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Report

Comparison of Helium–Alternative Carrier Gases for Thermal Desorption–Gas Chromatography–Mass Spectrometry of Official Test Methods for Indoor Air Quality Guidelines in Japan

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As part of our ongoing study on verification of helium–alternative carrier gases in the official test method using gas chromatography–mass spectrometry (GC–MS) for chemicals in indoor air, we examined the applicability of hydrogen and nitrogen to thermal desorption (TD)–GC–MS. A comparison of the signal–to–noise ratios of standard solutions of volatile organic compounds (VOC) and Phthalate esters showed that detection sensitivities of hydrogen and nitrogen analyses were sufficient for the official test method. Measurements using these alternative carrier gases showed good linearity and could quantify less than 1/100th of Japanese guideline values for indoor air concentrations. Therefore, hydrogen and nitrogen gases can be applied to the official test method using TD–GC–MS for VOC and Phthalate esters in indoor air as alternative carrier gases to helium.

Key words indoor air, helium, alternative carrier gas, volatile organic compounds, phthalate esters, thermal desorption

INTRODUCTION

Chemical substances in indoor air are widely analyzed by GC–MS, with helium being the most frequently used carrier gas due to its inertness, non–flammability, and high analytical performance. However, Japan relies entirely on imported helium, and its procurement has become increasingly difficult because of recent global supply constraints.[1–4] In response, hydrogen and nitrogen have attracted attention as alternative carrier gases, as they are domestically available and stably supplied. Several studies have reported their applicability in GC–MS analysis.[5–8] In addition, GC–MS systems compatible with hydrogen and nitrogen are now available from various manufacturers.

The Ministry of Health, Labour and Welfare (MHLW) revised the official analytical manual for chemicals in indoor air, in which both the solvent extraction (SE) method and the thermal desorption (TD) method have been stipulated.[9] Previously, we verified the application of hydrogen and nitrogen as alternative carrier gases for SE–GC–MS and confirmed their feasibility.[10] However, TD–GC–MS has not been investigated.

In the present study, we examined the applicability of hydrogen and nitrogen as helium–alternative carrier gases in the official test method using TD–GC–MS for VOC and Phthalate esters in indoor air.

MATERIALS AND METHODS

Chemicals Standard solutions were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan), Fujifilm Wako Pure Chemicals Co. (Osaka, Japan), and Kanto Chemical Co. (Tokyo, Japan). Toluene–d_8 (Fujifilm Wako Pure Chemicals Co., Osaka, Japan) for VOC, di-*n*-butyl phthalate-d_4 (DnBP-d_4) and di-2-ethylhexyl phthalate-d_4 (DEHP-d_4) for phthalate esters were used as internal standard substances. Methanol 5,000 for pesticide residue and poly chlorinated biphenyl analysis was purchased from Fujifilm Wako Pure Chemicals Co. (Osaka, Japan) and Kanto Chemical Co. (Tokyo, Japan).

Instruments A TD unit (TD100–xr, Markes International Ltd., Llantrisant, UK) was coupled to a GC–MS (5977B GC–MSD, Agilent Technologies, Inc., CA, USA) equipped with an Extractor ion source and an integrated leak check system. Hydrogen (purity: 99.99996 vol%) was generated using a hydrogen generator (The NM Plus 160 Hydrogen Generator, Airtech Co., Kanagawa, Japan). Helium (purity: ≥99.999 vol%) and nitrogen (purity: ≥99.9995 vol%) were supplied through a centralized gas delivery system.

Analytical Methods The analytical conditions for GC were determined in accordance with the “Manual for Measuring Indoor Air Chemical Substances” set by MHLW[10]. The helium condition followed the official manual (total run time: 53 min), whereas the hydrogen condition adopted a fast-anal-

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ysis condition (25 min). The nitrogen condition was translated from the hydrogen parameters using the EZGC Method Translator and Flow Calculator (Restek Corporation, PA, USA), where the translation was based on equivalent linear velocity and retention behavior to maintain comparable chromatographic performance. However, because the Height-Equivalent-to-a-Theoretical-Plate markedly increased under identical linear velocity, the carrier gas flow rate for nitrogen was adjusted to 0.5 mL /min, resulting in a total run time of 53 min.

