

High sensitivity detection method for polycyclic aromatic hydrocarbons using GC-MS/MS

Product used: Mass Spectrometer (MS)

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds produced not only by industrial activities but also by the combustion of substances in human activities and natural phenomena such as home heating, cooking, and forest fires. It has been recognized that PAHs have strong carcinogenicity or mutagenicity. Because they are produced in various combustion processes, there is a possibility that PAHs are contained not only in environmental pollution but also in various substances around human activity. The government organizations of several territories have already controlled and regulated contaminant level of PAHs from various points of view.

In Japan, the PAHs level in environmental pollutants is controlled and regulated, and the contamination levels of PAHs in various household products are also controlled and regulated by law (Act on Control of Household Products Containing Harmful Substances).

In Europe, the contamination level of PAHs in familiar products such as toys and furniture is controlled and regulated by GS mark certification from the perspective of safety certification. The European Food Safety Authority (EFSA) sets maximum acceptable levels for PAHs in food. Various regulations concerning PAH contamination levels have been in place, and there is a possibility to create new regulations about PAHs from different interests.

In the United States, the U.S. Environmental Protection Agency (EPA) regulates PAHs pollution levels in soil and water, and the Food and Drug Administration (FDA) sets limits for PAH contamination levels in food. In addition, each state and local government may implement its own regulations, and it is expected that the scope of regulations will continue to expand in the future.

Several methods have been proposed to measure trace amounts of PAHs. Gas chromatography- triple quadrupole mass spectrometry (GC-Triple QMS) is commonly used for high sensitivity measurement methods for specific PAHs in complex matrices. Twenty kinds of PAHs shown in Table 1 (left) were measured using JMS-TQ4000GC (JEOL Ltd.) and those the results are reported in this application note.



JMS-TQ4000GC

Table 1. Target compounds, Internal Standard compounds and SRM conditions

Compound Name of Target		R.T.	Q Transition		I Transition	
			SRM	Codition	SRM	Codition
1	Phenanthrene	6.07	178	> 176	30	178 > 152
2	Anthracene	6.14	178	> 176	30	178 > 152
3	Fluoranthene	8.83	202	> 200	35	202 > 152
4	Pyrene	9.70	202	> 200	25	202 > 152
5	Benzo (C) fluorene	10.85	216	> 189	40	216 > 214
6	Benzo(a)anthracene	14.14	228	> 226	30	228 > 202
7	Cyclopenta(c,d)pyrene	14.45	226	> 224	35	226 > 200
8	Chrysene	14.47	228	> 226	30	228 > 202
9	5-methylchrysene	16.41	242	> 240	30	242 > 226
10	Benzo(b)fluoranthene	19.58	252	> 250	35	252 > 226
11	Benzo(k)fluoranthene	19.58	252	> 250	35	252 > 226
12	Benzo(j)fluoranthene	19.58	252	> 250	35	252 > 226
13	Benzo(a)pyrene	21.73	252	> 250	35	252 > 226
14	Indeno(1,2,3,-c,d)pyrene	25.37	276	> 274	40	276 > 272
15	Dibenzo (a,h) anthracene	25.34	278	> 276	35	278 > 252
16	Benzo(g,h,i)perylene	26.61	276	> 274	40	276 > 272
17	Dibenzo(a,i)pyrene	31.81	302	> 300	45	302 > 298
18	Dibenzo(a,e)pyrene	33.93	302	> 300	45	302 > 298
19	Dibenzo(a,l)pyrene	35.13	302	> 300	45	302 > 298
20	Dibenzo(a,h)pyrene	35.75	302	> 300	45	302 > 298

Compound Name of Internal Standard		R.T.	Transition	
			SRM	Codition
1	Phenanthrene ¹³ C ₆	6.07	184	> 182
2	Anthracene ¹³ C ₆	6.14	184	> 182
3	Fluoranthene ¹³ C ₆	8.82	208	> 206
4	Pyrene ¹³ C ₆	9.70	205	> 203
5	Benzo(a)anthracene ¹³ C ₆	14.14	234	> 232
6	Chrysene ¹³ C ₆	14.47	234	> 232
7	Benzo(b)fluoranthene ¹³ C ₆	19.58	258	> 256
8	Benzo(k)fluoranthene ¹³ C ₆	19.58	258	> 256
9	Benzo(a)pyrene ¹³ C ₆	21.74	256	> 254
10	Indeno(1,2,3,-c,d)pyrene ¹³ C ₆	25.37	282	> 280
11	Dibenzo (a,h) anthracene ¹³ C ₆	25.34	284	> 282
12	Benzo(g,h,i)perylene ¹³ C ₁₂	26.61	288	> 286
13	Dibenzo(a,e)pyrene ¹³ C ₆	33.93	308	> 306
14	Dibenzo(a,l)pyrene ¹³ C ₁₂	35.13	314	> 312

Experimental

The GC and MS/MS measurement conditions are shown in Table 2. The JMS-TQ4000GC has two different SRM modes: (1) 'high-speed mode' in which monitoring channels can be switched with high speed and (2) 'high-sensitivity mode' in which high-sensitivity measurements can be achieved by expanding ion accumulation time with normal switching speed for SRM channels. The high-speed mode was applied for this measurement in anticipation of an increase in the number of target compounds in the future. A 'Select PAH' column (Agilent Technology) dedicated to PAH analysis was used and the oven heating rate program was finely implemented to achieve chromatographic separation of PAHs with similar structures. Also, as shown in Table 1 (Right side), several ¹³C-labeled PAHs were used as internal standards.

