II.1.9 Components of gasoline and kerosene

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Introduction

The petroleum fuels are a group of hydrocarbons refined and modified from the crude oil, and include more than 100 kinds of aliphatic and aromatic hydrocarbons. They are roughly classified into petroleum gas, gasoline, kerosene, light oil, heavy oil and others [1]. This chapter deals with analysis of hydrocarbons of C_3–C_{16} being included in automobile gasoline, purified kerosene (No.1 kerosene), automobile light oil for a diesel engine and liquefied petroleum (LP) gas.

The petroleum oils, such as gasoline and kerosene, are frequently detected from specimens in fire cases. The detection of petroleum components from human specimens is especially important in legal medicine as a proof of vital reaction [2, 3]. In the field of police science, the discrimination analysis among gasoline, kerosene and other products is being made for specimens of a fire and of environmental pollution; the detection of each component serves as an objective and important evidence for an accident or an incident [4]. Although such specimens can be grouped into biological ones and non-biological ones such as fire debris and polluted materials, the methods to be presented in this chapter are usable for both groups of specimens.

Since the petroleum components are generally volatile with the exception of some fluids such as heavy oil, the methods of headspace extraction [2–8], liquid-liquid extraction using hexane [9], purge-and-trap extraction [10, 11], dynamic headspace extraction [12] and solid-phase microextraction (SPME) [13–18] are being employed as pretreatments; their analysis is being made by GC with FID or GC/MS.

As medicolegal application, a GC/MS method for discrimination among LP gas, gasoline and kerosene is also presented for a gas sample obtained from the trachea of a cadaver [19].

Reagents and their preparation

Reagents are of analytical grade obtainable from many manufacturers. The organic solvents to be used for extraction should be of ultra-pure grade. Toluene-d_6 can be purchased from Merck (Darmstadt, Germany) and other companies. The 0.001 % *n*-butylbenzene solution is prepared by dissolving 1.0 μL *n*-butylbenzene in 100 mL distilled water.

Instrumental conditions

i. GC (/MS) conditions-1 [8, 19]

Column: a DB-1 fused silica wide-bore capillary column (30 m × 0.53 mm i. d., film thickness 1.5 μm or 5.0 μm, J&W, Scientific, Folsom, CA, USA)[a], DB-17 (15 m × 0.53 mm i. d., film thickness 1.0 μm, J&W, Scientific)[a]; column temperature: 40 °C (1 min)→16 °C/min→250 °C (10 min); injection temperature: 250 °C; splitless mode: 60 s; carrier gas[b] (flow rate): N_2 (1 mL/min), He (15 mL/min); FID conditions[b]: H_2 (35 mL/min), air (400 mL/min); detector temperature: 300 °C; MS conditions[c]: positive ion EI; accelerating voltage: 3 kV; electron energy: 70 eV; ionization current: 0.3 mA; interface temperature: 250 °C.

ii. GC conditions-2

Column: 1.5 % GE SE-30 Chromosorb W (2 m × 2.6 mm i. d., glass column, GL Sciences, Tokyo, Japan, and similar columns obtainable from other manufacturers); column temperature: 60 °C (2 min)→2 °C/min→120 °C (5 min); carrier gas[b] (flow rate): N_2 (40 mL/min), He (40 mL/min); detector temperature: 140 °C

iii. GC/MS conditions-3 (cold trap)

Instrument: a QP-5000 GC/MS instrument equipped a cryogenic oven trapping system with liquefied carbon dioxide (Shimadzu Corp., Kyoto, Japan); column: an XTI-5 fused silica capillary column (30 m × 0.25 mm i. d., film thickness 0.25 μm, Restek, Bellefonte, PA, USA); column temperature: 40 °C (1 min) → 30 °C/min → 290 °C (5 min); carrier gas (flow rate): helium (2.1 mL/min); MS conditions: positive ion EI; electron energy: 70 eV; interface temperature: 260 °C; scan range: *m/z* 33–200, 0.35 s/cycle.

