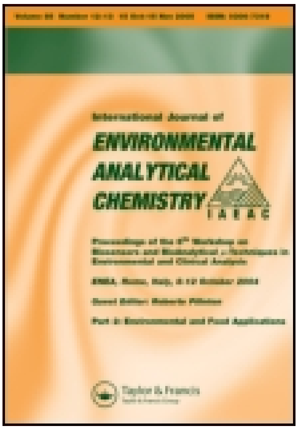

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Application of urea adduction technique to polluted urban aerosols for the determination of hydrogen isotopic composition of *n*-alkanes

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We examined an applicability of an improved urea adduction technique for the determination of hydrogen isotopic composition (δD) of homologous series of *n*-alkanes present in polluted urban aerosols using GC/TC/IRMS. Unresolved complex mixture (UCM) of hydrocarbons that interferes with accurate isotope measurements of *n*-alkanes was removed from *n*-alkane fraction by a urea adduction method. Recoveries of C_{20} to C_{30} *n*-alkanes during the urea adduction procedure were greater than 90% when the concentrations of total *n*-alkanes exceed 6.1 $\mu g\,mL^{-1}$. Our compound-specific D/H ratios confirm the absence of significant hydrogen isotope fractionation in *n*-alkanes during urea adduction and recovery of the purified *n*-alkane fraction. We applied this technique to the urban aerosols that contain a large quantity of UCM to measure δD of C_{20} to C_{35} *n*-alkanes in urban aerosols from Tokyo and Sapporo with an accuracy less than 10‰. We found that the δD values widely ranged from −38 to −179‰. Based on the δD values of individual *n*-alkanes in aerosol samples, we can obtain further information on the sources of aerosol *n*-alkanes and their source regions, and the atmospheric processes such as long-range transport and atmospheric mixing of air masses of different origin.

Keywords: hydrogen isotope; *n*-alkane; urban aerosol; urea adduction

1. Introduction

Homologous series of *n*-alkanes are one of ubiquitous organic compounds in environmental samples including atmospheric aerosols [1]. In general, *n*-alkanes in terrestrial higher plant waxes are dominated by longer chain homologues (C_{25} to C_{35}) with a significant predominance of odd carbon numbers [2], whereas those in fossil fuels are characterised by C_{10} to C_{35} homologues with no carbon number preference [3]. Hence, carbon preference index (CPI; odd/even ratios) of *n*-alkanes is often used to distinguish their origin and discuss transport processes of aerosols [4,5]. For example, contemporary observations of odd/even ratios of *n*-alkanes in urban aerosols in Tokyo, Japan, have revealed a major contribution from higher plant waxes during spring to summer, while anthropogenic emission of petroleum hydrocarbons was dominant in winter [6].

Stable carbon isotopic composition (δ^{13}C) of individual *n*-alkanes in aerosols provides additional information on their sources. In particular, large variations (up to 20‰) in δ^{13}C are reported for plant leaf wax *n*-alkanes due to the difference in photosynthetic pathways

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between C_3 and C_4 plants, and their $\delta^{13}C$ signature is often used to evaluate relative contribution of C_3/C_4 plants to organic aerosols [7,8]. However, the relatively narrow range of *n*-alkane $\delta^{13}C$ values in crude oil [9] compared with those in plants lowers their resolution to distinguish source differences in the mixture of plant *n*-alkanes and anthropogenically emitted hydrocarbons in urban aerosols.

For the last decade, hydrogen isotopic composition (δD) of individual organic molecules in various biological and geological samples has been intensively studied using gas chromatography/thermal conversion/isotope ratio mass spectrometer (GC/TC/IRMS). The δD studies of hydrocarbons in crude oils revealed much larger variations than those of the $\delta^{13}C$ by reflecting their source organic matter, source water and post depositional processes [9–12]. For example, the δD values of hydrocarbons derived from marine and terrestrial source rocks exhibit isotopic differences of more than 100%, which potentially provide a useful tool for oil-source correlation and paleoenvironmental reconstructions [9,11]. On the other hand, the δD of terrestrial higher plant leaf waxes was revealed to respond sensitively to the δD of the precipitation waters and local and regional meteorology (evapotranspiration, relative humidity and soil moisture) [13–15]. Further, their records in sediments have been used as the proxy for past hydrological changes [16,17].

