Applications note

MS
MSTips No. 466
GC-TQMS Application

Residual solvent analysis in cosmetic ingredient using single QMS mode and alternative carrier gases in GC/MS/MS

Product used : Mass spectrometer(MS)

Introduction

The gas chromatograph triple quadrupole mass spectrometer JMS-TQ4000GC UltraQuad™ TQ (Fig. 1) can be used as QMS by single QMS mode in addition to qualitative and quantitative analysis of trace components by MS/MS mode. We have already reported quantitative analysis in water samples and qualitative analysis in material samples in MSTips No. 443 and 450. In this time, we report the analysis of residual solvents in cosmetic ingredient using the single QMS mode. Residual solvents in cosmetic ingredient, like residual solvents in pharmaceuticals, are classified as Class 1-3 solvents by the International Council for Harmonization of Technical Requirements for Pharmaceuticals for Human Use(ICH). Class 1 solvents: Solvents to be avoided in the manufacture of pharmaceuticals. Class 2 solvents: Solvents to be limited in pharmaceuticals. Class 3 solvents: Solvents with low toxic potential[1]. In this application note, we report the analysis of residual solvents in ethanol solution using nitrogen gas as an alternative carrier gas for seven solvent components classified as Class 1 and 2, as well as the quantitative analysis of 1,4-Dioxane in cosmetic ingredient.

Fig. 1 JMS-TQ4000GC UltraQuad™ TQ

Method

The measurement was performed using a MS-62071STRAP trap-type HS and GC triple quadrupole mass spectrometer JMS-TQ4000GC UltraQuad™ TQ. The measurement conditions are shown in Table 1, and the target components and their SIM monitoring ion are shown in Table 2.

Table 1 Measurement condition

Sample	
Sample 1	Standard 7 mix in EtOH (Mixture of Methyl alcohol, Methylene chloride, Trichloromethane, Benzene, 1,4-Dioxane, Toluene and Xylene including Ethylbenzene. Concentration levels for each compound range from 0.2-100 ppm.)
Sample 2	Cosmetic ingredient including 1,4-Dioxane at about 1 ppm
HS condition	
Sample Volume	Sample 1: 2 µL, Sample 2: about 1g with 1,4-Dioxane 4 µL and d8-Dioxane 4 µL
Sample Temp.	Sample 1: 100 °C, Sample 2: 80 °C
Sampling mode	Loop mode
Heating time	Sample 1: 60 min, Sample 2: 30 min
GC condition	
Column	Rxi-624(30 m length, 0.25 mm i.d., 1.4 µm film thickness)
Inlet	Split/Splitless
Inlet Temp.	200 °C
Flow	He carrier gas 1 mL/min, Constant flow N_2 carrier gas 1 mL/min, Constant flow
Injection Mode	Split (50 :1)
Oven Program	35 °C (5 min) → 10 °C/min → 250 °C (5min)
MS condition	
Ion Source Temp.	200 °C
Interface Temp.	200 °C
Ionization Mode	EI+, 70 eV(He carrier gas), 20 eV(N_2 carrier gas)
Measurement Mode	SIM

Table 2 Monitoring ion of SIM

Component	Quantitative ion	Reference ion 1	Reference ion 2
Methyl Alcohol	31	29	32
Methylene chloride	84	49	86
Trichloromethane	83	85	118
Benzene	78	77	52
d8-Dioxane	96	64	46
1,4-Dioxane	88	58	43
Toluene	91	92	65
Ethylbenzene	91	106	65
m,p-Xylene	91	106	65
o-Xylene	91	106	65

Result

- Measurement result of sample 1

The observed EIC peaks of each component by He carrier gas and N_2 carrier gas are shown in Fig. 2. All target components were observed by both carrier gases. On the other hand, when focusing on methyl alcohol, the EIC peak of *m/z* 29 is buried in the baseline for the N_2 carrier gas. It is supposed that baseline was higher than that of the He carrier gas by stable isotope(^{15}N) of N_2. The comparison result of S/N value is shown in Table 3. Generally, it is said that the sensitivity of N_2 carrier gas is about 1/10 lower than that of He carrier gas. However, for this measurement, the S/N values of 8 out of 9 components were within 1/5. It is assumed that the ionization energy of 20 eV suppressed the generation of nitrogen ion, which is a factor in sensitivity reduction, and as a result, good sensitivity was obtained.