The targeted chemicals were toluene, xylene, styrene, ethylbenzene, 1,4-dichlorobenzene, and tetradecane as VOC, and di–*n*–butyl phthalate (DnBP) and di-2-ethylhexyl phthalate (DEHP) for phthalate esters. These quantifier and qualifier ions are shown in Table 1. These chemicals were measured using Selected Ion Monitoring (SIM) modes. The concentration ranges of the calibration curves were 0.1–100 ng for VOC and 0.1–5 ng for phthalate esters. *m*-, *p*-xylenes, parts of the three isomers of xylene, were quantified as overlapping peaks. The chromatograms were processed with PRISM 10 (GraphPad Software, CA, USA). The limits of quantification (LOQ) were calculated as 10–fold the standard deviation of six analyses of the lowest concentration samples (0.1 ng), respectively, and were further divided by the expected sampling volume according to the official test method specified by MHLW.[10] The detailed measurement conditions are shown in Tables 2-3.

Table 1. Target and Qualifier Ions

Chemicals	Quantifier Ion	Qualifier Ion
Toluene	91	65, 92
Ethylbenzene	91	51, 106
Xylene	91	105, 106
Styrene	104	78, 103
1,4–Dichlorobenzene	146	75, 111
Tetradecane	57	43, 71
DnBP	149	223
DEHP	149	167
Toluene-d_8	98	70, 100
DnBP-d_4	153	227
DEHP-d_4	153	171

DnBP: di-*n*-Butyl phthalate
DEHP: di-2-Ehylhexyl phthalate

RESULTS AND DISCUSSION

The SIM chromatograms of the standard solutions for the targeted chemicals demonstrated well-separated peaks, suitable for qualitative and quantitative analysis with all tested carrier gases (Fig. 1). The signal-to-noise (S/N) ratios of the measurements with 100 ng of the targeted chemicals are shown in Table 4. The S/N ratio was generally highest with helium. For most compounds, hydrogen provided comparable or even superior S/N ratios, although a moderate decrease (up to ~45%) was observed for some VOC such as toluene and xylenes. Nitrogen yielded the lowest S/N ratios, with a reduction of 15%–77% compared with helium. While helium generally provided the highest S/N ratios, some compounds exhibited irregular behavior when hydrogen or nitrogen was used as the carrier gas. For instance, DnBP and tetradecane showed markedly higher S/N ratios with hydrogen than with helium, whereas DEHP exhibited slightly higher sensitivity with nitrogen. These variations can be attributed to compound-specific factors such as volatility, adsorption/desorption characteristics, or ionization efficiency under varying carrier gas properties and vacuum conditions.

The coefficients of determination (R^2) of the calibration curves are shown in Table 5. Most of the chemicals showed good linearities, with more than R^2 of 0.9990 in the concentration range of 0.1–100 ng for VOC and 0.1–5 ng for phthalate esters, except the R^2 of DnBP was below 0.999.

A comparison of the LOQ and guideline values for indoor air concentrations is shown in Table 6. Measurements using all carrier gases can quantify less than 1/100th of the guideline values for the indoor air concentrations of all tested chemicals. Moreover, since the LOQ values for TD–GC–MS were generally lower than those for SE–GC–MS, confirming the higher sensitivity of the thermal desorption method.

Table 3. Measurement Conditions of TD

Carrier gases	He	H_2	N_2
Tube desorption	280 °C, 10 min, 50 mL/min		
Primary tube desorption	splitless		
Cold trap	–10 °C, 50 mL/min, 1 min		
Trap desorption	300 °C, 5 min		
Trap desorption split flow	29 mL/min	29 mL/min	splitless

Table 2. Measurement Conditions of GC-MS for VOC and Phthalate Esters

Carrier gases	He	H_2	N_2
Column	DB–1ms Ultra Inert (0.25 mm i.d. x 60 m, 0.25 µm)		
Time	53 min	25 min	53 min
Temperature program	40°C (0 min) → (5°C/min) → 250°C (3 min) → (20°C/min) → 300°C (3 min)	40°C (5 min)→(10°C/min)→ 130°C (0 min)→(25°C/min)→ 280°C (5 min)	40°C (0 min)→(5°C/min)→ 250°C (5 min)→(20°C/min)→ 300°C (3 min)
Inlet temperature	250°C		
Source temperature	280°C		
Quad temperature	150°C		
Linear velocity (cm/sec)	20.3	25.5	12.7
flow (mL/min)	1	1	0.5
Inlet pressure (kPa)	136.2	75.3	75.9
Acquisition type	SIM/Scan		
Range (*m/z*)	35–450		