Procedures

i. Headspace method [2–8, 19]

i. Liquid samples, such as blood and urine, are directly subjected to analysis. Organ specimens, after being frozen, are rapidly minced into small pieces with a scalpel or a knife, or emulsified with a closed-type homogenizer.
ii. A fixed amount (0.5–2 mL or g) of a specimen is placed in a glass vial[d] containing an internal standard (IS)[e] solution, if necessary, capped airtightly and heated[f] at a temperature (55–65 °C) for a period (15–30 min).
iii. A volume (0.5–1.0 mL) of the headspace vapor is drawn into a gastight syringe (or a glass syringe), which has been also heated at the same temperature (55–65 °C), and injected into GC[f] [GC(/MS) conditions-1].

ii. Liquid-liquid extraction method [9]

i. A 5 mL volume of blood and IS solution (0.001 % *n*-butylbenzene, 0.2 mL[g] are placed in a glass centrifuge tube with a ground-in stopper.
ii. A 7 mL volume of *n*-pentane is added to the mixture, shaken vigorously and centrifuged at 3,000 rpm for 5 min.
iii. The upper organic layer is carefully transferred to a vial and condensed into about 200 μL[h]. A 3–5 μL aliquot of it is injected into GC (GC conditions-2).

iii. Headspace SPME method

i. A human blood or other specimen (0.2–2 mL or g) is placed in a 10–15 mL volume vial with a screw cap[d] containing IS solution, if necessary (toluene-d_8[g], in case of GC/MS analysis).
ii. An SPME device (100 μm polydimethylsiloxane, Supelco, Bellefonte, PA, USA) is injected into the vial for exposure of a fiber, heated at 55 °C for 15 min and then cooled at 5 °C for 15 min.
iii. The device is pulled out of the vial and injected into GC port [GC (/MS) conditions-1].

iv. Headspace SPME-cold trap method [18]

i. A human blood or other specimen (0.2 g), IS solution (toluene-d_8, 0.2 or 1 μg) and 0.8 mL distilled water are placed in a 12 mL volume screw-cap vial and capped with a Teflon-coated silicone rubber septum.
ii. A 100 μm polydimethylsilicone fiber (Supelco) is exposed in the headspace of the vial at 5 °C for 30 min for adsorption of target compounds.
iii. The SPME device is pulled out of the vial, injected into GC/MS and left there for 3 min (1 min for sampling and 2 min for purging) (GC/MS conditions-3).

v. Analysis of intratracheal gas (direct injection method) [19]

i. The front skin of the neck of a cadaver is incised to expose the trachea; a needle of a 2 mL volume glass syringe is inserted into the trachea to obtain the intratracheal gas.
ii. The tip of the needle is capped with the septum of GC injection; it is injected into a GC port as soon as possible [GC (/MS) conditions-1].

