汽车罩光漆的同位素比值分析及保存条件影响研究

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摘要：本文通过检验汽车油漆最外层罩光漆的同位素实现不同样品的区分，并考察保存条件对样品同位素的影响。实验共收集了10种汽车罩光漆样品，分别在室温避光、60 ℃高温、−20 ℃低温和强紫外线条件下保存6个月，然后用元素分析仪-同位素比值质谱(EA-IRMS)检测样品的碳、氢、氧同位素比值。结果表明：油漆样品在不同保存条件下发生碳、氢、氧同位素分馏，样品的$\delta^{13}C$值在高温和低温保存后向负值偏移，强紫外线照射的影响微弱；$\delta^{2}H$值在3种条件下均向正值偏移，受紫外线照射影响最大；$\delta^{18}O$值在3种条件下均向负值偏移，但不同种类树脂样品之间$\delta^{18}O$值的偏移幅度不同，在3类样品中，聚甲基丙烯酸甲脂类树脂样品分子中由于氧含量最少其偏移值最小。稳定同位素分析方法可为油漆样品分析提供高区分度的三维指纹，在油漆识别与区分方面具有较大的潜力，可用于油漆物证的溯源分析。

关键词：稳定同位素；汽车油漆；保存条件；同位素分馏；同位素比值质谱(IRMS)
中图分类号：O657.63　　**文献标志码**：A　　**文章编号**：1004-2997(2023)01-0113-08
doi：10.7538/zpxb.2022.0041

Isotope Ratio Analysis and Environmental Impact Study of Automotive Vanish

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Abstract: Due to the different sources of raw materials and manufacturing processes, different automotive paint samples have different isotopic signatures, which can be used as the basis for distinguishing similar paint samples. The varnish is the paint applied on the outermost layer of the car, which is easily affected by the storage conditions. Therefore, the isotope ratios of different varnish samples under different storage conditions were analyzed. Ten automotive varnish samples were collected and stored for 6 months at room temperature away from light, high temperature of 60 ℃, low temperature of −20 ℃ and strong ultraviolet light. After that, the samples were analyzed by elemental analyzer-isotope ratio mass spectrometry (EA-IRMS). The carbon, hydrogen and

国家自然科学基金(42063002)；贵州省科技计划项目(黔科合支撑[2019]2884号)
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oxygen isotope values were determined. The results showed that the carbon, hydrogen and oxygen isotope ratios of different paint samples can be used to distinguish different samples, the potential of identification and differentiation of paint samples using stable isotopes of carbon, hydrogen and oxygen were demonstrated. The carbon, hydrogen and oxygen isotope fractionation of the paint samples occurred under different storage conditions. The $\delta^{13}C$ value of the samples shifted to a negative value after storage at high temperature and low temperature, greater variation of samples occurred at high temperature, and the influence of strong ultraviolet radiation was weak, which meant that UV light had little effect on the $\delta^{13}C$ value of the paint samples. The $\delta^{2}H$ value shifted to a positive value under the three conditions, which was most affected by ultraviolet radiation, and minimal change in the condition of high temperature. The $\delta^{18}O$ value shifted to more negative under the three conditions. But the shift amplitude of the $\delta^{18}O$ value was different between samples of different resin types. Among the three resin types of samples, polymethyl methacrylate lipid resin samples had the smallest offset due to the least oxygen content in the molecules, the variation ranges of glyceryl elaidate and sorbitan monostearate paint samples had little difference under the three storage conditions. Stable isotope analysis method can provide high resolution three-dimensional fingerprints for paint samples, which has great potential in paint identification applications, and can be applied to traceability analysis of paint physical evidence.

Key words: stable isotopes; car paint; storage condition; isotope fractionation; isotope ratio mass spectrometry (IRMS)

汽车油漆是指在汽车表面起保护和装饰作用的表面涂层。油漆的主要成分包括树脂、颜料、稀释剂、固化剂等。其中,树脂是油漆的主要成膜物质,也是油漆的主要成分;颜料是油漆的次要成膜物质;稀释剂和固化剂是辅助油漆成膜的物质。按树脂成分不同,可将油漆分为反油酸甘油酯类、聚甲基丙烯酸甲酯类、山梨醇酐单硬脂酸酯类、聚氨基甲酸酯类、聚苯乙烯和聚氯乙烯类等。对油漆逐层分离后,主要使用红外[1-3]、扫描电镜-能谱[4-5]和裂解-气相色谱[6]等仪器进行分析,可得到油漆的化学成分、层序、颜色和添加剂等信息,但分析结论往往是同类判定,无法确定具有相同成分的油漆样品是否来源于同一辆车。因此,能否实现样品的同一认定,对案件侦查、审讯起到重要作用。