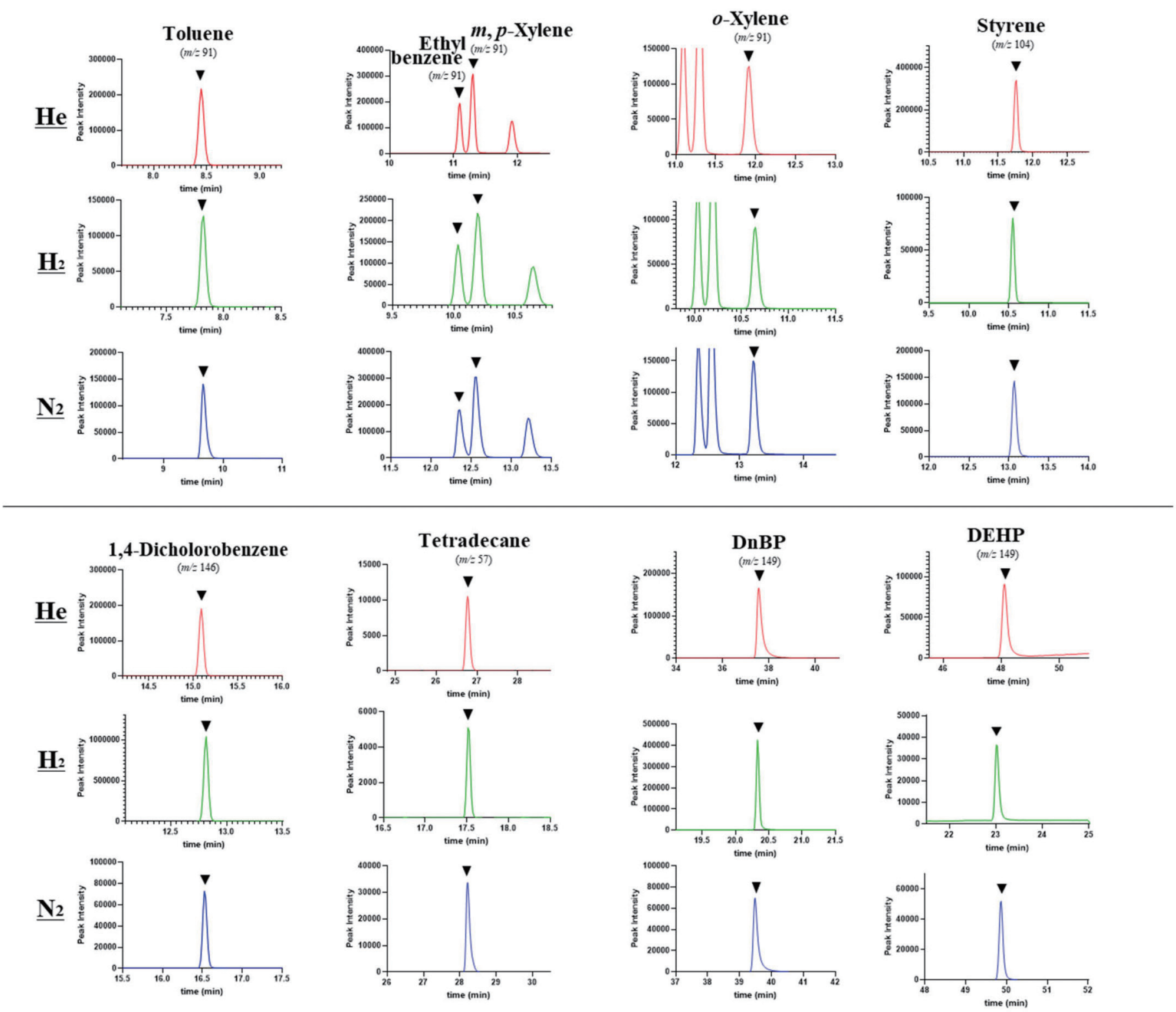

Fig. 1. SIM Chromatograms of the Target Chemicals for Each Carrier Gas

Table 4. S/N Ratios of the Targeted Chemicals

Chemicals	S/N ratio*		
	He	H_2	N_2
Toluene	4,260	2,345	1,200
Ethylbenzene	4,084	2,583	1,549
m, *p*–Xylene	6,298	3,931	2,606
Styrene	2,896	2,910	1,478
o–Xylene	2,547	1,667	1,276
1,4–Dichlorobenzene	2,457	4,156	1,947
Tetradecane	1,497	3,978	338
DnBP	800	4,620	673
DEHP	441	550	502

* 100 ng

Table 5. Coefficients of Determination for the Targeted Chemicals

Chemicals	R^2		
	He	H_2	N_2
Toluene	0.9997	0.9997	0.9996
Ethylbenzene	0.9994	0.9994	0.9995
m, *p*–Xylene	0.9993	0.9995	0.9991
o–Xylene	0.9993	0.9997	0.9990
Styrene	0.9996	0.9994	0.9990
1,4–Dichlorobenzene	0.9993	0.9993	0.9993
Tetradecane	0.9997	0.9998	0.9993
DnBP#	0.9998	0.9996	0.9933
DEHP#	0.9997	0.9996	0.9993

0.1–100 ng
#0.1–5 ng

Table 6. Comparison of LOQ and the Guideline Values for Indoor Air Concentration

Chemicals	LOQ [#] ($\mu g/m^3$)						Guideline values ×10^{-2} ($\mu g/m^3$)
	SE [*1, §]			TD [*2]			
	He	H_2	N_2	He	H_2	N_2	
Toluene	0.21	0.11	3.40	0.11	0.08	0.33	2.6
Ethylbenzene	0.65	0.49	2.30	0.03	0.03	0.06	3.7
Xylene	2.40	0.90	7.20	0.06	0.03	0.10	2
Styrene	1.80	0.47	1.20	0.05	0.01	0.05	2.2
1,4–Dichlorobenzene	2.30	0.56	1.50	0.02	0.01	0.04	2.4
Tetradecane	0.96	0.66	5.90	0.02	0.02	0.03	3.3
DnBP	0.0047	0.039	0.059	0.01	0.06	0.02	0.17
DEHP	0.0080	0.010	0.059	0.02	0.02	0.01	1

[#] 0.1 ng injection at six times repeatedly

[*1] Divided by specified collection volume (VOC; 144 L, Phthalate esters; 4,320 L)

[*2] Divided by specified collection volume (VOC; 20 L, Phthalate esters; 144 L)

