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Tracing the Source of Cooking Oils with an Integrated Approach of Using Stable Carbon Isotope and Fatty Acid Abundance

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ABSTRACT: We report a new approach to identify swill-cooked oils that are recycled from tainted food and livestock waste from commercial vegetable and animal oils by means of carbon isotope values and relative abundance of fatty acids. We test this method using 40 cooking oil samples of different types with known sources. We found significant differences in both total organic carbon isotope as well as compound-specific isotope values and fatty acid C_{14}/C_{18} ratios between commercial vegetable oils refined from C_3 plants (from −35.7 to −27.0‰ and from 0 to 0.15) and animal oils (from −28.3 to −14.3‰ and from 0.1 to 0.6). Tested swill-cooked oils, which were generally refined by mixing with animal waste illegally, fall into a narrow $\delta^{13}C$/fatty acid ratio distribution: from −25.9 to −24.1‰ and from 0.1 to 0.2. Our data demonstrate that the index of a cross-plotting between fatty acid $\delta^{13}C$ values and C_{14}/C_{18} ratios can be used to distinguish clean commercial cooking oils from illegal swill-cooked oils.

KEYWORDS: *Vegetable oil, swill-cooked oil, animal fat, fatty acid, carbon isotope*

INTRODUCTION

Swill-cooked oils, which are also called illegal cooking oils, refer to oils extracted from kitchen waste and/or rotten animal fat and viscera. Adding swill-cooked oil illegally in edible commercial vegetation oils or selling swill-cooked oils directly is one of the major problems regarding the safety of edible cooking oils.[1,2]

Because of improved techniques employed for refining swill-cooked oils, the traditional oil safety monitoring indices, such as the degree of overoxidation, acid values, heavy metal contents, and triglyceride and polycyclic aromatic hydrocarbon (PAH) contents,[3−5] might be less effective in distinguishing swill-cooked oils from commercial vegetation oils. Despite many attempts being made recently to develop test method(s) to identify swill-cooked oils,[2,6,7] an efficient way of distinguishing swill-cooked oils and commercial vegetation oils is still lacking.[8,9]

Stable isotope technologies have been applied as effective ways to trace the source of food or drug products,[10−12,22−24] such as for testing the contamination of honey[13,14] and source of milk.[15,16] Here, we analyzed cooking oils from different sources, including commercial vegetation oil, animal oils, and illegal swill-cooked oils and explore if stable isotope techniques, with the support of other methods, can be used as a potential approach in distinguishing these oil products.

MATERIALS AND METHODS

Materials. Both edible commercial vegetation oil (14 samples) and animal oils (14 samples) were purchased from a supermarket in Xi'an, northern China. Swill-cooked oils (12 samples), seized at the scene of inspection by city food inspection officials, were obtained from the National Research Center for Certified Reference Material (Table 1). The clear defined source of samples ensured us a meaningful comparison of biochemical and isotope variations between the real "swill-cooked oil" and clean commercial vegetation oils.

Methods. *Total Organic Carbon (TOC) Isotope.* All organic chemical and isotope analyses were carried out in the Stable Isotope Laboratory at the Institute of Earth Environment of the Chinese Academy of Sciences in Xi'an, China. Carbon isotope ratios ($\delta^{13}C$) of TOC were measured using MAT-251 gas mass spectrometer with a dual inlet system. Approximately 0.1 g of sample (edible commercial vegetation oil or animal oil) was combusted for 4 h at 850 °C in a vacuum-sealed quartz tube in the presence of Pt, cupric oxide, and copper.[17] The CO_2 gas was extracted and purified cryogenically, and the isotope composition of the extracted CO_2 gas was then analyzed. A routine laboratory work standard with a known $\delta^{13}C$ value was also measured every day. The analytical precision with standards (MAT-251) was 0.2‰.