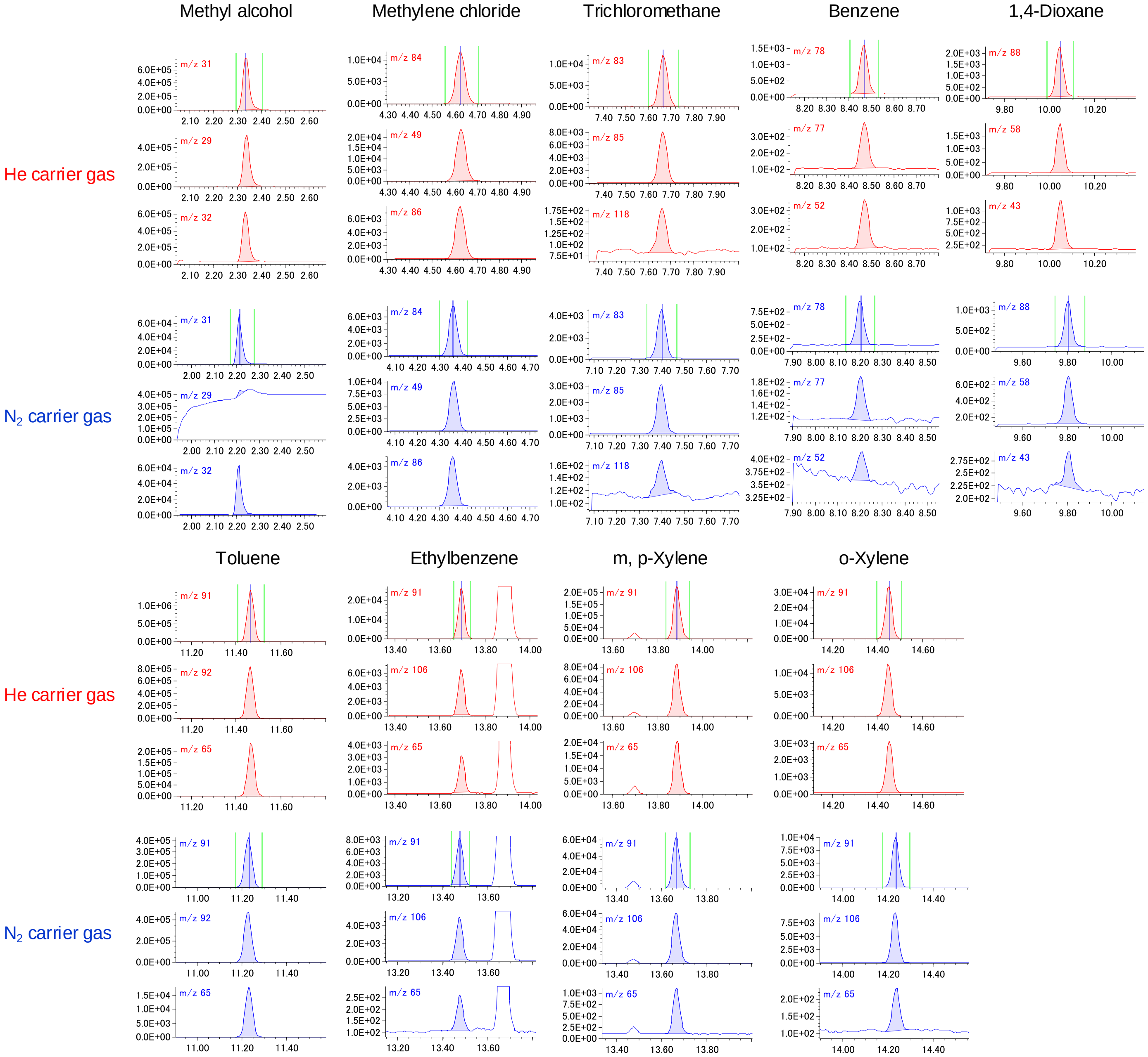

Fig. 2 The observed EIC peaks of each component by He carrier gas and N_2 carrier gas

