC/NPD

other organic amines, has been identified as a major contributor to malodor pollution. At room temperature, TMA occurs in a gaseous form, and is the result of the manufacture, use and disposal of a variety of materials utilized in sewage treatment plants, landfills, petroleum refineries, agricultural and food industries. Owing to the low odor threshold of TMA, complaints associated with poor air quality are often associated with TMA. Thus, many countries and organizations have released rules and regulations setting permissible exposure limits (PELs) for TMA, and have also developed sample collection and preparation methods, as well as instrument parameters for the analysis of TMA. Examples of regulations include the Offensive Odor Control Laws in both Japan and South Korea, which regulate offensive odors emitted from businesses, and testing methods such as the U.S. Occupational Safety and Health Administration (OSHA) Method 2060 and China environmental protection standard HJ 1042-2019.

Introduction

Trimethylamine (C_3H_9N or TMA) is a volatile organic compound which, along with hydrogen sulfide, organic sulfide, phenol, organic acids and



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OSHA Method 2060 details a procedure for TMA analysis in which air samples are collected in 10% phosphoric acid coated XAD-7 tubes, desorbed with 1 mL of a 1:1 solution of deionized water:methanol with 30 minutes shaking, and subsequently analyzed utilizing a gas chromatogram (GC) equipped with a flame ionization detector (FID). In the Japanese and Korean methods, sulfuric acid is utilized in the collection of the air samples, and target compounds are decomposed by KOH solution and absorbed in a cold trap, with identification and quantification achieved by GC/FID. Chinese standard HJ 1042-2019 is also established for the determination of TMA in ambient air and waste gas by solvent absorption-HS-GC/FID or NPD.

The study presented herein demonstrates the determination of TMA in the exhaust gas of a station pollution source utilizing a PerkinElmer TurboMatrix™ HS-40 sampler, and a PerkinElmer Clarus® GC with nitrogen phosphorus detector (NPD). Detailed instrument method parameters are presented with precision, recovery, linearity and detection limit results. This application note demonstrates that the TurboMatrix HS-40 and Clarus GC/NPD meets or exceeds the performance criteria set out in HJ1042-2019 and OSHA Method 2060.

Experimental

Reagent

TMA calibration gas was purchased from Dalian Special Gases Co. Ltd, and diluted utilizing a dynamic diluter (Entech Instruments). Trimethylamine hydrochloride standard was purchased from the Institute for Environmental Reference Materials (IERM) of the Ministry of China National Environmental Protection. Hydrochloric acid (GR), sodium chloride (GR), ammonia water (AR), sodium hydroxide (GR) and potassium sulfate (GR) were obtained from Sinopharm Chemical Reagent Co. Ltd. The pure water utilized in the experiment was produced by Mini-Q.

The collecting solution of 10 mL of HCl ($\rho=1.189 \text{ g/mL}$) was diluted with water by 10 times. The reagent decomposition of 50 g of NaOH was dissolved in water and diluted to 50 mL. The stock standard solution of 0.1620 g trimethylamine hydrochloride was dissolved in the collecting solution, and diluted to 100 mL.

The primary dilution standard solution of 1 mL of stock standard solution was diluted with the collecting solution by 100 times.

Sample Preparation

The sample preparation procedure used is as follows:

1. The TMA gas standard was diluted by nitrogen and filled in a Tedlar bag.
2. Two collection bottles were cascaded with 10 mL of collecting solution in each of the bottles.
3. 20 L of TMA gas was exhausted through the collection bottles using of flow rate of 0.5 L/min.
4. The collecting solution, which was washed inside the bottle, was transferred into a 10 mL colorimetric tube, and added to a volume of 10 mL.

5. The solution was transferred from the colorimetric tube to a 22 mL glass headspace vial containing 3.2 g of NaCl and 1.0 g of K_2SO_4 .
6. 500 μL of NaOH solution and 100 μL of ammonia water were added to the vial.
7. The vial was sealed with the PTFE side of the septum facing toward the sample.