Extraction and Purification of Fatty Acids (FAs). Each sample (ca. 10 mg of oil and ca. 0.1 g of animal fat) was freeze-dried and extracted 3 times with 20 min for each, with a mixture of dichloromethane (DCM) and MeOH (9:1, v/v) using an ultrasonic method.[18] The extract was concentrated under a gentle N_2 stream and then transferred to a screw-top test tube. For methylation, an acetyl chloride in MeOH (5‰) was added and the mixture was immediately heated (70 °C and >12 h). After this acid-catalyzed transesterification, NaCl (5% aqueous, 2 mL) was added. The mixture was then extracted with hexane 3 times. The total extraction was separated by way of silica gel chromatography, using hexane and then DCM as the eluent. The fatty acid methyl esters (FAMEs) were collected in the second fraction after elution with DCM. The total FAME compounds (including saturated and unsaturated FAMEs) were separated by way of column

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Table 1. Carbon Isotope Ratios [$\delta^{13}C_{TOC}$, $\delta^{13}C_{16}$, and $\delta^{13}C_{18}$, Expressed as Parts Per Thousand (‰) versus PDB] and the Relative Abundance Ratios (C_{14}/C_{16} and C_{14}/C_{18}) of Three Groups of Oil Samples

number	sample	type	material	$\delta^{13}C_{TOC}$ (‰)	$\delta^{13}C_{16}$ (‰)	$\delta^{13}C_{18}$ (‰)	C_{14}/C_{16}	C_{14}/C_{18}
1	PO12-1	vegetable oil	sesame	−29.0	−29.4	−29.4	0.006	0.012
2	PO12-2	vegetable oil	canola	−29.9	−30.4	−29.8	0.015	0.042
3	PO12-3	vegetable oil	soybean	−30.3	−30.6	−30.8	0.008	0.019
4	PO12-4	vegetable oil	peanut	−29.9	−30.1	−32.6	0.004	0.010
5	PO12-7	vegetable oil	peanut	−29.5	−29.8	−31.7	0.000	0.000
6	PO12-8	vegetable oil	peanut	−30.2	−30.4	−32.0	0.003	0.010
7	PO12-9	vegetable oil	corn	−15.4	−15.7	−16.7	0.003	0.023
8	PO12-10	vegetable oil	sunflower seed	−28.5	−28.7	−29.6	0.008	0.010
9	PO12-11	vegetable oil	soybean	−30.4	−30.5	−31.1	0.007	0.022
10	PO12-12	vegetable oil	peanut	−29.9	−30.2	−30.4	0.003	0.008
11	PO12-13	vegetable oil	sesame	−27.3	−27.6	−27.0	0.000	0.000
12	PO12-14	vegetable oil	olive	−29.0	−29.3	−29.5	0.000	0.000
13	PO12-15	vegetable oil	rice bran	−33.3	−33.6	−35.7	0.012	0.144
14	PO12-16	vegetable oil	camellia seed	−29.5	−30.7	−30.7	0.005	0.021
15	AO12-1	animal oil	butter	−22.8	−21.6	−22.6	0.192	0.199
16	AO12-2	animal oil	lard oil	−17.0	−16.5	−15.4	0.061	0.096
17	AO12-3	animal oil	butter	−20.4	−18.2	−20.8	0.147	0.241
18	AO12-4	animal oil	lard oil	−27.7	−27.5	−26.5	0.064	0.177
19	AO12-5	animal oil	mutton fat	−25.7	−24.7	−24.5	0.125	0.200
20	AO12-7	animal oil	lard oil	−16.5	−15.9	−14.3	0.075	0.193
21	AO12-8	animal oil	butter	−18.7	−23.0	−19.0	0.157	0.203
22	AO12-9	animal oil	lard oil	−22.3	−23.1	−20.7	0.148	0.444
23	AO12-10	animal oil	lard oil	−17.9	−18.1	−17.8	0.321	0.516
24	AO12-11	animal oil	lard oil	−24.1	−24.4	−23.0	0.107	0.359
25	AO12-12	animal oil	butter	−22.7	−21.8	−23.6	0.139	0.373
26	AO12-13	animal oil	butter	−20.7	−18.8	−20.6	0.139	0.239
27	AO12-14	animal oil	butter	−17.0	−16.2	−16.7	0.147	0.318
28	AO12-15	animal oil	lard oil	−17.1	−16.9	−15.1	0.255	0.437
29	WO12-1	illegal cooking oil	swill-cooked dirty oil	−27.8	−27.2	−24.7	0.041	0.167
30	WO12-2	illegal cooking oil	swill-cooked dirty oil	−27.8	−26.9	−24.5	0.042	0.171
31	WO12-3	illegal cooking oil	swill-cooked dirty oil	−27.4	−26.8	−24.1	0.051	0.206
32	WO12-4	illegal cooking oil	swill-cooked dirty oil	−28.3	−27.4	−25.9	0.041	0.133
33	WO12-5	illegal cooking oil	swill-cooked dirty oil	−28.4	−27.5	−25.9	0.032	0.108
34	WO12-6	illegal cooking oil	swill-cooked dirty oil	−27.2	−25.5	−24.2	0.044	0.156
35	WO12-7	illegal cooking oil	swill-cooked dirty oil	−29.9	−30.0	−30.4	0.033	0.129
36	WO12-8	illegal cooking oil	swill-cooked dirty oil	−34.4	−34.4	−34.7	0.027	0.253
37	WO12-9	illegal cooking oil	swill-cooked dirty oil	−27.6	−27.1	−24.5	0.043	0.148
38	WO12-10	illegal cooking oil	swill-cooked dirty oil	−27.4	−27.0	−24.4	0.035	0.137
39	WO12-11	illegal cooking oil	swill-cooked dirty oil	−27.5	−26.9	−24.2	0.032	0.122
40	WO12-12	illegal cooking oil	swill-cooked dirty oil	−27.2	−25.6	−24.6	0.039	0.118