同位素分析能够检测稳定同位素组成的微小变化,提供相关物证的来源信息。目前,稳定同位素分析已广泛应用于食品[7-8]、农林业[9-10]、环境科学[11-12]等领域,在法庭科学上的研究包括毒品[13-21]、法医学[22-24]、助燃剂[25-27]、爆炸物[28-34]、土壤[35]、棉纤维[36-37]以及纸张[38-42]等。Reidy和Farmer等[43-44]对建筑涂料中的稳定性同位素进行分析,确定了同位素分析在同种类型涂料物证中比对区分的能力。但目前尚未见对汽车油漆的同位素分析报道。

罩光漆涂敷在汽车油漆的最外层,受环境影响较大,本研究使用元素分析仪-同位素比值质谱(EA-IRMS)对10个汽车罩光漆样品进行碳氢氧同位素分析,根据结果区分不同样品,并考察其在高温、低温、强紫外线3种极端条件下的同位素变化规律。

1 实验部分

1.1 主要仪器与试剂

Mat253同位素比质谱仪、Flash EA 1112元素分析仪:美国Thermo公司产品;NB-UVB 9W紫外线灯:波兰飞利浦公司产品;电热鼓风干燥箱:上海一恒科学仪器有限公司产品;冰箱:青岛海尔公司产品;Molsieve填充柱(1 m×5 mm×2 mm):美国Agilent公司产品。

IAEA-600($\delta^{13}C=-27.71‰$),乙酰苯胺($\delta^{13}C=-26.85‰$),USGS-40($\delta^{13}C=-26.39‰$),

EMA-P1 ($\delta^{18}O = 20.99‰$, $\delta^2H = -25.30‰$), EMA-P2 ($\delta^{18}O = 26.88‰$, $\delta^2H = -87.80‰$), IAEA-601($\delta^{18}O=23.3‰$), NBS22($\delta^2H=-120‰$)稳定同位素标准品:购自北京瑞利君利发展有限公司。

1.2　样品采集与处理

10个汽车罩光漆样品的详细情况列于表1。使用相同的固化剂和稀释剂将罩光漆样品按固定比例进行稀释(罩光漆:固化剂:稀释剂=2∶1∶0.5,$V/V/V$),用涡旋混合器混匀。先后用去离子水和丙酮清洗载玻片,干净后置于60 ℃烘箱中烘干,将混合好的油漆均匀地涂在载玻片上,每个样品涂4份。将所有样品置于室温避光条件下保存6个月,待完全干燥后,将4份样品分别置于室温避光、60 ℃高温、−20 ℃低温和紫外灯照射条件下保存6个月,最后用手术刀从载玻片中心位置取0.5 cm×0.5 cm样品进行$\delta^{13}C$、δ^2H、$\delta^{18}O$分析。

表1　样品信息

Table 1　Information of samples

样品编号 No.	油漆品牌 Paint brand	生产厂家 Manufacturer	树脂类型 Resin type
1	芬凯尔	未知	反油酸甘油酯类
2	易涂	广东易涂汽车材料有限公司	反油酸甘油酯类
3	科迈迪	广东欣辰汽车用品有限公司	聚甲基丙烯酸甲脂类
4	易涂	广东易涂汽车材料有限公司	聚甲基丙烯酸甲脂类
5	未知	广东好尔威化工有限公司	山梨醇酐单硬脂酸酯类
6	易涂	广东易涂汽车材料有限公司	山梨醇酐单硬脂酸酯类
7	卡纳尔	广东万丰涂料有限公司	山梨醇酐单硬脂酸酯类
8	易涂	广东易涂汽车材料有限公司	山梨醇酐单硬脂酸酯类
9	都邦	广东万丰涂料有限公司	山梨醇酐单硬脂酸酯类
10	易涂	广东易涂汽车材料有限公司	山梨醇酐单硬脂酸酯类