The application of compound-specific δD analyses for *n*-alkanes in atmospheric aerosols would therefore provide further information on their sources and source regions reflecting the hydrological conditions that control δD of leaf wax *n*-alkanes. Nevertheless, no study is available so far for the δD of *n*-alkanes in urban aerosols, partly because of the difficulty in obtaining accurate δD data due to the presence of co-eluting unresolved complex mixture (UCM) of branched and cyclic hydrocarbons on GC chromatograms [5,6,18]. Several methods are known to refine *n*-alkanes in petroleum for the compound-specific isotope measurement; i.e. those utilise various types of molecular sieves, clathrates of urea and thin layer chromatography with urea [19–21]. In the case of the $\delta^{13}C$, it is generally known that no isotopic fractionation occurs during the procedures [20–22]; however, the examination of δD isotopic fractionation is only limited to the preliminary report by Pedentchouk *et al.* [23].

In this study, we investigate an applicability of urea adduction technique, one of the simplest and the least hazardous methods to purify *n*-alkanes in crude oils, for the measurements of δD of hydrocarbons in urban aerosols. Here we describe the analytical procedure for the δD measurement, report for the first time the δD values for homologous series of *n*-alkanes in urban aerosols, and discuss the advantage of this technique in the application to environmental chemistry of atmospheric aerosols.

2. Experimental

2.1 *Urea adduction of n-alkanes*

Isolation of homologous series of *n*-alkanes from unresolved complex mixture of branched and cyclic hydrocarbons was performed by urea adduction technique [22,24]. A saturated solution of urea in methanol (1.5 mL) was added to the aliphatic hydrocarbon fraction dissolved in a *n*-hexane/acetone (2 : 1) mixture (4.5 mL) and gently stirred in a tightly closed glass vial (10 mL) overnight at room temperature using a mechanical stirrer to complete the formation of urea adduct. After the adduction, the solvent was pipetted out from the urea crystals, which were rinsed with fresh solvent (*n*-hexane/acetone 2 : 1

mixture) for three times to remove non-adducted hydrocarbons. The urea crystals were dried under N_2 flow, then the adducted *n*-alkanes were recovered with *n*-hexane after dissolving the crystals in pure water at room temperature.

The *n*-alkanes were analysed on a Hewlett-Packard 6890 gas chromatograph equipped with an on-column injector, CP-Sil 5 CB fused silica capillary column (60 m × 0.32 mm i.d., 0.25 μm film thickness) and flame ionisation detector (FID). Helium was used as a carrier gas. The GC oven temperature was ramped from 50 to 120°C at 30°C min^{-1}, and to 310°C at 5°C min^{-1}, and then held isothermally for 45 min. GC data were processed for quantification by the Chemstation software using an external standard (C_{29} *n*-alkane).

2.2 *Principles of δD measurement for n-alkanes using GC/TC/IRMS*

Compound-specific hydrogen isotopic compositions (δD) of individual *n*-alkanes were determined using a Hewlett-Packard GC (HP 6890) connected to a Finnigan MAT Delta Plus XL mass spectrometer via a Finnigan MAT thermal conversion ceramic tube. The GC was equipped with an on-column injector and DB-5MS fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 50 to 120°C at 10°C min^{-1}, and to 310°C at 4°C min^{-1}, and then held isothermally for 45 min. Helium was used as a carrier gas at a flow rate of 1.8 mL min^{-1}. The *n*-alkanes were isolated and transferred to a thermal conversion furnace maintained at 1450°C, where hydrocarbons were converted to hydrogen molecules and graphite. The mass-2 and mass-3 signals were monitored by the mass spectrometer. The D/H ratios for individual compounds were calculated by integrating the two signals after correcting the contribution of H_3^+ to the mass-3 beam [25]. The H_3^+ factor was determined based on the changes in the (mass-3)/(mass-2) ratio under the different H_2 pressures. The H_3^+ factor during the measurement was typically between 7.8 and 8.5 ppm nA^{-1}. The hydrogen isotopic compositions of individual compounds are reported in the delta notation with respect to the Vienna Standard Mean Ocean Water (VSMOW) as follows:

$$\delta\mathrm{D}(‰) = [(\mathrm{D/H})_{\mathrm{sample}}/(\mathrm{D/H})_{\mathrm{VSMOW}} - 1] \times 1000$$

For a calibration purpose, a mixture of C_{16} to C_{30} *n*-alkanes with known isotopic compositions acquired from Indiana University, USA (further information is available at http://mypage.iu.edu/~aschimme/hc.html), was used. Prior to the sample measurement, the solution was injected to the GC/TC/IRMS system to check the data quality and to ensure the analytical error to be ±5‰.

