A Novel Method to Identify Illegal Diesel Fuel, II: the Use of [1-D] *n*-Alkane with Stable Hydrogen Isotope Analysis

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We demonstrated a novel identification method of illegal diesel fuel by using a deuterium (D) labeled *n*-alkane ([1-D] *n*-alkane) as a new chemical marker instead of coumarin. In a mixing system of diesel fuel with marker-labeled kerosene, kerosene content is quantitatively determined by D-enrichment of a target *n*-alkane in a mixed oil using compound-specific stable hydrogen isotope analysis. Thus, [1-D] *n*-alkane will become a high potential chemical marker instead of coumarin.

We recently have a big concern that diesel fuel is often illegally adulterated with kerosene or crude oil to evade a specific excise on diesel fuel trade. In Japan, the estimated lost tax is at least one hundred and fifty billion yen (≈sixteen or seventeen billion dollars) per year. Moreover, diesel engine is strongly damaged when illegal diesel fuel is used as normal fuel. Furthermore, by using it diluted with crude oil, a large amount of particular matter (PM) and nitrogen oxides (NO_x) are discharged. Such dirty exhaust is a cause of significant air pollution and associated respiratory diseases (including lung cancer).[1]

In order to identify the oils contaminated into diesel fuel, coumarin has been artificially added by 1 ng/μL as a chemical marker into kerosene and crude oil in Japan. Low concentration (>0.1 ng/μL) of coumarin in oils can be detected by conventional fluorescence analysis.[2] However, coumarin in oils is easily removed by sulfuric acid treatment. An acidic effluent, termed sulfate pitch, is also produced as a by-product during this treatment.[3] The illicit abandonment of the sulfate pitch to the natural environments (e.g., forests and mountains) causes further significant pollution for soil and atmosphere.[4]

Therefore, a new chemical marker is required to solve the both economic and environmental problems related to illegal diesel fuel production. A new marker must satisfy that it cannot be removed by chemical and physical treatments (especially, by sulfuric acid treatment). In a previous study, we demonstrated another novel identification method of illegal diesel fuel by using adamantane (tricyclo[3,3,1,1,^{3,7}]decane) or [1, 2-D_2] *n*-tetradecane as a new chemical marker.[5] These markers have specific ion fragments on gas chromatography/mass spectrometry (GC/MS) analysis, which allows kerosene content in illegal diesel fuel to be quantitatively determined. Although these markers have a high advantage that they cannot be removed by sulfuric acid treatment, its poor detection limit (7–15 ng/μL) shows a defect that the marker must be employed with higher concentration by approximately one or two orders of magnitude than coumarin.

In this study, we demonstrated a novel method using a [1-D] *n*-alkane as a chemical marker with stable hydrogen isotope analysis, in order to improve the defect in the previous study.[5] *n*-Alkanes are major components of diesel fuel as well as kerosene and crude oil. By addition of [1-D] *n*-alkane into kerosene and crude oil, D content of a target *n*-alkane (which is the same carbon-numbered *n*-alkane to the [1-D] *n*-alkane marker) in the oils increases specifically. It is expected that detection of this D-enriched *n*-alkane from diesel fuel becomes an undoubted proof of its adulteration with kerosene or crude oil and that the degree of the D-enrichment represents the mixing ratio between the oils. Deuterium content of oil *n*-alkanes can be determined by compound-specific stable hydrogen isotope analysis using GC/isotope ratio mass spectrometry (GC/IRMS). GC/IRMS is a tool to measure a quite small variation of natural isotope abundance (D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{18}O/^{16}O$) of organic molecules, and has widely been used for various studies such as geochemistry, biochemistry, environmental chemistry, and petroleum chemistry.[6–11]

As the first attempt, this study focuses on a mixing system between diesel fuel and kerosene, and we used [1-D] *n*-hexadecane (*n*-C_{16}) or [1-D] *n*-octacosane (*n*-C_{28}) as a chemical marker. [1-D] *n*-C_{16} was available as a product from SIGMA-ALDRICH. [1-D] *n*-C_{28} was synthesized from 1-octacosanol (SIGMA- ALDRICH) according to previous studies.[12]

Abundance and carbon-number of oil *n*-alkanes were identified and quantified by GC/MS.[5] Compound-specific stable hydrogen isotope analysis was carried out by GC/pyrolysis/IRMS.[9] Hydrogen isotopic composition (δD) is reported in per mill (‰) as defined in eq 1:

$$\delta D\ (‰) = (R_{sam} - R_{std})/R_{std} \cdot 1000, \quad (1)$$

where R_{sam} and R_{std} are the D/H ratio of the sample and international standard [Standard Mean Ocean Water (SMOW)], respectively. The δD measurement for oil *n*-alkanes was always better than 7‰ (as 1σ, standard deviation).

In the case of diesel fuel diluted by kerosene with [1-D] *n*-C_{16}, δD value of *n*-C_{16} in mixed oil well correlates with the kerosene content. For example, by the use of kerosene with 7 ng/μL of [1-D] *n*-C_{16}, δD value of *n*-C_{16} in mixed oil is enriched in D by 39‰ (kerosene content of 40%) and 75‰ (kerosene content of 60%) relative to that of normal diesel fuel (kerosene content of 0%) (Figure 1). This D-enrichment is consistent with the expected value from an isotopic mass balance calculation on the mixing model. Thus, kerosene content in mixed oil can be quantitatively determined by D-enrichment on the target *n*-alkane, in which the uncertainty is estimated to be less than ±7% on the basis of analytical error of the δD measurement. The marker concentration of 7 ng/μL is, however, still larger than that of coumarin.