1.3　实验条件

1.3.1　样品前处理　取样品置于研钵中,持续加入液氮研磨后过60目筛网,密封保存。

1.3.2　仪器条件　碳同位素分析:He流速200 mL/min,O_2流速40 mL/min,氧化管温度950 ℃,还原管温度620 ℃,色谱柱温度60 ℃。

氢、氧同位素分析:He流速90 mL/min,高温裂解管温度1 380 ℃,色谱柱温度60 ℃。

1.3.3　数据校正与分析　将标准物质的$\delta^{13}C$、δ^2H和$\delta^{18}O$测定值与真实值进行线性拟合,得出线性校正方程。通过线性校正方程和油漆样品$\delta^{13}C$、δ^2H和$\delta^{18}O$的测定值计算真实值。

1.4　同位素比值表示方法

以维也纳拟箭石(Vienna pee dee belemnite, VPDB)作为$\delta^{13}C$和$\delta^{18}O$值的标准,维也纳标准平均海水(Vienna standard mean ocean water, VSMOW)作为δ^2H值的标准,计算公式示于式(1):

$$\delta(‰) = (R_{sample}/R_{standard} - 1) \times 1\,000 \quad (1)$$

式中,R_{sample}、$R_{standard}$分别是样品和标准品中重同位素与轻同位素的丰度比。

2　结果与讨论

2.1　样品均匀性考察

按树脂种类,可将10个油漆样品分为3类,分别是反油酸甘油酯类(1～2号)、聚甲基丙烯酸甲脂类(3～4号)和山梨醇酐单硬脂酸酯类(5～10号)。随机选择1个每种树脂的油漆样品,分别从载玻片的4个角和中心位置取0.5 cm×0.5 cm样品进行分析,结果列于表2。3个样品$\delta^{13}C$、δ^2H、$\delta^{18}O$值的最大测量不确定度分别为0.11‰、0.96‰、0.88‰;在相同条件下,对标准物质IAEA-600重复测试5次,得到$\delta^{13}C$值的测量不确定度为0.17‰;对标准物质EMA-P1重复测试5次,得到δ^2H和$\delta^{18}O$值的测量不确定度分别为1.2‰和0.86‰;除2号样品的$\delta^{18}O$和4号样品的δ^2H的不确定度与标准品重复测定的不确定度相当外,其他样品的

表 2 样品均匀性考察

Table 2 Examination of sample homogeneity

取样位置 Sampling position	2 号样品 Sample 2			4 号样品 Sample 4			9 号样品 Sample 9		
	$\delta^{13}C$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$\delta^{13}C$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰	$\delta^{13}C$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰
左上	−29.28	−77.41	15.20	−28.22	−92.84	14.19	−28.6	−93.71	13.48
右上	−29.26	−76.42	15.41	−28.13	−92.63	14.28	−28.58	−94.16	14.16
中心	−29.28	−77.87	15.32	−28.16	−91.14	13.89	−28.75	−93.31	14.27
左下	−29.25	−76.11	14.37	−28.31	−91.58	13.77	−28.77	−92.68	14.33
右下	−29.30	−78.39	16.37	−28.12	−93.62	14.95	−28.62	−94.58	14.95
平均值	−29.27	−77.24	15.33	−28.19	−91.96	14.22	−28.66	−93.69	14.24
不确定度	0.024	1.19	0.88	0.097	1.24	0.57	0.11	0.92	0.65

测量不确定度均低于标准品。因此，认为油漆被均匀地涂在载玻片上。

2.2 室温避光条件下保存油漆的同位素信息

每个样品平行测定 3 次，取 3 次测量结果的平均值用于分析。10 个样品的碳、氢、氧同位素数据列于表 3。

表 3 室温避光条件下 10 个样品的$\delta^{13}C$、$\delta^{2}H$和$\delta^{18}O$值

Table 3 $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ values of 10 samples stored at room temperature away from light

样品编号 No.	$\delta^{13}C$/‰	$\delta^{2}H$/‰	$\delta^{18}O$/‰
1	−28.83	−101.40	15.33
2	−29.28	−77.89	15.32
3	−28.50	−82.87	12.09
4	−28.16	−91.14	13.89
5	−27.91	−107.19	14.27
6	−27.59	−91.37	18.52
7	−29.32	−95.81	16.20
8	−29.09	−90.85	15.32
9	−28.75	−95.31	14.27
10	−29.16	−105.88	16.23