2.3 *δD measurements of authentic n-alkanes before and after urea adduction*

A solution containing fifteen *n*-alkanes (C_{16} to C_{30}) at concentrations of 11.1 to 62.4 ng μL^{-1} of individual compounds, the same solution used for calibration, was used in this study. Four fractions that contain 4.4, 9.9, 27.5 and 68.8 μg of total *n*-alkane compounds each were used for recovery tests during the urea adduction procedure. The recovered *n*-alkanes were then determined by GC-FID to evaluate a potential loss of the compounds and by GC/TC/IRMS to evaluate potential isotopic fractionation that may occur during the urea adduction procedure.

2.4 *Application to aerosol samples*

Three urban aerosol samples (QFF38; QFF39; QFF43) used in this study were collected in Setagaya, Tokyo, Japan, using a high-volume air sampler (Shibata HV1000) and pre-combusted quartz filter (Pallflex 2500QAT, 20 cm × 25 cm) on the roof of the Science building of Tokyo Metropolitan University during November 1988 to January 1989 [6]. Aerosol samples were also collected in Sapporo, Japan, in July and December 2008 using a high-volume air sampler (Kimoto AS-810) and quartz filter on the roof of the Institute of Low Temperature Science of Hokkaido University. Filter samples were stored in a clean glass jar with a Teflon-lined cap and preserved in a freezer (−20°C) until the analyses.

An aliquot of filter sample was extracted with 0.1 M KOH-methanol solution (10 mL) for three times using DIONEX ASE-200, and the residue was further extracted by ultrasonication with methylene chloride for 10 min. The extracts were combined and concentrated down to ca. 0.5 mL using a rotary evaporator under vacuum, and separated into neutral and acidic fractions by the method of Kawamura [26]. The neutral fraction was further separated into four sub-fractions on silica gel column chromatography (Merck 230–400 mesh; activated at 400°C and then deactivated with 1% H_2O) using a Pasteur pipette. Aliphatic hydrocarbons were obtained by elution with 1.7 mL *n*-hexane on the column. Homologous series of *n*-alkanes were then purified using urea adduction and were determined by GC-FID for their concentrations. One to two microliters of samples that contain ca. 300 ng of individual compounds on average were co-injected with an internal standard (C_{13} *n*-alkane; $\delta D = -79 \pm 1‰$) into the GC/TC/IRMS. All the measurements were duplicated.

3. Results and discussion

3.1 *Procedural blank and recovery test*

Blank tests showed that no laboratory contamination of *n*-alkanes was detected during urea adduction procedure. Figure 1 plots recoveries of authentic *n*-alkanes (C_{16} to C_{30}) during urea adduct experiments against their carbon numbers. The recoveries were in a range of 5.2 to 99.4% with the lowest value for C_{16} *n*-alkane in every experiment. We found that the recoveries gradually increase with an increase in carbon chain-length of *n*-alkanes and reach a plateau when *n*-alkanes ≥ C_{23} (Figure 1). Such a chain-length

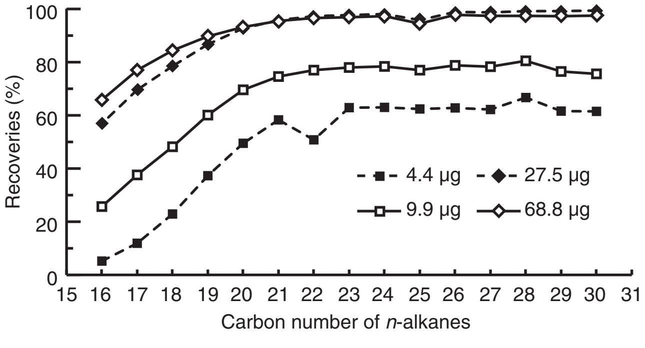

Figure 1. Recoveries (%) of C_{16} to C_{30} *n*-alkanes in urea adduct experiments with solutions that contain 4.4, 9.9, 27.5 and 68.8 µg of total *n*-alkanes each.