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Although VOC and phthalate esters had generally required separate analytical conditions, the present approach could achieve their simultaneous analysis under a unified method. Compared with our previous SE–GC–MS method, the present approach greatly reduced the analysis time while allowing the application of three different carrier gases on a single column. To the best of our knowledge, no published studies have evaluated helium, hydrogen, and nitrogen as carrier gases using the same GC–MS column. Because hydrogen has a relatively high gas-phase diffusion coefficient, columns with thicker stationary-phase films and narrower internal diameters are generally recommended. Increasing the film thickness enhances analyte retention; however, it also extends the diffusion path within the column and impairs mass transfer between the stationary and mobile phases. In contrast, thinner films offer improved separation efficiency at higher linear velocities. Therefore, when hydrogen is used as the carrier gas under high linear velocity conditions, a thinner stationary-phase film might be more advantageous, provided that adequate retention is achieved.

Our findings demonstrated that using hydrogen as a carrier gas produced results comparable to those with helium, and in some cases, hydrogen even outperformed helium. Therefore, hydrogen is a promising alternative to helium in the official test method using TD–GC–MS for VOC and phthalate esters in indoor air. Nitrogen was also applicable in the official TD–GC–MS method for indoor air chemicals, demonstrating quantifiability for the targeted analyses despite its somewhat lower sensitivity.

Conclusion This study revealed that hydrogen and nitrogen gases can be applied to the official test method using TD–GC–MS for VOC and Phthalate esters in indoor air as alternative carrier gases to helium.

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Conflict of interest The authors declare no conflict of interest.

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