Table 2. Measurement Conditions

GC Condition		MS Condition	
GC	8890GC (Agilent)	Mass Spectrometer	JMS-TQ4000GC (JEOL Ltd.)
Injection mode	Pulsed splitless	SRM Mode	High Speed Mode
	Purge On time : 1min, Purge Flow : 20mL/min	Ion source temp	280°C
Injection Temp	300°C	GC Interface temp	300°C
Column	Select PAH (Agilent) 30m X 0.25mm I.D. 0.15µm F.T.	Ionization Voltage	70V
Oven	110°C (1 min) > 60°C/min > 220°C (0min) > 5°C/min > 270°C (0min) > 3°C/min > 295°C (0min) > 20°C/min > 330°C (10min) > 2°C/min > 340°C (0min)		
He Flow	1mL/min (Constant Flow mode)		

Results

Calibration curves in the range of 5–250 µg/L for 20 kinds of PAHs were created. The calibration curves for all 20 PAHs gave good linearity with more than 0.999 value as coefficient of determination (r^2). The SRM chromatograms of the three benzo(a)fluoranthenes (b, k, j) and the two ^{13}C -labeled benzo(a)fluoranthenes (b, k) that were used as internal standards were shown in Fig.1.

Since the three benzo(a)fluoranthenes (b, k, j) are structural isomers with the same elemental composition, the SRM conditions to monitor those three benzo(a)fluoranthene were exactly same. But chromatographic separation for those three benzo(a)fluoranthene (b, k, j) could be achieved by using the Select PAH column

The limit of quantification (LOQ) values for the 20 PAHs were calculated as the peak with $S/N = 10$ based on S/N values (Peak-to-Peak) of each PAHs peaks at 5 µg/L that was measured as lowest calibration point and were summarized in Table 3 together with S/N values at the 5 µg/L calibration point. LOQ values less than 0.3 µg/L were obtained for 18 PAHs, excluding dibenzo(a,h)pyrene and dibenzo(a,h)pyrene, and the detection limit values less than 1 µg/L were obtained for those two PAHs. It could be concluded that the SRM measurement using the JMS-TQ4000GC (JEOL Ltd.) could achieve highly sensitive detection for the 20 PAHs.

Benzo (b, k, j) fluoranthene

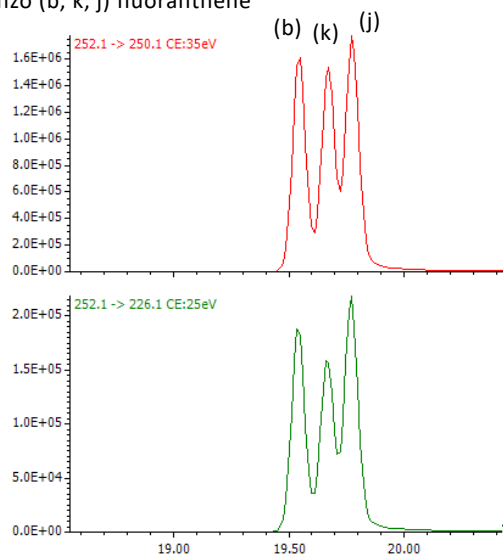
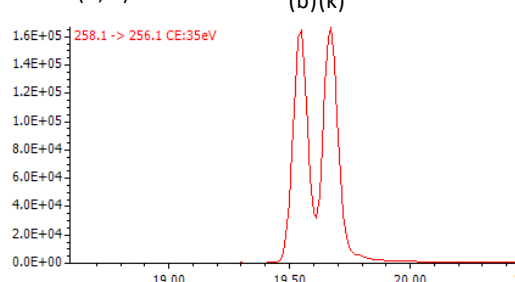
 ^{13}C -Benzo (b, k) fluoranthene

Figure 1. SRM chromatograms of 3 benzo(a)fluoranthenes (b, k, j) and ^{13}C labelled benzo (b, k) fluoranthenes

Table 3. Linearity of calibration curve and detection limit for each target PAHs

	Compound name	R^2	LOQ µg/L (S/N 10)	$S/N(P-P)$
1	Phenanthrene	0.99997	0.08	636.6
2	Anthracene	0.99993	0.06	855.6
3	Fluoranthene	0.99997	0.11	456.4
4	Pyrene	0.99999	0.09	546.3
5	Benzo (c) fluorene	0.99999	0.13	381.5
6	Benzo(a)anthracene	0.99999	0.09	535.5
7	Cyclopenta(c,d)pyrene	0.99995	0.16	315.6
8	Chrysene	0.99997	0.27	185.4
9	5-methylchrysene	0.99996	0.21	244.0
10	Benzo(b)fluoranthene	0.99997	0.07	698.3
11	Benzo(k)fluoranthene	0.99998	0.08	615.4
12	Benzo(j)fluoranthene	0.99970	0.08	623.5
13	Benzo(a)pyrene	0.99999	0.10	510.9
14	Indeno(1,2,3,-c,d)pyrene	0.99999	0.09	586.0
15	Dibenzo (a,h) anthracene	0.99999	0.07	696.4
16	Benzo(g,h,i)perylene	0.99991	0.13	391.0
17	Dibenzo(a,i)pyrene	0.99991	0.15	324.8
18	Dibenzo(a,e)pyrene	0.99999	0.22	228.7
19	Dibenzo(a,l)pyrene	0.99975	0.59	84.9
20	Dibenzo(a,h)pyrene	0.99920	0.50	100.2

Conclusion

We have used the JMS-TQ4000GC SRM high-speed mode in this study for considering the possibility that the number of target analytes may increase in the future, and it was possible to detect all PAHs with high sensitivity. The results show that the JMS-TQ4000GC can be fully utilized for quantitative analysis of PAHs.