Assessment of the methods

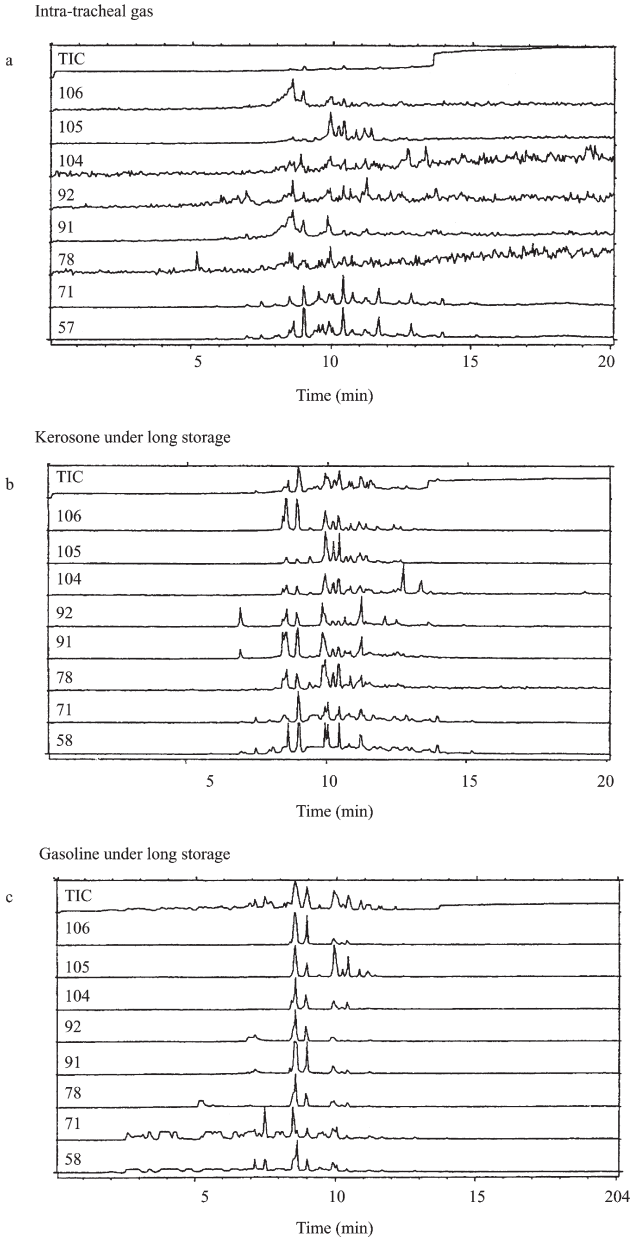
The gasoline/kerosene analysis is frequently made for the purpose of discrimination between them. The most common method for such analysis is the one by liquid-liquid extraction. However, it is somewhat complicated, tedious and occasionally suffers from interference by compounds with low boiling points being contaminated in an organic solvent used. It is also a problem that some compounds with low boiling points to be analyzed may be lost during the condensation step.

Therefore, the headspace method, without the need of an organic solvent for extraction, is widely used; it is very suitable for analysis of volatile compounds, such as LP and butane gas [2–8]. However, this method is not suitable for compounds with relatively high boiling points (larger than C_{10}) and not useful for discrimination between kerosene and light oil.

Since the static headspace method is based on the equilibrium of a compound between gas and aqueous phases, its sensitivity is sometimes not sensitive enough. To overcome this problem, the dynamic headspace and purge-and-trap[i] methods have been developed in recent years. The volatile compounds are purged from a specimen to be trapped by activated charcoal or a column of Tenax[j], followed by desorption of the compounds by (pulse) heating and introduction into GC (/MS) for analysis. However, these methods require special instrumental devices; and they also suffer from adsorption of water to the activated charcoal, or from difficulty in desorption of compounds with relatively high boiling points from the Tenax column.

Recently, the headspace SPME method [method (3)] and the combined method [method (4)] have been developed as useful methods for analysis of volatile compounds.

Figure 9.1



GC/MS analysis of intratracheal gas in an actual case. TICs and mass chromatograms for each ion are shown. The data on kerosene and gasoline are shown for comparison; the profiles showed that the intratracheal gas contained kerosene. The GC/MS conditions-1 described in the text with a column of DB-1 (30 m × 0.53 mm i. d., film thickness 5 μm) were used. For the panels b and c, each headspace gas was injected into GC/MS. TIC: total ion chromatogram; the numbers shown at the left corners of each panel are mass numbers of ions (*m/z*) used for mass chromatography.

As an application to an actual forensic case, the analysis of intratracheal gas was performed (*Fig. 9.1*, in which kerosene could be detected); it is possible to discriminate among LP gas, gasoline, kerosene and others by the simple direct gas analysis[k] [19], and the presence of such components in the trachea can be regarded as an indicator of vital reaction.