chromatography using $AgNO_3$ on silica gel (10%, w/w), and the saturated FAMEs, which were eluted first with hexane/DCM (4:1, v/v) solution, were analyzed for gas chromatography (GC) and compound-specific carbon isotope.

GC. GC analysis was performed to measure compound abundances with an Agilent 6890 series instrument equipped with a split injector using an Agilent HP1-ms GC column (60 m, 0.32 mm inner diameter, and 0.25 μm film thickness) with a flame ionization detector. Samples were injected in the split mode with a GC inlet temperature of 310 °C and a flow rate of 1.2 mL/min. The temperature program was 40 °C for 1 min, to 150 °C at 10 °C/min, then to 310 °C at 6 °C/min, and held for 20 min. For quantification, peak areas of straight-chain FA (*n*-FA) were compared to those of an external standard mixture of FAMEs (C_{12}–C_{24}, even carbon numbers).

Measurement of FA Carbon Isotope. About 300 ng of the FAMEs was dissolved in toluene and then injected into a Thermo Tracer GC instrument in splitless mode with an inlet temperature of 280 °C (approximately equivalent to 310 °C with an Agilent 6890 GC instrument). FAs were separated in a GC column and converted to CO_2 using a high-temperature oxidization furnace at 980 °C before measured in Delta-V isotope ratio mass spectrometer. A standard laboratory mixture of *n*-alkanes was used as a routine measurement after every three samples; the $\delta^{13}C$ value of the working standard was obtained by offline analysis. Meanwhile, FAME reference substances obtained from Indiana University were also measured to evaluate the analysis accuracy. The standard deviation of the *n*-alkane working standards was <0.2‰. During the measurement of FAs (as FAMEs), the $\delta^{13}C$ values were corrected by mathematically removing the isotopic contributions of the added methyl (ca. −50.5‰)

$$\delta^{13}C_{FAs} = [(n + 1)\delta^{13}C_{FAMEs} - \delta^{13}C_{methyl}]/n \quad (1)$$

where *n* is carbon number of the FA.

Each sample was analyzed in duplicate, and the standard deviation was usually <0.3‰.

RESULTS AND DISCUSSION

Carbon Isotope Values as an Indication of Sources. Among our tested samples, with the exception of the corn oil specimen (PO12-9), the TOC $\delta^{13}C$ values of other edible

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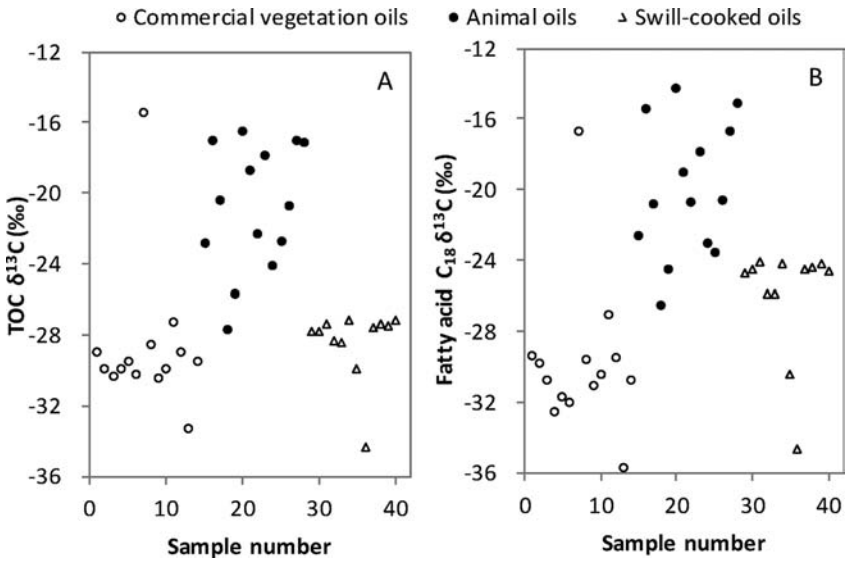

