

Off-flavor analysis in natural rubber by using HS-GC/MS/MS

Product used : Mass spectrometer (MS)

Introduction

Natural rubber is used in a wide range of products from daily necessities such as shoe soles and hoses to industrial products such as tires. It is important to control off-flavor components in natural rubber, because the sap of natural rubber trees has a strong odor. In general, the SCAN/SIM measurement by HS-GC/MS is used for this analysis. However, it has possibility that the SIM measurement is affected by matrix components, because some natural rubbers contain many matrix components. Therefore, it is difficult to analyze off-flavor components contained in trace amounts by using the SIM measurement. On the other hand, the SRM measurement of GC/MS/MS use a combination of selected precursor ion and generated product ion from its selected precursor ion, so selectivity of detection ion and detection sensitivity will be improved. As a result, the influence of matrix components can be reduced, and it is possible to detect components contained in trace amounts. In this application, we report the analysis of off-flavor components in natural rubber by using HS-GC/MS/MS.

Measurement

The measurement was performed using a MS-62071STRAP trap-type HS and GC triple quadrupole mass spectrometer JMS-TQ4000GC UltraQuad™ TQ. Natural rubber (Sample A and B) was used as the measurement sample. Off-flavor components content of sample A is larger than that of Sample B. The amount of measurement sample was reduced from 200 mg to 50 mg, because the combination of chemical trap mode of JEOL's HS and SRM measurement enable more sensitive measurement. The measurement conditions is shown in Table 1, and the target components and their SRM transition are shown in Table 2.

Table 1 Measurement condition

HS condition	
Sample Temp.	150 °C
Sampling mode	Trap mode
Heating time	20 min
Trap tube	AQUATRAP1 (GL Sciences Inc.)
GC condition	
Column	VF-5MS(30 m length, 0.25 mm i.d., 0.25 µm film thickness)
Inlet	Split/Splitless
Inlet Temp.	250 °C
Flow	2 mL/min, Constant flow
Injection Mode	Split (20 :1)
Oven Program	40 °C (3 min) → 3 °C/min → 100 °C (1min) → 8 °C/min → 250 °C
MS condition	
Ion Source Temp.	200 °C
Interface Temp.	250 °C
Ionization Mode	EI+, 70 eV
Measurement Mode	SCAN/SRM
Mass range	<i>m/z</i> 10-500
Collision Gas	N ₂ , 10%

Table 2 SRM transition

Component	R.T.(min)	Quantitative ion	Reference ion 1	Reference ion 2
Acetic acid	1.7	60->43 CE:5	60->45 CE:10	60->60 CE:5
Isovaleric aldehyde	2.1	44->43 CE:15	58->57 CE:10	58->58 CE:5
Propionic acid	2.6	74->55 CE:15	74->73 CE:15	57->57 CE:5
Isobutyric acid	3.6	73->55 CE:10	88->73 CE:15	73->73 CE:5
Toluene	3.7	91->65 CE:15	92->91 CE:15	92->92 CE:5
Butyric acid	4.5	60->42 CE:10	73->55 CE:10	60->60 CE:5
Isovaleric acid	6.2	60->42 CE:15	87->69 CE:10	60->60 CE:5
Valeric acid	7.9	60->42 CE:10	73->55 CE:10	60->60 CE:5
Skatole	28.6	130->77 CE:20	130->130 CE:10	131->130 CE:15

Result

● SCAN measurement result of sample A and B

The TICC and EIC of sample A are shown in Fig. 1. The chromatogram peaks of the target component were clearly observed by SCAN measurement, because sample A content a lot of off-flavor components. Similarly, the chromatogram peaks of sample B were confirmed at the same RT, although the peak intensity was low.