Figure 9.2 shows the results of GC/MS analysis of gasoline, kerosene and light oil commercially available by the methods of headspace [method (1)], headspace SPME [method (3)] and direct injection. By the headspace method, the discrimination among LP gas, gasoline and kerosene could be achieved [19], but that between kerosene and light oil was somewhat difficult. By the headspace SPME method, the discrimination among gasoline, kerosene and light oil was possible; but there was a trend of low recoveries of compounds with low boiling points. Therefore, by combining the headspace methods with the headspace SPME method, the discrimination of almost all petroleum gas and liquids is possible and applicable to forensic science practice[l].

In conclusion, for screening of petroleum fuels, such as gasoline, kerosene and others, the headspace GC-FID should be used first. When the peaks are too small by the headspace method to discriminate the petroleum fuels, the GC patterns obtained after liquid-liquid extraction seem useful. In the near future, the automated analysis by the headspace SPME/GC (/MS) will be probably used widely for components of gasoline and kerosene.

Toxic and fatal concentrations

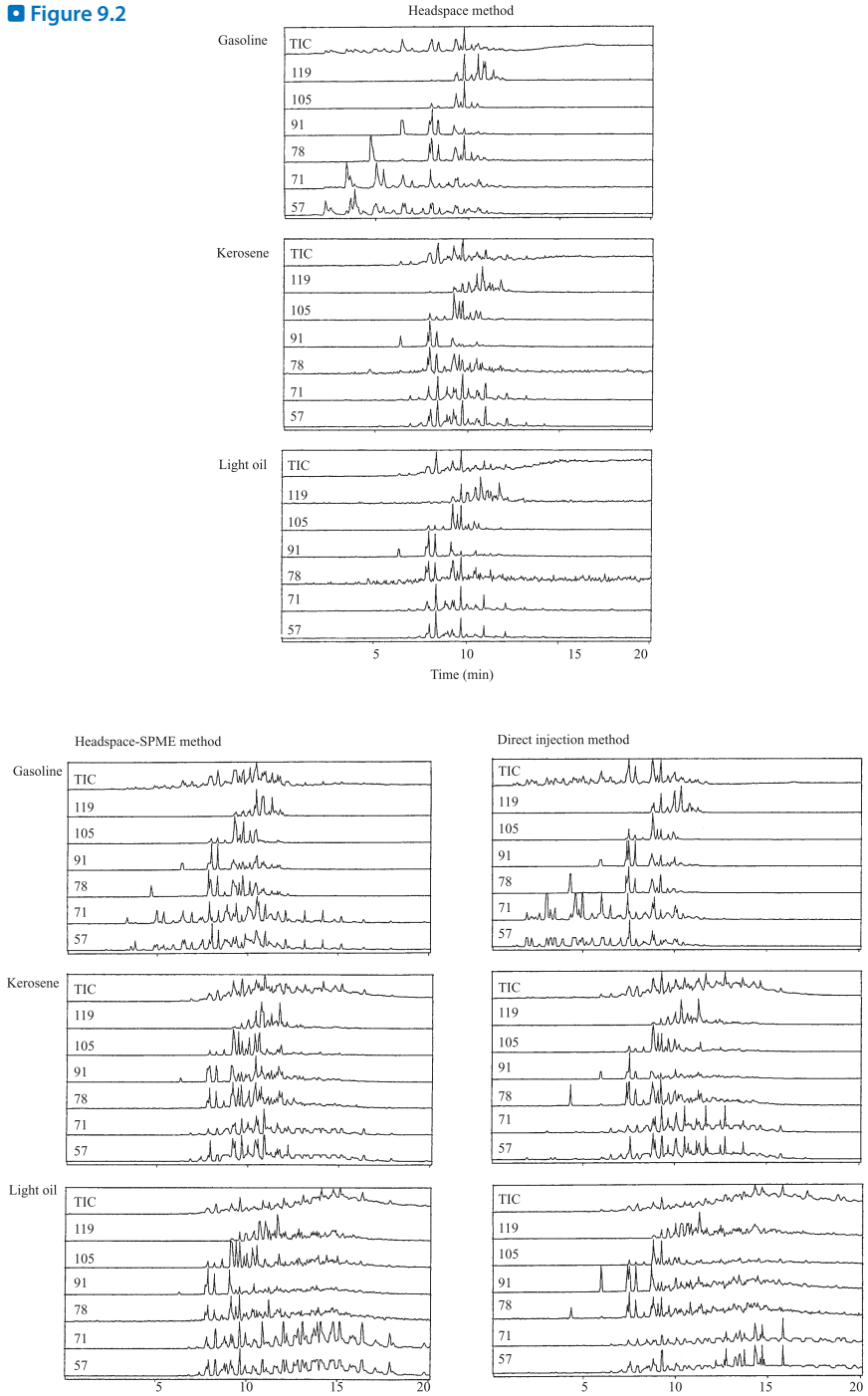
The poisoning cases with gasoline or kerosene are not rare. The most frequent acute poisoning is caused by their oral ingestion [20]. The acute poisoning symptoms by the oral ingestion are causalgia of the oral cavity and the stomach, nausea, vomiting, cyanosis, aspiration pneumonia and lung edema [21]. In the case of aspiration of petroleum fluids into the lung, the symptoms are said to be severer than those caused by the oral ingestion [20]; severe causalgia of the chest, respiratory disturbance, bronchitis and pneumonia appear [21].