结果表明，10 个样品的$\delta^{13}C$值−29.59～−27.82，平均值−28.66‰；$\delta^{2}H$值−106.03～−80.40，平均值−93.97‰；$\delta^{18}O$值 12.09～17.45，平均值 15.14‰。10 个样品的碳、氢、氧同位素分布图示于图 1。可见，在室温避光条件下保存的 10 个样品很容易被区分开。

根据厂商、品牌或油漆树脂种类等信息对样品进行比对分析，与 Famer 等[44]的研究结果类似，同一厂商的样品之间和相同种类的油漆样品之间均不存在显著相关（$P>0.05$）。

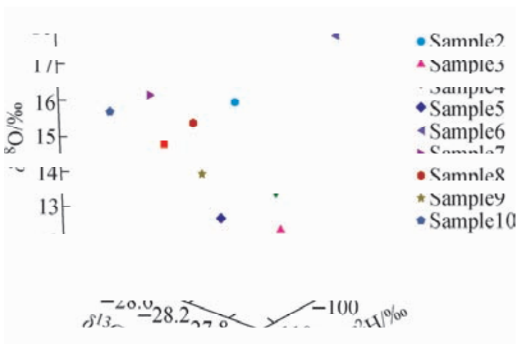

图 1 10 个样品的$\delta^{13}C$、$\delta^{2}H$和$\delta^{18}O$分布图

Fig. 1 $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ values of 10 samples

汽车油漆是由树脂、固化剂和稀释剂组成的混合物，在样品制备过程中所有样品均使用同种固化剂和稀释剂，且用量相同，因此，分析结果差异即油漆树脂成分同位素的差异。树脂可由油漆制造商自主制造或者从供应商处采购，但无论是哪种来源，树脂合成原料或者合成过程中发生的细微变化均可能影响油漆样品的同位素分析结果。上述比对结果表明，碳、氢、氧同位素的分析结果为不同油漆样品提供了可实现高度区分的三维指纹，突出了利用碳、氢、氧稳定同位素识别和区分油漆样品的潜力。

2.3 不同保存条件下样品的同位素变化

在 6 个月的高温、低温和强紫外线照射的保存条件下，样品的$\delta^{13}C$、$\delta^{2}H$和$\delta^{18}O$值发生了变化，与室温避光保存样品的差值列于表 4。

表4　样品在3种极端条件下的同位素变化

Table 4　Isotopic variation of samples under 3 extreme conditions

样品编号 No.	与室温避光保存的差值 Different value from room temperature								
	$\delta^{13}C$			$\delta^{2}H$			$\delta^{18}O$		
	60 ℃/‰	−20℃/‰	UV/‰	60℃/‰	−20℃/‰	UV/‰	60℃/‰	−20℃/‰	UV/‰
1	−0.23	−0.11	−0.01	1.30	1.11	2.54	−0.90	−0.66	−0.92
2	−0.15	−0.04	0.01	0.80	1.26	2.27	−1.63	−0.64	−0.68
3	−0.14	−0.16	−0.01	0.74	1.46	3.52	−0.10	0.00	−0.10
4	−0.23	−0.18	−0.11	0.84	1.47	3.69	−0.11	−0.03	−0.11
5	−0.10	−0.15	0.02	0.88	1.16	4.32	−1.27	−1.09	−0.54
6	−0.23	−0.04	−0.11	0.80	1.58	3.27	−1.88	−1.06	−1.55
7	−0.28	−0.27	−0.1	0.78	1.38	2.75	−1.20	−0.46	−0.23
8	−0.24	−0.17	−0.09	0.94	1.03	2.78	−1.09	−0.41	−0.33
9	−0.13	−0.04	−0.01	0.96	1.24	3.09	−1.36	−0.86	−0.83
10	−0.27	−0.13	−0.06	0.88	0.92	3.28	−1.01	−1.32	−1.64
最大值	−0.28	−0.20	−0.11	1.30	1.47	2.27	−1.88	−1.32	−1.64
最小值	−0.10	−0.04	0.02	0.40	0.91	4.32	−0.10	0.00	−0.10
均值	−0.20	−0.13	−0.047	0.89	1.26	3.15	−1.06	−0.65	−0.69