dependence on the recovery is consistent with the previous observation that the urea adduction did not complete for *n*-alkanes with less than 20 carbons [20]. Sun *et al.* [27] reported an increase in the recovery under low experimental temperature. The lower recoveries are also probably due to an evaporative loss of low molecular weight hydrocarbons during the concentration process using a rotary evaporator under vacuum and a nitrogen blow-down system under ambient temperature conditions.

Although a repeated urea adduction was required to increase the recovery of *n*-alkanes in the previous method [22], we confirmed that most of the *n*-alkanes were urea adducted by stirring the mixture overnight at room temperature, because there is no remaining *n*-alkane detected in non-adducted fraction (*n*-hexane/acetone solution). However, the recoveries were found to be dependent on the total amount of authentic *n*-alkanes used (Figure 1). In the solution containing 4.4 µg of total *n*-alkanes, the recovery gradually increased from 5.2% at C_{16} *n*-alkane to 58.3% at C_{21} *n*-alkane; however, it did not exceed 66.7% even in the longer-chain ($>C_{23}$) homologues. In contrast, in the solution that contains more than 27.5 µg of total *n*-alkanes, recoveries reached greater than 90% for longer chain *n*-alkanes ($\geq C_{20}$) (Figure 1). This indicates that the recoveries are high enough when the concentration of total *n*-alkanes in our urea adduct experimental system are $\geq 6.1\ \mu g\ mL^{-1}$.

3.2 *Examination of possible isotopic fractionation during analytical procedure*

To evaluate possible isotopic fractionation that may occur during the incorporation of *n*-alkanes into urea crystals and/or evaporative loss during the procedure, hydrogen isotopic compositions (δD) of *n*-alkanes were measured before and after the urea adduction using sufficient amount (27.5 and 68.8 µg of total *n*-alkanes) of authentic *n*-alkane mixtures (averaged recoveries of each *n*-alkane range from 61.4 to 98.4% (Table 1)). Table 1 presents δD values of authentic *n*-alkanes with and without the urea adduct treatment that were measured in our GC/TC/IRMS system, together with the isotopic differences ($\Delta\delta D$). Reproducibility of the δD measurement is generally good with an accuracy of ±5‰ (2–4‰ on average), but it is not good (up to 14‰) when the amount of *n*-alkanes injected to GC is not enough. Based on repeated analyses of authentic standards, we concluded that ca. 35 ng of hydrogen are required to be injected to our GC/TC/IRMS system for each compound to perform accurate measurements of δD with ±5‰ error.

The $\Delta\delta D$ of each authentic *n*-alkanes between before and after urea adduction ranges from −12 to 7‰ and does not exhibit any statistically significant correlation with the recoveries (Table 1), although the $\Delta\delta D$ values for C_{16} *n*-alkanes are slightly larger than the other *n*-alkanes. Since Wang and Huang [28] reported a decrease in δD values for *n*-alkanes along with their evaporations, the larger $\Delta\delta D$ values may reflect potential effect of evaporation on the δD. However, similar values in the δD of the C_{16} *n*-alkanes between two experiments (b and c in Table 1) confirms that serious isotopic fractionation does not occur in the *n*-alkane homologues during the urea adduction procedure, even for C_{16} *n*-alkanes.

3.3 *Application of the method to aerosol samples*

Aliphatic hydrocarbons separated from urban Tokyo aerosols are composed of homologous series of *n*-alkanes (C_{17} to C_{40}) and enormous amounts of unresolved complex

Table 1. Replicated measurements of δD of authentic *n*-alkanes before and after urea addution.