Method precision was measured by analyzing six replicates at concentrations of 5 $\mu\text{g}/\text{m}^3$, 25 $\mu\text{g}/\text{m}^3$ and 300 $\mu\text{g}/\text{m}^3$. Method recovery was investigated by six replicates at concentrations of 50 $\mu\text{g}/\text{m}^3$, 200 $\mu\text{g}/\text{m}^3$ and 400 $\mu\text{g}/\text{m}^3$. The method detection limit (MDL) was determined by analyzing seven replicate samples at the lowest concentration level of the calibration solution. The TMA unit, $\mu\text{g/L}$, was converted to a $\mu\text{g}/\text{m}^3$, with a sampling volume of 20 L.

Instrumentation

A PerkinElmer Clarus GC/NPD with TurboMatrix HS-40 sampler was used to perform this experiment, with the conditions presented in Table 1. An Rtx-Volatile Amine column (30 m x 0.32 mm x 5.0 μm) was used for separation of the volatile amine components. Samples were collected using a calibrated personal sampling pump.

Table 1. Analytical parameters.

HS Parameters	
Needle Temperature	110 °C
Transfer Line Temperature	115 °C
Oven Temperature	80 °C
Thermostating Time	30 min
Pressurization Time	2 min
Injection Time	0.08 min
Mode	Constant
Column Pressure	20 psi
GC Parameters	
Inlet Temp	280 °C
Carrier Gas Flow	1.0 mL/min
Split Ratio	10:1
Initial Oven Temp	65 °C
Oven Hold	5 min
Ramp	10 °C/min to 150 °C
2nd Oven Temp	5 min
NPD Temperature	300 °C
H ₂ Flow	2 mL/min
Air Flow	100 mL/min

Calibration

The primary dilution standard solution was diluted sequentially with collecting solution to the required concentration. It was then added to vials containing 3.2 g of NaCl and 1.0 g of K₂SO₄. The calibration levels are presented in Table 2.

Results and Discussion

A nonpolar Rtx-Volatile Amine column was used for the analysis of polar amine compounds in this study.

It was observed that a small amount of ammonia can effectively avoid peak tailing for amines. The chromatogram shows good peak shapes for TMA, and good resolution between TMA and the other five amine compounds (Figure 1).

TMA is very soluble in water, resulting in a partition coefficient (K) of TMA that is large and difficult to extract from water. Inorganic

salts were added to the collecting solution to decrease the value of K, and increase the concentration of TMA in the headspace phase. The collecting solution approached saturation for NaCl when 3.2 g of NaCl was added to the 10 mL of collecting solution. Then, K₂SO₄ was added to the solution to further increase the TMA response. The peak area for TMA was no longer increasing when the amount of K₂SO₄ was greater than 1.0 g.

The calibration curve was plotted as the peak area versus the amount of TMA. The determination coefficients (r^2) was over 0.9989, showing the reliability of the analysis in the calibration range. Table 3 presents the results for linearity, precision (%RSD), method detection limits (MDL) and percent recovery. The method detection limit of TMA exceeds the minimum method requirements as shown in Table 4.

Table 2. Analytical parameters.

Compound Name	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
TMA (µg/L)	5	10	20	50	100	200	500