样品在高温和低温条件下保存6个月后发生碳同位素分馏，$\delta^{13}C$向负值偏移，从偏移的平均值和最大值来看，高温下样品的$\delta^{13}C$值变化幅度较低温条件更大；而强紫外线照射条件下样品的$\delta^{13}C$值偏移有正有负，且偏移幅度均较小，所以认为紫外线对油漆样品的$\delta^{13}C$值影响较小。此外，不同树脂种类的油漆之间$\delta^{13}C$值未发现明显的规律性变化。

样品的$\delta^{2}H$值在高温、低温和强紫外线照射条件下均发生同位素分馏，^{2}H发生了显著的富集，较室温避光保存下样品的$\delta^{2}H$向正值偏移，不同树脂种类的油漆在不同保存条件下未表现出明显的规律；从变化幅度上看，紫外线照射对样品的$\delta^{2}H$值影响最大，其次是低温，高温条件对样品的$\delta^{2}H$值影响最小。

样品的$\delta^{18}O$值在高温、低温和强紫外线照射条件下均发生同位素分馏，较室温避光保存下样品的$\delta^{18}O$向负值偏移，与另外2种树脂油漆样品的$\delta^{18}O$值相比，聚甲基丙烯酸甲脂类树脂的$\delta^{18}O$在高温保存条件下的变化更小。这可能与聚甲基丙烯酸甲脂类树脂分子中含有更少的氧有关，极端的保存条件使油漆中的氧发生同位素分馏，由于聚甲基丙烯酸甲脂类树脂分子中含有更少的氧，其$\delta^{18}O$值变化更不明显。此外，除聚甲基丙烯酸甲脂类树脂外，反油酸甘油酯类和山梨醇酐单硬脂酸酯类油漆样品的$\delta^{18}O$值变化幅度在3种保存条件下的差别不大。

3　结论

本文以涂敷在汽车油漆最外层的罩光漆样品为研究对象，对10个样品的$\delta^{13}C$、$\delta^{2}H$和$\delta^{18}O$值进行分析，并考察60 ℃、−20 ℃和强紫外线照射等极端环境条件与室温避光保存条件下样品的同位素变化。结果表明，油漆的碳、氢、氧同位素可以作为油漆的区分或同一认定的依据，同一厂商或相同树脂类型的油漆样品之间不存在显著的相关性。在不同保存条件下，油漆的碳、氢、氧同位素比值会发生变化，其中，$\delta^{13}C$值受高温影响最大，几乎不受紫外线照射的影响；$\delta^{2}H$值受紫外线照射的影响最大，而高温条件对其影响最小；$\delta^{18}O$值在3种保存条件下的变化值相当，但不同树脂种类样品之间$\delta^{18}O$值的变化有区别，含有更多氧原子的样品分子在相同条件下会发生更大的分馏变化。

参考文献：

[1] 苗作章，王启明. 油漆的红外光谱分析[J]. 刑事技术，1981(3)：45-49.

MIAO Zuozhang, WANG Qiming. Infrared

spectroscopic analysis of paint[J]. Forensic Science and Technology, 1981(3): 45-49(in Chinese).

[2] 路春清,何洪源,贾艳超,张淑芳,陈占合. 交通肇事案中油漆物证的傅里叶变换红外光谱分析[J]. 中国人民公安大学学报(自然科学版), 2009,15(1):18-20.
LU Chunqing, HE Hongyuan, JIA Yanchao, ZHANG Shufang, CHEN Zhanhe. Fourier transform infrared spectrum analysis of paint evidence in traffic accident cases[J]. Journal of People's Public Security University of China (Science and Technology), 2009, 15(1): 18-20(in Chinese).

[3] 张美多. 扫描电镜/能谱仪法分析车漆成分[J]. 化工设计通讯,2019,45(10):172-173.
ZHANG Meiduo. Analysis of the paint by SEM/EDS[J]. Chemical Engineering Design Communications, 2019, 45(10): 172-173(in Chinese).

[4] 王玉鹏,季军宏,唐佳瑜,万雪期. 扫描电镜能谱仪在涂料中的应用研究[J]. 涂料工业,2016,46(3):57-63.
WANG Yupeng, JI Junhong, TANG Jiayu, WAN Xueqi. Research on application of scanning electron microscope energy spectrometer in coatings[J]. Paint & Coatings Industry, 2016, 46(3): 57-63(in Chinese).