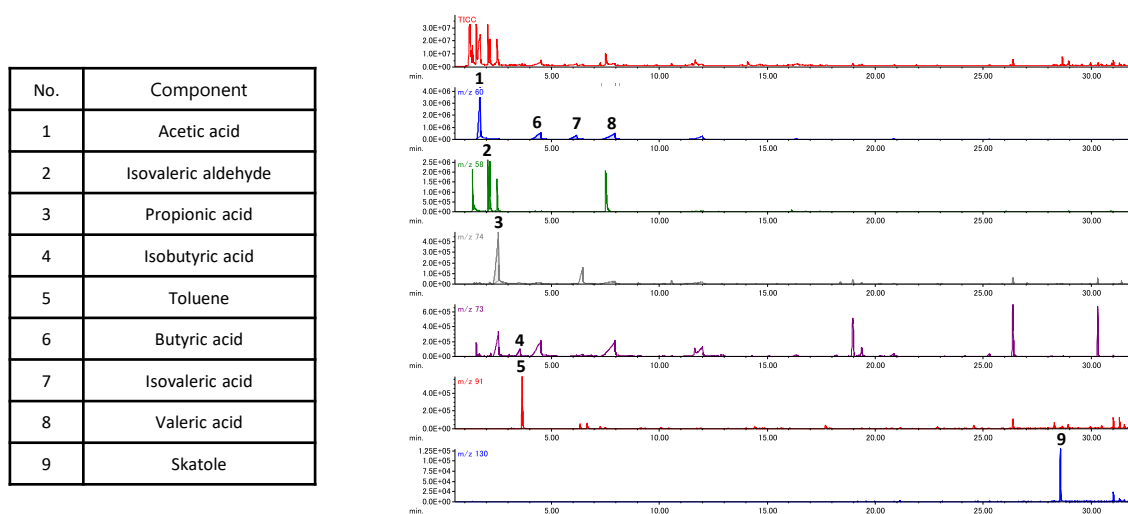


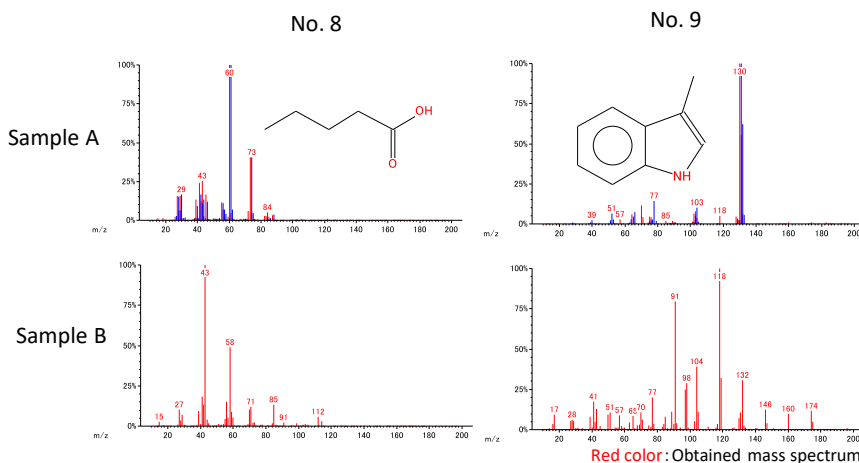
Fig. 1 TICC and EIC of Sample A

● NIST library search result of sample A and B

The M.F. value in the NIST library search result is shown in Table 3, and the mass spectra of peak No. 8 and peak No. 9 are shown in Fig. 2. Sample A has a high M.F. value of 820 to 938 due to the higher concentration of off-flavor components. On the other hand, sample B contain lower concentration of off-flavor components, and more than half of the NIST library search results showed low M.F. value or no result for the target component. As shown in Fig. 2, the mass spectra of peak No. 8 and peak No. 9 obtained from sample B were significantly different from those of sample A and the NIST library data. The chromatogram peaks observed from sample B were mainly composed of matrix components. Since single QMS measurements such as SCAN and SIM are expected to be greatly affected by matrix components, SRM measurement, which can suppress the effect of matrix components, might be a suitable for measurement method.

Table 3 NIST library search result

No.	Component	M.F.	
		Sample A	Sample B
1	Acetic acid	932	892
2	Isovaleric aldehyde	932	933
3	Propionic acid	845	731
4	Isobutyric acid	868	725
5	Toluene	938	940
6	Butyric acid	822	618
7	Isovaleric acid	900	853
8	Valeric acid	859	-
9	Skatole	820	-



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- Repeatability of peak area of each component in Sample B

The repeatability of peak area value obtained by SCAN measurement is shown in table 4, and the repeatability of peak area value obtained by SRM measurement is shown in table 5. The result of SCAN measurement showed overall high coefficients of variation especially Skatole and Butyric acid. This may be due to lower peak intensity or the influence of matrix components. On the other hand, the result of SRM measurement showed good repeatability and a coefficient of variation range from 0.1 to 8.6% due to the suppression of the influence of matrix components and improved sensitivity.