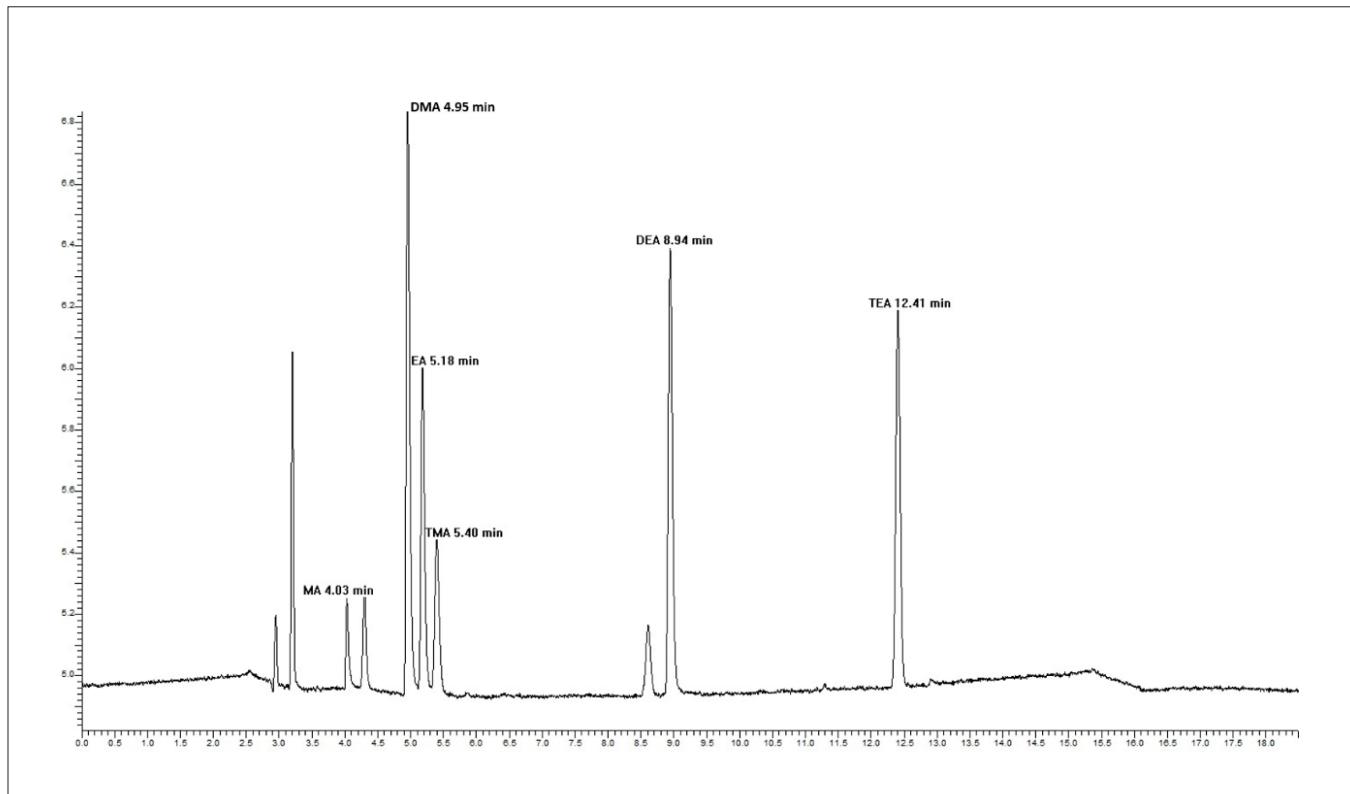


Figure 1. The chromatogram with six organic amine compounds. (The retention time is 4.03 min for methylamine, 4.95 min for dimethylamine, 5.18 min for ethylamine, 5.40 min for trimethylamine, 8.94 min for diethylamine and 12.41 min for triethylamine.)

Table 3. Summarized results of TMA.

Compound	Linearity		RSD%			MDL		Recovery%		
	Calibration Curve	r^2	5 µg/m³	25 µg/m³	300 µg/m³	µg/L	µg/m³	50 µg/m³	200 µg/m³	400 µg/m³
TMA	685321x+1764	0.9989	7.69	6.73	4.18	0.92	0.46	96.67	106.58	101.05

Table 4. Method detection limits of TMA using different methods.

Method Name	Sample Volume	Method Detection Limit
Offensive Odor Control Law in Japan	50 L	-
OSHA PV2060	10/20 L	0.2 mg/m ³ (200 µg/m ³)
HJ 1042-2019	20 L	0.7 µg/m ³
In This Study	20 L	0.46 µg/m ³

Summary

In this study, the determination of TMA in an exhaust pollution source was easily performed utilizing a TurboMatrix HS-40 and Clarus GC/NPD system. The superior detection limit, stability and linearity presented herein ensures a reliable TMA determination.

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