Figure 1. Distribution of (left) TOC $\delta^{13}C$ and (right) C_{18} FA $\delta^{13}C$ among the commercial vegetation oils, animal oils, and swill-cooked oils.

commercial vegetation oil samples were from −33.3 to −27.3‰ (Table 1). As a C_4 plant, corn produces oil with a C_4 plant carbon isotope signature (−15.4, −15.7, and −16.7‰ for TOC and *n*-C_{16} and *n*-C_{18} FA $\delta^{13}C$ values, respectively) that made the sample PO12-9 stand out among all tested commercial vegetation oils (Figure 1). In contrast, TOC $\delta^{13}C$ values of animal oils were higher than commercial vegetation oils, ranging from −27.7 to −16.5‰. TOC $\delta^{13}C$ values of swill-cooking oils (except for two samples) fell into a narrow range between −28.4 and −27.2‰ (left panel of Figure 1). Meanwhile, the distribution of carbon isotope ratios of *n*-C_{18} FA showed that $\delta^{13}C$ values were from −35.7 to −27.0‰ for normal edible commercial vegetation oils, from −28.3 to −14.3‰ for animal oils, and from −25.9 to −24.1‰ for swill-cooking oils (except for two samples) (right panel of Figure 1). The distribution of *n*-C_{16} acid showed that $\delta^{13}C$ values were from −33.6 to −27.6‰ for normal vegetation oils, from −27.5 to −15.9‰ for animal oils, and from −27.5 to −25.5‰ for swill-cooking oils (except for two samples).

The applications of stable carbon isotope technologies had been used to compare organic milk and conventional milk, thus protecting consumers from wrongly labeled dairy products.[15,16] The primary principle of carbon isotope tracing was that conventional milk produced by cows fed by artificial feedstuff was mainly based on corn, a C_4 plant, whereas organic milk was produced by livestock that consumed nature grasses, which were primarily composed of C_3 plants, hence, with a profound difference in carbon isotope signals. The carbon isotope of animal products was mainly controlled by the source of feeds, although it often had somewhat positive $\delta^{13}C$ values compared to their plant diet.[25]

Edible commercial vegetation oils were mainly extracted from seeds of natural plants, which mostly belong to C_3 plants. On the contrary, animal oils mainly came from fat of dairy livestock (cows, sheep, and pigs) that were primarily fed corn, a C_4 plant. Because of different photosynthesis pathways, there were large differences on carbon isotopic values between tissues of C_3 and C_4 plants,[19] with a mean $\delta^{13}C$ value of −27‰ for C_3 plants and a mean $\delta^{13}C$ value of −13‰ for C_4 plants.[20] Thus, the $\delta^{13}C$ values of oils extracted from livestock fat were inherited from the more positive carbon isotope signature of C_4 plants (e.g., corn, etc.). The $\delta^{13}C$ values of the retailed edible commercial vegetation oils reflected the more negative carbon isotope signature of C_3 plants (Figure 1).

The $\delta^{13}C$ values of swill-cooking oils lay in a relatively narrow range between that of edible commercial vegetation oils and animal oils (Figure 1). A possible explanation for the narrow range of carbon isotope values for swill-cooking oil was that swill-cooking oils were composed of a mixture of vegetable oils and animal oils that enable them to average the $\delta^{13}C$ values of C_3 plants and animal fats. Being a multi-source mixture, the swill-cooking oils carried a carbon isotope signature that was influenced by both commercial vegetation oils and animal oils. Meanwhile, the carbon isotope values of *n*-C_{18} acid provided a better separation among oils from the three different sources than TOC $\delta^{13}C$ values (Figure 1). In general, *n*-C_{18} acid $\delta^{13}C$ values of commercial vegetation oils were below −28‰, *n*-C_{18} acid $\delta^{13}C$ values of animal oils were above −24‰, and the $\delta^{13}C$ values of swill-cooked oils were between −26 and −24‰.