Table 3 Comparison S/N value by He carrier gas with S/N value by N_2 carrier gas

Component	S/N value by He carrier gas	S/N value by N_2 carrier gas
Methyl Alcohol	105022.7	24079.0
Methylene chloride	14312.2	10044.2
Trichloromethane	7131.1	5385.4
Benzene	2288.3	1065.5
1,4-Dioxane	3098.7	913.9
Toluene	1365053.9	256462.1
Ethylbenzene	33704.9	4821.1
m,p-Xylene	99506.4	33379.6
o-Xylene	20814.7	9726.1

- Measurement result of sample 2

The quantitative value of 1,4-Dioxane was calculated by the standard addition method. The ratio of peak area value of 1,4-Dioxane and d8-Dioxane by both carrier gases are shown in Table 4. The EIC peaks and calibration curves of 1,4-Dioxane obtained from cosmetic ingredient by both carrier gases are shown in Fig. 3. The EIC peaks of *m/z* 88 of 1,4-Dioxane was observed with a good peak shape from the cosmetic ingredient, and the calibration curve showed a linearity of more than 0.99. The quantitative value of 1,4-Dioxane was 1.13 ppm by He carrier gas and 1.11 ppm by N_2 carrier gas. These values were close to the indicated concentration.

Table 4 The ratio of peak area value of 1,4-Dioxane to peak area value of d8-Dioxane

Added concentration of 1,4-Dioxane	Ratio of peak area value by He	Ratio of peak area value by N_2
0 ppm	0.645	0.620
250 ppm	1.268	1.259
500 ppm	1.822	1.786

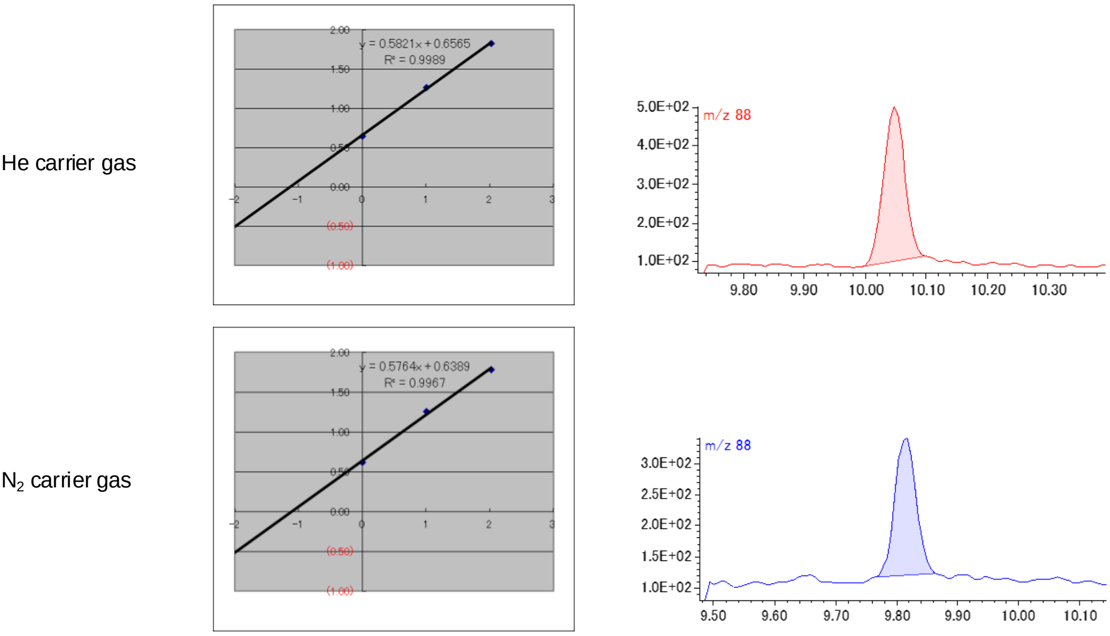

Fig. 3 Calibration curve by standard addition method and the peak of 1,4-Dioxane in cosmetic ingredient

Conclusion

It was shown that residual solvent analysis is possible using the single QMS mode of the JMS-TQ4000GC. Regarding the SIM measurement by N_2 carrier gas, it was confirmed that the peak intensity was sufficient for residual solvent analysis. Furthermore, the JMS-TQ4000GC can perform single QMS mode as well as MS/MS mode with a single instrument. Thus, it is possible to select the measurement mode according to the amount of matrix in the sample, making it applicable to a wider range of application fields.

Acknowledgments

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References

[1] Japanese Pharmacopoeia 18th Edition (2.46 Residual Solvents)