Although the toxic concentrations of gasoline in human blood could be hardly found in the literature, the minimum fatal oral dose of gasoline was reported to be 10–50 mL; and that by aspiration not more than several mL [21].

Gasoline and kerosene are composed of many toxic compounds, which are somewhat different according to their brands and even to their lots. Therefore, it seems not desirable to express the toxic and fatal concentrations simply as the amounts of gasoline or kerosene itself. However, toluene and xylene, the most toxic components of gasoline and kerosene can be indicators for their toxicity. In *Fig. 9.3*, the analytical results by GC for a 28-year-old male, who died by inhalation of gasoline gas inside a automobile trunk with suicidal intent, are shown [8]; each peak appearing in the TICs was identified by GC/MS. The analytical results of this victim are shown in *Table 9.1* together with those appearing in some reports [5, 6, 8, 22].

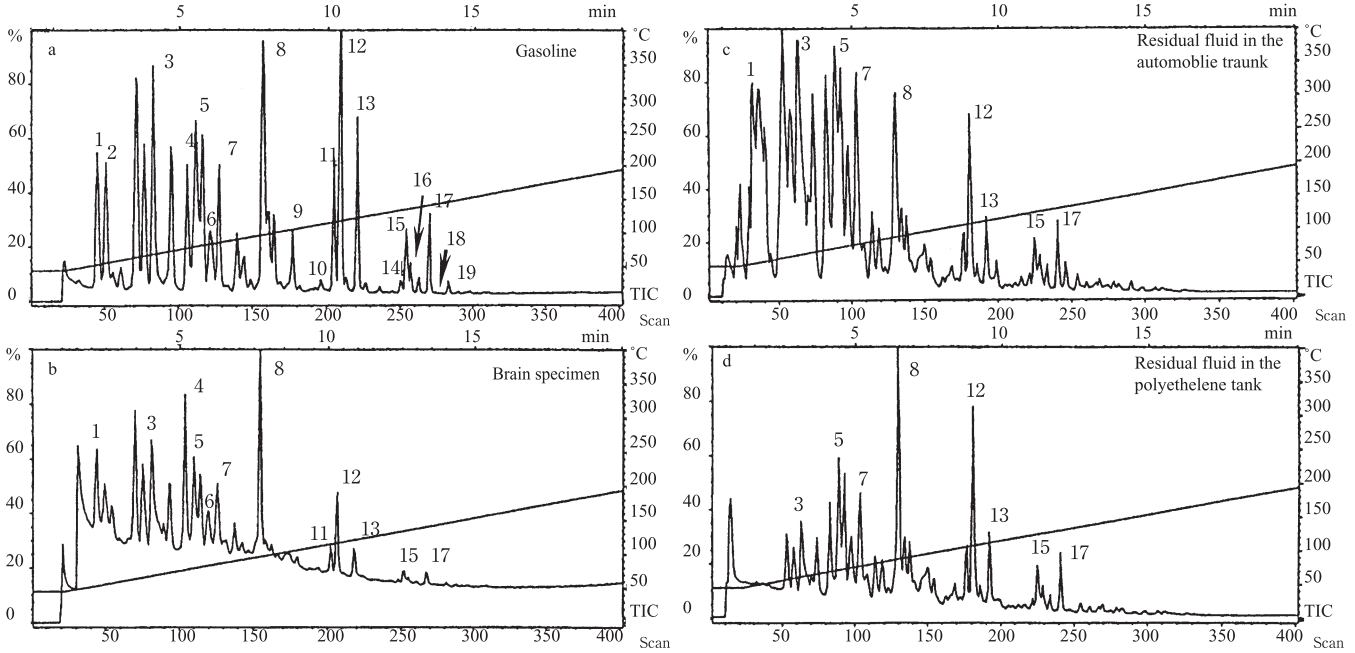
Carnevale et al. [5] reported that the gasoline concentration in blood of a 25-year-old male, who had died of gasoline poisoning, was 52 μg/mL (ppm). Matsumoto et al. [7] reported a case, in which a male had been discovered alive in an automobile filled with gasoline vapor; he died 9 days later. They measured gasoline concentrations in his blood at 39 and 63 h after the exposure, and estimated the initial gasoline concentration in blood to be 247 μg/mL. In the above case [8], the blood concentrations of toluene and xylene were 7.66 and 12.6 μg/mL, respectively, which were almost fatal.

Figure 9.2