Thus, our results indicated that both total organic as well as compound-specific carbon isotope ratios from different oils can be applied to indicate the source of these oil products as commercial vegetation oils, animal oils, and swill-cooked oils, which fall into different $\delta^{13}C$ value ranges. However, it should be noticed that there were overlaps of value ranges among the three types of oils, and a few exceptions made the carbon isotope method fall short of "bullet proof".

Relative Abundance of FAs as an Indication of Sources. To further support the differentiation of sources using carbon isotope ratios, we also explored the use of the relative abundance of *n*-C_{14} acid (myristic acid), *n*-C_{16} acid (palmitic acid), and *n*-C_{18} acid (stearic acid). It had been shown that abundance ratios between these FAs (C_{16}/C_{18} and C_{14}/C_{18}) can be used to discriminate cooking oils of different sources because of the more C_{14} abundance in animal oils.[21] In our investigation, the C_{14}/C_{18} ratio was less than 0.15 for commercial vegetation oils, from 0.1 to 0.6 for animal oils, and from 0.1 to 0.3 for the tested swill-cooked oils (Figure 2). The patterns of relative abundance ratios of FAs derived from animal fat and commercial vegetation oils were consistent with previous findings,[21] while the ratios for tested swill-cooked oils were in between, with some overlappings with animal oils but

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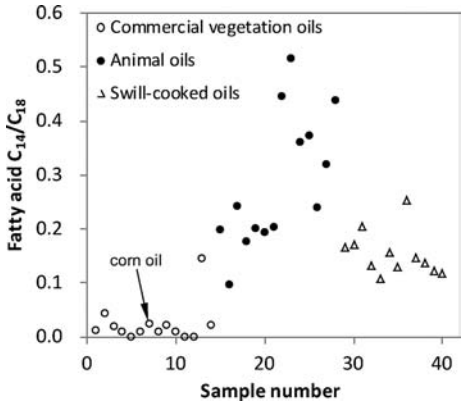

Figure 2. Distribution of FA C_{14}/C_{18} among commercial vegetation oils, animal oils, and swill-cooked oils.

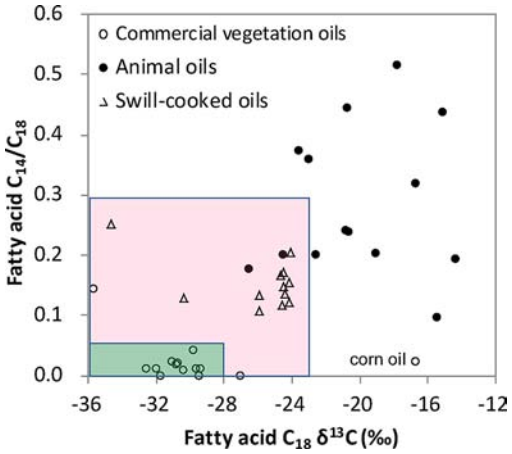

Figure 3. Identification of commercial vegetation oils and swill-cooked oils based on a combined method using carbon isotope ratios and relative abundance of FAs. Green area, commercial vegetation oils; red area, swill-cooked oils.

distinct from commercial vegetation oils. Therefore, the relative abundance of FAs (e.g., C_{14}/C_{18} ratio) can be used as an auxiliary index to distinguish edible commercial vegetation oils and swill-cooked oils, suggesting a distribution zone of the C_{14}/C_{18} ratio between 0.1 and 0.3 for these swill-cooked oils. Although the precise mechanism of the variation of the C_{14}/C_{18} ratio among different cooking oils was not completely understood, the higher C_{14}/C_{18} ratios found in swill-cooked oils were probably due to more animal fat added to the dirty oils during their recycling process.