			Experiment 1 (27.5 μg*)					Experiment 2 (68.8 μg*)				
		δD values before adduction	δD values after adduction					δD values after adduction				
n-Alkanes	Aver. recovery (%)	(a) ($n = 5$)	First	Second	Aver. (b)	1σ	$\Delta\delta$D (a−b)	First	Second	Aver. (c)	1σ	$\Delta\delta$D (a−c)
C$_{16}$	61.4	−70 ± 3	nd**	−59	−59	–	−11	−50	−67	−58	12	−12
C$_{17}$	73.3	−135 ± 3	−124	−141	−133	12	−2	−137	−137	−137	0	2
C$_{18}$	81.5	−55 ± 1	−58	−59	−59	1	4	−58	−56	−57	2	2
C$_{19}$	88.2	−121 ± 1	−125	−126	−126	1	5	−122	−122	−122	0	1
C$_{20}$	93.0	−51 ± 1	−58	−54	−56	2	5	−52	−51	−52	0	1
C$_{21}$	95.7	−206 ± 2	−198	−218	−208	14	2	−201	−203	−202	1	−4
C$_{22}$	96.9	−60 ± 3	−68	−63	−66	4	6	−59	−62	−60	2	0
C$_{23}$	97.3	−47 ± 2	−50	−50	−50	0	3	−47	−47	−47	0	0
C$_{24}$	97.7	−55 ± 1	−60	−59	−59	1	4	−56	−56	−56	0	1
C$_{25}$	95.2	−260 ± 1	−263	−266	−265	3	5	−260	−262	−261	1	1
C$_{26}$	98.4	−60 ± 5	−72	−63	−67	6	7	−56	−63	−60	5	0
C$_{27}$	98.1	−229 ± 0	−225	−233	−229	6	0	−229	−231	−230	1	1
C$_{28}$	98.3	−55 ± 1	−57	−57	−57	0	2	−55	−56	−55	1	0
C$_{29}$	98.2	−184 ± 1	−190	−187	−189	2	5	−181	−185	−183	3	−1
C$_{30}$	98.4	−48 ± 2	−56	−50	−53	4	5	−48	−48	−48	0	0

Note: *Total amount of *n*-alkanes used in experiments; **nd, not determined.

mixture (UCM) (Figure 2a) [6]. Two other samples from Tokyo (QFF 39 and 43) also showed a gas chromatogram similar to that of OFF 38 (Figure 2a). Similar distribution was also found in the winter aerosols from Sapporo (Figure 2e). Shorter chain *n*-alkanes (C_{17} to C_{24}) in the aerosols from both cities exhibit no odd/even carbon number predominance, suggesting a significant contribution of fossil fuel hydrocarbons. This is consistent with high UCM concentrations (616–2343 ng m^{-3}; Table 2). In contrast, longer chain *n*-alkanes (C_{25} to C_{35}) show a weak odd/even carbon number predominance ($CPI_{25-35} = 1.3$–2.5), suggesting a mixed contribution from higher plant leaf waxes and fossil fuel combustion residues (Figure 2a, e). On the other hand, the summer aerosols from Sapporo (July 2008) showed a predominance of longer chain odd-carbon number *n*-alkanes (C_{25} to C_{35}) ($CPI_{25-35} = 8.4$) (Figure 2c), suggesting a strong contribution from terrestrial higher plant waxes.

As shown in Figures 2b, d and f, the gas chromatograms of aliphatic hydrocarbon fraction purified by the urea adduction treatment prove a complete removal of the UCM. This purification step enables us to perform accurate measurements of hydrogen isotopic compositions (δD) of individual *n*-alkanes. Table 2 presents the δD values of C_{20} to C_{35} *n*-alkanes in the urban aerosols collected from Tokyo and Sapporo. Replicate analyses show that reproducibility of the δD measurements of *n*-alkanes was generally less than 10‰ (4‰ on average). Although mono-methyl alkanes remain in the *n*-alkane fractions after the urea adduction step, they can be isolated from *n*-alkanes on the capillary GC chromatogram (e.g. Figure 2b). We could not detect any serious co-elution of these homologues on *n*-alkanes on the GC/TC/IRMS traces.