GC/MS analysis of gasoline, kerosene and light oil commercially available by the methods of headspace extraction, headspace-SPME and direct injection. The GC/MS conditions-1 described in the text were used with the same column as specified in *Fig. 9.1*.

Figure 9.3



TICs obtained by headspace GC/MS for specimens collected from an actual case of gasoline poisoning. The GC/MS conditions-1 described in the text were used with the same column as specified in Fig. 9.1. Each peak was identified by measurements of mass spectra as follows. 1: isopentane, 2: *n*-pentane, 3: *n*-hexane, 4: benzene, 5: 2,4-dimethylpentane, 6: 1-heptene, 7: *n*-heptane, 8: toluene, 9: *n*-octane, 10: 2-octane, 11: *o*-xylene, 12: *m,p*-xylene, 13: ethylbenzene, 14: *n*-propylbenzene, 15: 4-ethyltoluene, 16: 1,3,5-trimethylbenzene, 17: 1,2,4-trimethylbenzene, 18: *n*-decane, 19: 1,2,3-trimethylbenzene (from reference [8] with permission).

Table 9.1

Concentrations of gasoline and its components in blood and organs in fatal cases of gasoline poisoning

Case	Age	Sex	Compound identified	Concentration (μg/mL or g)								
				Blood	Brain	Lung	Liver	Kidney	Sceretal muscle	Adipose tissue	Oil used	Ref
1	18	M	Gasoline (a peak, RT 1 min)	–	300–400	–	–	–	–	–	Gasoline	[22]
2	18	M	Gasoline (a peak, RT 1 min)	+	+	400	700	+	–	–	Gasoline	[22]
3	25	M	Gasoline (2-methyl pentane)	51.5	44.2	457	663	51.5	–	–	Gasoline	[5]
4	44	M	Isopentane *n*-Pentane 2-Methyl-2-butene 2-Methylpentane 3-Methylpentane *n*-Hexane Ethanol	0.051 0.241 0.284 0.186 0.222 0.447 2.21 (mg/mL)	–	–	–	–	–	–	Gasoline	[6]
5	28	M	Toluene Xylene	7.66 12.6	40.8 40.7	5.34 14.6	27.9 23.1	5.38 7.49	14.8 12.9	15.3 12.2	Gasoline	[8]