Integrated Index. The above-discussed carbon isotope approach and the application of relative abundance ratios between FA C_{14}/C_{18} had the marked difference between commercial vegetation oils and swill-cooked oils. Especially, the carbon isotope approach seems more reliable as the mechanism for using $\delta^{13}C$ to trace the source of oils that had been better characterized. However, because of overlaps, none of the above method alone produced satisfactory separation of these oil products. Therefore, we proposed an integrated index using cross-plotting data from compound-specific carbon isotope ($\delta^{13}C$ value of stearic acid, *n*-C_{18} acid) and the relative abundance ratio between myristic acid and stearic acid (C_{14}/C_{18}). The combined data sets produced a more reliable approach to identify swill-cooked oils.

This integrated approach was illustrated in Figure 3, which gave a distribution range from −36 to −28‰ for $\delta^{13}C$ values of FA *n*-C_{18} and from 0 to 0.05 for the C_{14}/C_{18} ratio for clean normal edible commercial vegetation oils from our investigation. The next range from −28 to −23‰ for $\delta^{13}C$ values of FA *n*-C_{18} and from 0.05 to 0.25 for the C_{14}/C_{18} ratio bracket swill-cooked oils, and the area beyond this box, from −23 to −12‰ for $\delta^{13}C$ values of FA *n*-C_{18} and from 0.25 to 0.55 for the C_{14}/C_{18} ratio, indicated animal oils (except for the corn oil sample). This integrated index approach had a couple of advantages. In addition to clearly indicating a source of origin for each type of cooking oil, it had the potential to provide information on the source of possible contamination during the formation of the recycling process of making swill-cooked oils. For example, there were two commercial vegetation oil samples that fell inside of the swill-cooked oil range, one with slightly more positive $\delta^{13}C$ values and another possessing a higher C_{14}/C_{18} ratio. It was possible that these commercial vegetation oils might be contaminated with swill-cooked oils or animal fats at some point during their production. For the two animal oil samples that fell into the swill-cooked oil range, it was possible that these samples represent oils from livestock that had been fed with natural grasses composed of preliminary C_3 plants, resulting in more negative carbon isotope values. Further testing with more samples of known production history would help clarify these issues.

Because there was no other effective method to identify swill-cooking oils or illegal dirty oil addition to commercial cooking oils, our integrated approach might provide a new solution to identify potential swill-cooked oils and to detect the possibility of whether commercial cooking oils had been contaminated with the mixing of illegal swill-cooking oils, thus contributing to the better protection of the safety of cooking oils and the consumers.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Sonia, E.; GianFrancesco, M.; Roberto, S.; Ibanez, R.; Agnese, T.; Stefania, U.; Maurizio, S. Monitoring of virgin olive oil volatile compounds evolution during olive malaxation by an array of metal oxide sensors. *Food Chem.* **2009**, *113*, 345−350.

(2) Zhou, Y. S.; Luo, S. P.; Kong, Y. Determination of cholesterol in drainage oil by solid phase extraction−gas chromatography−mass spectrometry. *Chin. J. Chromatogr.* **2012**, *30*, 207−210 (in Chinese with English Abstract).

(3) Gomes, T.; Caponio, F.; Delcuratolo, D. Fate of oxidized triglycerides during refining of seed oils. *J. Agric. Food Chem.* **2003**, *51*, 4647−4651.

(4) Martin-Polvillo, M.; Marquez-Ruiz, G.; Dobarganes, M. C. Oxidative stability of sunflower oils differing in unsaturation degree during long-term storage at room temperature. *J. Am. Oil Chem. Soc.* **2004**, *81*, 577−583.

(5) Chen, H.; Yang, M.; Zhu, R.; Zhang, Y.; Qiao, B.; Pu, X. Ultra performance liquid chromatography with electrospray tandem mass spectrometry in the determination of cholesterol in hotpot oil,