On the other hand, in the case of diesel fuel diluted by kerosene with 0.35 ng/μL of [1-D] *n*-C_{28}, the kerosene content can be determined by δD value of *n*-C_{28} in mixed oil with the uncer-

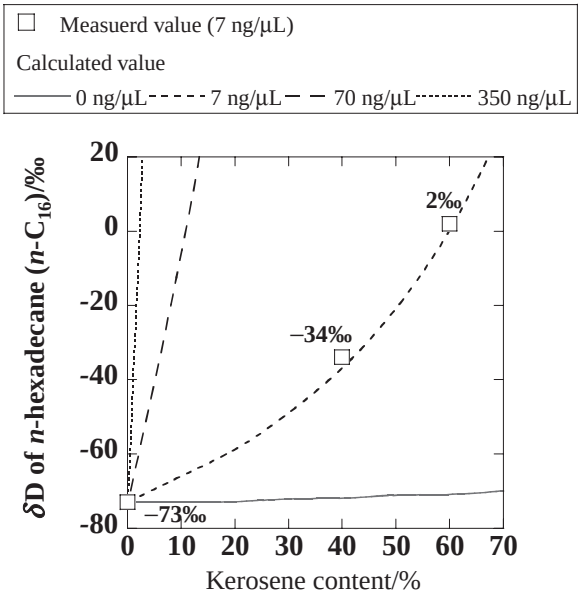

Figure 1. D-Enrichment of n-C_{16} in diesel fuel diluted by kerosene labeled with [1-D] n-C_{16}.

tainty being less than ±4% (Figure 2). The marker concentration is thus smaller than that of coumarin. n-C_{16} is a major n-alkane of diesel fuel (≈40 μg/μL), whereas n-C_{28} is a minor one (≈0.2 μg/μL). Therefore, the latter is easily labeled by its [1-D] derivative with lower concentration than the former. These results suggest that original concentration of a target n-alkane in oils is a further important point to reduce adding volume of [1-D] n-alkane marker.

As same as the previous study,[5] it should be mentioned that [1-D] n-alkane cannot be eliminated from mixed oil and that δD variation during sulfuric acid and charcoal treatments is identical within the analytical error (<±7‰) (Table 1). Thus, sulfuric acid and charcoal treatments have no substantial effect on the D content of oil n-alkanes, being in agreement with theoretical idea on the isotopes that the same molecule with distinct isotopic compositions cannot be easily separated because of their substantial the same physical and chemical properties.

This study clearly demonstrated that D-enrichment of a target n-alkane represents the kerosene content in mixed oil, and that the use of [1-D] n-alkane as a chemical marker with compound-specific hydrogen isotope analysis can improve the defect (i.e. requirement of high concentration marker) in the previous study.[5] Moreover, because [1-D] n-alkane is almost the same molecule to an n-alkane in oils except deuterium contents, it should be expected that the artificial addition of it has no significant effect on oil quality and safety. Thus, we strongly suggest

Table 1. δD change of n-C_{16} in the mixed oil (60% kerosene with 7 ng/μL of [1-D] n-C_{16}) during sulfuric acid or charcoal treatment

Treatment	Measured δD/‰	$\Delta_{\text{after treatment - before treatment}}$ /‰
Control	+2	
Sulfuric acid	+13	+11
Charcoal	+7	+5

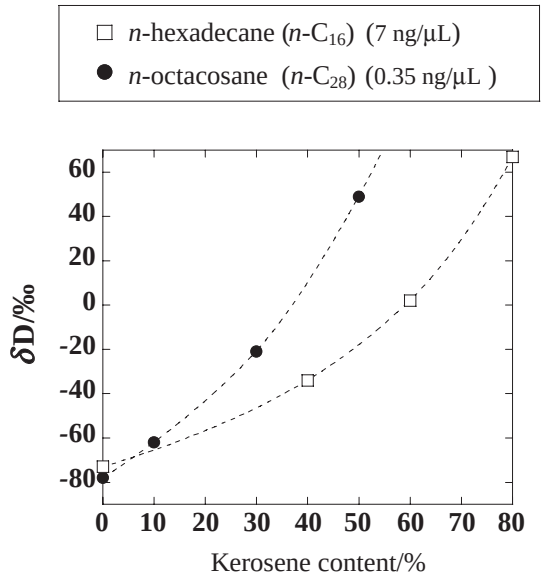

Figure 2. D-Enrichment of n-C_{16} and n-C_{28} in diesel fuel diluted by labeled kerosene (7 ng/μL of [1-D] n-C_{16} and 0.35 ng/μL of [1-D] n-C_{28}).

[1-D] n-alkane as a high potential chemical marker to identify illegal diesel fuel instead of coumarin, which will promise to prevent production of illegal diesel fuel, regain lost tax, and reduce environmental disruption.

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