Table 4 Repeatability of peak area by SCAN

Component	n = 1	n = 2	n = 3	Ave.	STDEV	C.V.(%)
Acetic acid(m/z 60)	26727058	23448580	30907431	27027690	3738502	13.8
Isovaleric aldehyde(m/z 58)	37894217	36797432	30177488	34956379	4174815	11.9
Propionic acid(m/z 74)	1118609	1169287	1238393	1175430	60128	5.1
Isobutyric acid(m/z 73)	441535	476884	494190	470870	26838	5.7
Toluene(m/z 91)	2066383	2268404	2248838	2194542	111419	5.1
Butyric acid(m/z 60)	540842	638348	465206	548132	86801	15.8
Isovaleric acid(m/z 60)	1623757	1962426	1671893	1752692	183223	10.5
Valeric acid(m/z 60)	505776	500742	414297	473605	51424	10.9
Skatole(m/z 130)	16467	10732	13107	13435	2882	21.4

Table 5 Repeatability of peak area by SRM

Component	n = 1	n = 2	n = 3	Ave.	STEDV	C.V.(%)
Acetic acid(60→43)	48198138	46441666	46676467	47105424	953573	2.0
Isovaleric aldehyde(44→43)	31611384	32652805	33453197	32572462	923531	2.8
Propionic acid(74→55)	1620757	1524801	1530497	1558685	53831	3.5
Isobutyric acid(73→55)	3658550	3502348	3510171	3557023	88012	2.5
Toluene(91→65)	8652579	8161044	8422329	8411984	245931	2.9
Butyric acid(60→42)	2326212	2132262	2092492	2183655	125049	5.7
Isovaleric acid(60→42)	4355087	4349861	4359477	4354808	4814	0.1
Valeric acid(60→42)	2327284	2243168	2132341	2234264	97776	4.4
Skatole(130→77)	50718	43135	44845	46233	3977	8.6

- Confirmation of Valeric acid and Skatole in sample B by SRM measurement

The SRM chromatogram peaks of Valeric acid and Skatole are shown in Fig. 3(a) and(b). Regarding Valeric acid and Skatole that the mass spectra of the target component could not be obtained by SCAN measurement, the observed peaks can be confirmed as the target component based on the multiple monitor ions and the relationship between precursor ion and product ion.

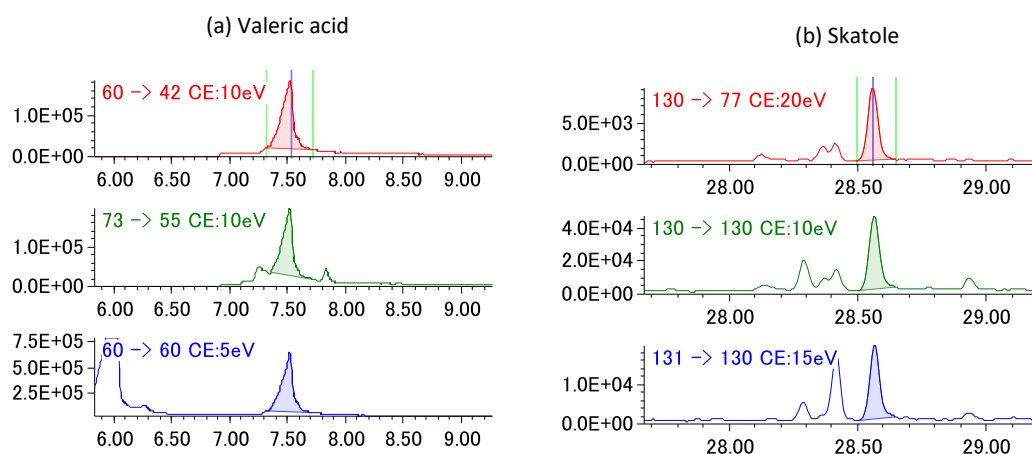


Fig. 3 SRM chromatogram peaks of valeric acid (a) and skatole (b)

Conclusion

The SCAN/SRM measurement of GC/MS/MS is an effective measurement method for the off-flavor analysis in materials with many matrix components. In particular, the SRM measurement use a combination of selected precursor ion and generated product ion from its selected precursor ion, so selectivity of detection ion and detection sensitivity will be improved. As a result, the influence of matrix components can be reduced, and it is possible to detect components contained in trace amounts. In addition, HS-GC/MS/MS measurement combined with JEOL's HS enables higher sensitivity analysis and reduces the amount of sample for measurement.

Acknowledgments

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