hogwash oil and waste oil. *Chin. J. Food Hyg.* **2011**, *23*, 429−432 (in Chinese with English Abstract).
(6) Naz, S.; Siddiqi, R.; Sheikh, H.; Sayeed, S. A. Deterioration of olive, corn and soybean oils due to air, light, heat and deep-frying. *Food Res. Int.* **2005**, *38*, 127−134.
(7) Wei, Y. H.; Zhang, J. Y.; Dai, T. C. Determination of chlorine in hogwash oil and edible oil by ion chromatography. *Food Sci.* **2011**, *32*, 213−215 (in Chinese with English Abstract).
(8) Zhang, Q.; Chen, Q. S.; Liu, Y. T.; Meng, Z. F. Status of identification and detection of hogwash oil. *J. Cereals Oils* **2010**, *9*, 39−40 (in Chinese with English Abstract).
(9) Cao, W. M.; Xue, B.; Yang, B. T.; Ding, D. H.; Sun, X. H. Development and research of the hogwash oil detection technique. *Grain Sci. Tech. Econ.* **2011**, *36*, 41−44 (in Chinese).
(10) Ehleringer, J. R.; Casale, J. F.; Lott, M. J.; Ford, V. L. Tracing the geographical origin of cocaine. *Nature* **2000**, *408*, 311−312.
(11) Piasentier, E.; Valusso, R.; Camin, F.; Versini, G. Stable isotope ratio analysis for authentication of lamb meat. *Meat Sci.* **2003**, *64*, 239−247.
(12) Chesson, L. A.; Valenzuela, L. O.; O'Grady, S. P.; Cerling, T. E.; Ehleringer, J. R. Hydrogen and oxygen stable isotope ratios of milk in the United States. *J. Agric. Food Chem.* **2010**, *58*, 2358−2363.
(13) White, J. W.; Doner, L. W. Mass spectrometric detection of high-fructose corn syrup in honey by use of the $^{13}C/^{12}C$ ratio: Collaborative study. *J. Assoc. Off. Anal. Chem.* **1978**, *61*, 746−750.
(14) White, J. W.; Winters, K.; Martin, P.; Rossmann, A. Stable carbon isotope ratio analysis of honey: Validation of internal standard procedure for worldwide application. *J. AOAC Int.* **1998**, *81*, 610−619.
(15) Molkentin, J. Authentication of organic milk using $\delta^{13}C$ and the α-linolenic acid content of milk fat. *J. Agric. Food Chem.* **2009**, *57*, 785−790.
(16) Cui, L. L.; Liu, W. G. The application exploration of carbon stable isotope ratio in identification of fresh milks with different of sources. *J. Chin. Mass Spectrom. Soc.* **2011**, *32*, 164−169 (in Chinese with English Abstract).
(17) Cao, Y. N.; Liu, W. G.; Ning, Y. F.; Zhang, Q. L.; Wang, Z. Effects of soil sample preparation process on $\delta^{13}C$ of organic matter. *Geochimica* **2005**, *34*, 398−404 (in Chinese with English Abstract).
(18) Liu, W. G.; Huang, Y. S. Compound specific D/H ratios and molecular distributions of higher plant leaf waxes as novel paleoenvironmental indicators in the Chinese Loess Plateau. *Org. Geochem.* **2005**, *36*, 851−860.
(19) Denies, P. The isotopic composition of reduced organic carbon. In *Handbook of Environmental Isotope Geochemistry: The Terrestrial Environment*; Fritz, P., Fontes, J. C., Eds.; Elsevier: Amsterdam, The Netherlands, 1981; Vol. *1*, pp 329−406.
(20) Ehleringer, J. R. Implications of quantum yield differences to the distributions of C_3 and C_4 grasses. *Oecologia* **1978**, *31*, 255−267.
(21) Wang, J. F.; Yao, L. L.; Zhang, G. X. Discrimination examination between animal oil and vegetable oil. *Chem. Res. Appl.* **2008**, *20*, 1514−1519 (in Chinese with English Abstract).
(22) Angerosa, F.; Camera, L.; Cumitini, S.; Gleixner, G.; Reniero, F. Carbon stable isotopes and olive oil adulteration with pomace oil. *J. Agric. Food Chem.* **1977**, *45*, 3044−3048.
(23) Angerosa, F.; Bréas, O.; Contento, S.; Guillou, C.; Reniero, F.; Sada, E. Application of stable isotope ratio analysis to the characterization of the geographical origin of olive oils. *J. Agric. Food Chem.* **1999**, *47*, 1013−1017.
(24) Spangenberg, J. E.; Ogrinc, N. Authentication of vegetable oils by bulk and molecular carbon isotope analyses with emphasis on olive oil and pumpkin seed oil. *J. Agric. Food Chem.* **2001**, *49*, 1534−1540.
(25) Rogers, K. M. Stable isotopes as a tool to differentiate eggs laid by caged, barn, free range, and organic hens. *J. Agric. Food Chem.* **2009**, *57*, 4236−4242.