Nelm et al. [22] dared to use the values in terms of gasoline in the cases of gasoline poisoning (*Table 9.1*), but the analysis of each component is, of course, desirable to assess the toxicity.

For poisoning with kerosene, the symptoms were reported almost the same as those for gasoline [21]; the fatal oral dose in humans was estimated to be 90–120 g [21]. The analytical data of kerosene and its components in human specimens are not found, but are estimated to be similar to those of gasoline.

Notes

a) Retention times of petroleum components are, of course, different with different DB-17 and DB-1 columns and with different film thickness, which should be confirmed by each analyst. The retention times with an HP-17 column probably differ from those with the DB-17 column in spite of the same material, size and film thickness; this is also true between HP-1 and DB-1. By the use of GS-Q column (30 m × 0.53 mm i. d., J&W, Scientific), the discrimination among LP gas, gasoline and kerosene can be also made [19, 23].

b) The conditions are different in different types of instruments and are required for careful readjustment.

c) The MS conditions in the EI mode, which is most common, are shown. The positive EI mode gives the most reproducible, sensitive and stable results for both qualitative and quantitative analysis.

d) For headspace extraction, a vial cap with a septum made of materials containing rubber (including Teflon and silicon rubber) is to be avoided, if possible. The safest one is the vial with a screw cap with a cork disk coated with aluminum foil on the inside surface (Nichidenrika Glass, Tokyo, Japan and any other manufacturer). In this case, it is necessary to drill a hole through the central part of each plastic cap (not trough the cork disk) beforehand.

e) The petroleum fluids contain too many compounds to be quantitated by GC-FID with use of an IS. However, by GC/MS, the accurate quantitation of the components becomes possible with stable isotopic ISs, such as toluene-d_8 (at about 10 μg/mL, 10 ppm), $C_{10}D_{22}$, $C_{11}D_{24}$, $C_{12}D_{26}$, $C_{13}D_{28}$, $C_{14}D_{30}$ or $C_{15}D_{32}$ (Cambridge Isotope Lab., Woburn, MA, USA) [also see the below g)] .

f) With use of an autosampler for headspace extraction, accurate determination can be made even with caps with Teflon or silicone rubber septa, because highly reproducible measurements can be achieved with a fixed time and temperature for heating; however, butyl rubber septa cause too many impurity peaks and thus should not be used.

g) In GC/MS, 1–10 μg/mL of toluene-d_8 or $C_{10}D_{22}$ dissolved in 10 % (v/v) Tween-20 (polyoxyethylene sorbitan monooleate, Nacalai Tesque, Kyoto, Japan and other manufacturers) aqueous solution can be used as IS [also see the above e)].

h) The condensation is made under the stream of nitrogen without warming. Care should be taken not to dry or condense too much.

i) The examples of the purge-and-trap instruments are: Tekmar 3000J/4000J, CP 4020 PTI/TCT (GL Sciences) and Curie point headspace sampler (JHS-100, Nihon Bunseki Kogyo, Tokyo, Japan).

j) It is activated by heating at 260 °C for 30 min before use.
k) There are also reports dealing with the usefulness of intratracheal contents (not air) [24, 25].
l) The specimens obtained at the scene of a fire usually give profiles of peaks different from those of an oil actually used for ignition, because of the evaporation of low-boiling point components during burning and intervals after the fire; such changes should be taken into consideration upon each judgement. For identification of environmental pollutants, care should be taken for the possibility of the presence of multiple oils and of denaturation due to a long storage or use.

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