The δD values of *n*-alkanes in the Tokyo aerosols collected in winter ranged from −38 to −144‰. These values fall in a range of those reported from the *n*-alkanes in marine crude oils [9], except for C_{34} *n*-alkane. This suggests that *n*-alkanes in the Tokyo aerosols originate from anthropogenic emission of fossil fuel hydrocarbons. However, a significant negative excursion of δD values (up to ~50‰) was recognised for odd-carbon number *n*-alkanes (C_{27} to C_{33}) compared to even-carbon *n*-alkanes and a zigzag pattern was observed for longer chain *n*-alkanes (Figure 3). Because the leaf wax *n*-alkanes in contemporary Far East land plants are characterised by lower δD values (−149 to −171‰) than marine crude oils (−50 to −160‰) [10,14], the pattern should be caused by a superimposed contribution from higher plant waxes. In addition, the δD of C_{27}, C_{29} and C_{31} *n*-alkanes in Tokyo aerosols decreased as the CPI value of *n*-alkanes increased (Figure 3, Table 2), suggesting that the δD values of these *n*-alkanes in urban aerosols are significantly influenced by the input of higher plant wax.

On the other hand, the Sapporo winter aerosol sample (QFF 3323) showed much lower δD values (−101 to −179‰) (Figure 3), although the same zigzag pattern was found in the δD values of C_{25} to C_{31} *n*-alkanes as seen in the Tokyo samples. The δD values of C_{17} to C_{24} *n*-alkanes and even-carbon numbered C_{26} to C_{30} homologues ranged from −101 to −133‰, again suggesting that they originate from anthropogenic emission of fossil fuel hydrocarbons [9]. In contrast, the δD values of odd-carbon numbered C_{25} to C_{33} *n*-alkanes in the Sapporo aerosols ranged from −161 to −179‰ in both summer and winter samples (QFF 3323 and 3324, Figure 3), which are similar to those of leaf wax *n*-alkanes in Far East vegetation [10,14]. Hence, the odd-carbon numbered *n*-alkanes (C_{25} to C_{33}) in the Sapporo aerosols mainly originate from higher plant waxes.

It is important to emphasise that the values of Sapporo aerosols are 30 to 60‰ lower than those of Tokyo samples (Figure 3), despite the similarity of their GC chromatograms (Figures 2a, e). Because the atmospheric composition in Sapporo,

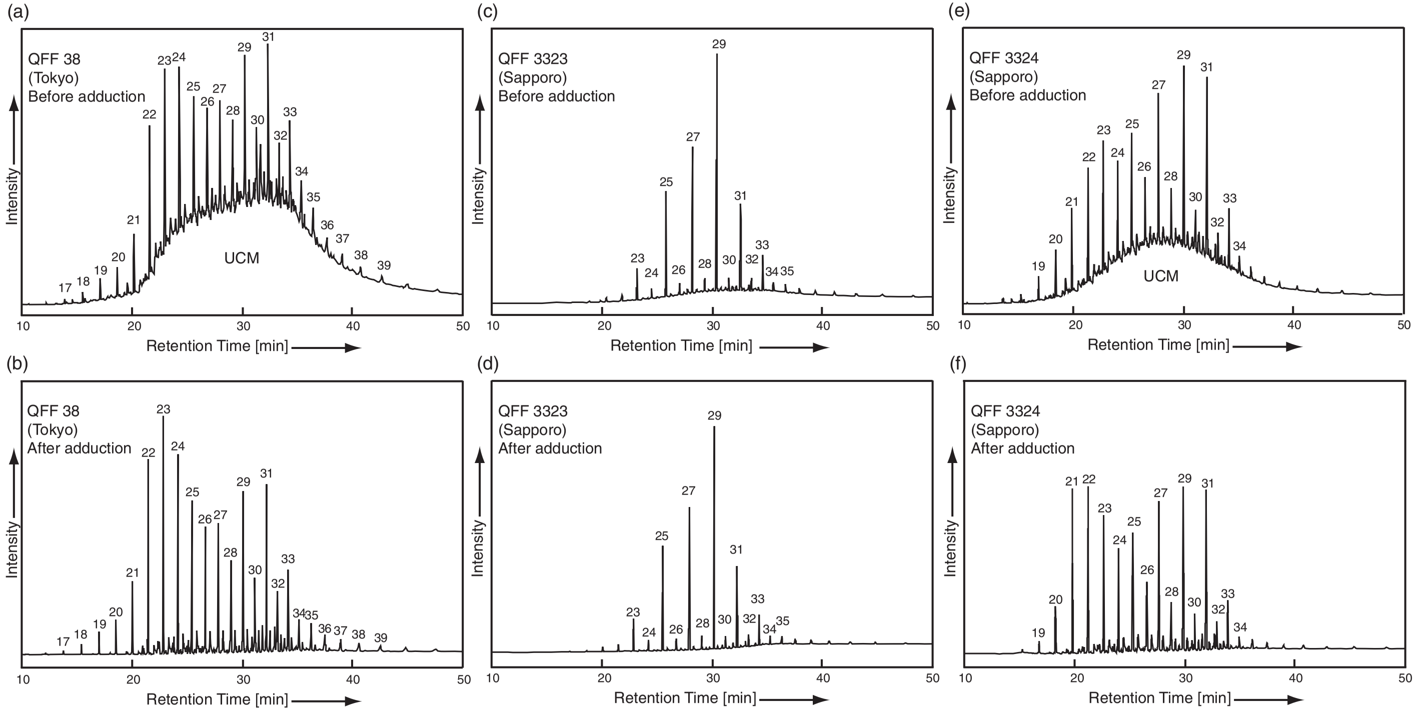

Figure 2. Typical gas chromatograms of aliphatic hydrocarbon fraction in Tokyo aerosol collected 21–22 November 1988 (a) before and (b) after the urea adduction, and (c, d) those of Sapporo aerosols collected 29–31 July 2008 and (e, f) 18–24 December 2008. (Numbers on the GC peaks indicate carbon chain length of *n*-alkanes, UCM = unresolved complex mixture of branched and cyclic hydrocarbons).

Table 2. Concentrations and hydrogen isotopic composition of *n*-alkanes in the aerosol samples collected in Tokyo and Sapporo, Japan.

	Tokyo, Japan						Sapporo, Japan			
	QFF38 (21–22 Nov. 1988)		QFF39 (15–16 Dec. 1988)		QFF43 (17–18 Jan. 1989)		QFF3323 (29–31 Jul. 2008)		QFF3324 (18–24 Dec. 2008)	
n-Alkanes	Concn. ng m_{air}^{-3}	δD	Concn. ng m_{air}^{-3}	δD	Concn. ng m_{air}^{-3}	δD	Concn. ng m_{air}^{-3}	δD	Concn. ng m_{air}^{-3}	δD
C_{20}	4.5	−56 ± 2	8.6	−69 ± 2	6.4	−47 ± 2	BDL*	nd**	2.8	−101 ± 11
C_{21}	9.5	−85 ± 1	20.6	−74 ± 4	17.7	−71 ± 6	BDL	nd	5.0	−112 ± 7
C_{22}	26.2	−79 ± 3	20.4	−70 ± 5	26.8	−71 ± 1	1.0	nd	7.0	−112 ± 6
C_{23}	30.8	−77 ± 3	14.7	−72 ± 4	26.9	−73 ± 4	4.8	nd	7.7	−133 ± 0
C_{24}	27.4	−77 ± 6	10.5	−69 ± 6	23.1	−72 ± 1	1.7	nd	5.8	−130 ± 3
C_{25}	21.3	−83 ± 5	8.0	−84 ± 3	18.3	−79 ± 2	15.9	−161	6.7	−162 ± 1
C_{26}	20.2	−83 ± 6	6.4	−85 ± 4	15.6	−76 ± 7	1.9	nd	4.1	−130 ± 3
C_{27}	20.3	−102 ± 5	7.5	−115 ± 10	16.2	−97 ± 2	22.4	−172 ± 3	8.7	−179 ± 0
C_{28}	16.6	−86 ± 1	5.3	−94 ± 7	12.1	−82 ± 4	2.1	nd	3.6	−129 ± 1
C_{29}	24.1	−126 ± 4	11.3	−144 ± 6	17.1	−110 ± 1	34.9	−179 ± 1	10.2	−178 ± 1
C_{30}	12.6	−79 ± 9	4.8	−81 ± 1	10.6	−59 ± 7	2.0	nd	2.2	−121 ± 6
C_{31}	24.1	−123 ± 8	10.9	−138 ± 6	17.6	−115 ± 5	13.7	−163	9.4	−178 ± 3
C_{32}	10.4	−74 ± 3	4.0	−75	8.7	−55 ± 6	2.0	nd	1.7	nd
C_{33}	12.4	−100 ± 0	5.4	−98 ± 2	13.0	−86 ± 13	5.1	nd	3.4	−150 ± 8
C_{34}	6.5	−38 ± 2	2.6	nd	6.2	nd	1.7	nd	1.3	nd
C_{35}	6.2	−56 ± 11	2.5	nd	4.9	nd	1.6	nd	0.9	nd
Total *n*-alkanes	273.0		143.4		241.2		110.8		80.2	
UCM	2343		933		1873		0		616	
CPI	1.4		1.6		1.3		8.4		2.5	

Note: *BDL, below detection limits; **nd, not determined.

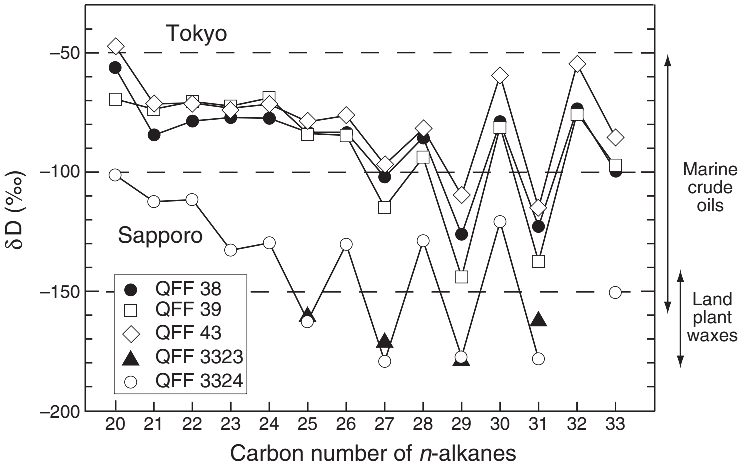

Figure 3. Variations in the δD values of *n*-alkanes with an increase in their carbon numbers for the urban aerosol samples collected in Tokyo and Sapporo. Ranges of δD values are indicated for *n*-alkanes in marine crude oils and terrestrial higher plant waxes.

northern Japan, is seriously affected by air masses from Asian continent via long-range atmospheric transport [29], more D-depletion of the *n*-alkanes in the Sapporo samples may indicate differences in source regions of aerosols. The detailed analyses of δD values of aerosol *n*-alkanes may further provide a novel tool to access the source regions and transport processes of anthropogenically emitted fossil fuel hydrocarbons in urban aerosols.

4. Conclusions

We examined a possible application of a urea adduction procedure to remove a large quantity of unresolved complex mixture (UCM) of cyclic and branched hydrocarbons for the accurate determination of hydrogen isotopic composition (δD) of individual *n*-alkanes in heavily polluted and less polluted urban aerosols using GC/TC/IRMS. The recoveries of C_{20} to C_{30} *n*-alkanes during the procedure were found to be greater than 90% when the concentrations of total *n*-alkanes are $\geq 6.1\,\mu g\,mL^{-1}$. Our compound-specific D/H ratios confirm the absence of significant hydrogen isotope fractionation in *n*-alkanes during urea adduction and recovery of the purified *n*-alkane fraction. Accuracy of the δD determination for authentic C_{17} to C_{30} *n*-alkanes is less than 7.3‰. This technique enables us to determine the δD of individual *n*-alkanes in urban aerosol samples after the complete removal of UCM. The δD of C_{20} to C_{35} *n*-alkanes in Tokyo winter aerosols range from −38 to −144‰, whereas those in Sapporo winter aerosols exhibits much lower values (−101 to −179‰). In both samples, a zigzag pattern of δD was found with higher δD values for even-carbon number *n*-alkanes. This study demonstrates that accurate measurements of δD of *n*-alkanes in aerosol samples may further provide information on their sources, source regions and atmospheric processes such as long-range transport and atmospheric mixing of air masses of different origin.

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