[5] 雷平. 交通事故中油漆物证的扫描电镜/能谱鉴定方法[J]. 电子显微学报,2014,33(4):373-376.
LEI Ping. The identification method of paint evidences in traffic accidents using SEM/EDS[J]. Journal of Chinese Electron Microscopy Society, 2014, 33(4): 373-376(in Chinese).

[6] 孙其然,罗仪文,徐彻. 裂解气相色谱-质谱法和红外光谱法对红色汽车油漆的比较分析[J]. 中国司法鉴定,2013(5):51-54.
SUN Qiran, LUO Yiwen, XU Che. Comparative analysis of red automobile paints by pyrolysis gas chromatography-mass spectrometry and infrared spectrometry[J]. Chinese Journal of Forensic Sciences, 2013(5): 51-54(in Chinese).

[7] 马玉华,唐方东,刘佳煜,忻智炜,曾友石,杜林,刘卫. 稳定同位素比技术用于橄榄油的掺假鉴定[J]. 质谱学报,2021,42(2):189-196.
MA Yuhua, TANG Fangdong, LIU Jiayu, XIN Zhiwei, ZENG Youshi, DU Lin, LIU Wei. Olive oil adulteration identification using stable isotope ratio technique[J]. Journal of Chinese Mass Spectrometry Society, 2021, 42(2): 189-196(in Chinese).

[8] 戴祁,钟其顶,王道兵,武竹英,陈珊珊,肖冬光. 散养与笼养鸡蛋中稳定碳氮同位素特征研究[J]. 质谱学报,2016,37(4):366-373.
DAI Qi, ZHONG Qiding, WANG Daobing, WU Zhuying, CHEN Shanshan, XIAO Dongguang. Study on stable carbon and nitrogen isotope characteristics of cage-free eggs and caged eggs[J]. Journal of Chinese Mass Spectrometry Society, 2016, 37(4): 366-373(in Chinese).

[9] LU X F, LIANG L L, WANG L X, JENERETTE G D, MCCABE M F, GRANTZ D A. Partitioning of evapotranspiration using a stable isotope technique in an arid and high temperature agricultural production system[J]. Agricultural Water Management, 2017, 179: 103-109.

[10] COLOMBANO N, MASTROCICCO M, CASTALDELLI G, ARAVENA R. Contrasting biogeochemical processes revealed by stable isotopes of H_2O, N, C and S in shallow aquifers underlying agricultural low lands[J]. Science of the Total Environment, 2019, 691: 1 282-1 296.

[11] CARREY R, BALLESTE E, BLANCH A R, LUCENA F, PONS P, LOPEZ J M, RULL M, SOLA J, MICOLA N, FRAILE J, ARRIDO T, MUNNE A, SOLER A, OTERO N. Combining multi-isotopic and molecular source tracking methods to identify nitrate pollution sources in surface and groundwater[J]. Water Research, 2021, doi: 10.1016/j.watres.2020.116537.

[12] TORRES-MARTINEZ J A, MORA A, MAHLKNECHT J, KAOWN D, BARCELO D. Determining nitrate and sulfate pollution sources and transformations in a coastal aquifer impacted by seawater intrusion-a multi-isotopic approach combined with self-organizing maps and a Bayesian mixing model[J]. Journal of Hazardous Materials, 2021, doi: 10.1016/j.jhazmat.2021.126103.

[13] MUCCIO Z, WOCKEL C, AN Y, JACKSON G P. Comparison of bulk and compound-specific $\delta^{13}C$ isotope ratio analyses for the discrimination between cannabis samples[J]. Journal of Forensic Sciences, 2012, 57(3): 757-764.

[14] MALLETTE J R, CASALE J F, JORDAN J, MORELLO D R, BEYER P M. Geographically sourcing cocaine's origin-delineation of the nine-

teen major coca growing regions in south america [J]. Scientific Reports, 2016, 6(1): 23 520.

[15] THOMPSON R A, MORELLO D R, PANICKER S, LI L, PANICKER S. Carbon and nitrogen isotopic analysis of morphine from opium and heroin samples originating in the four major heroin producing regions[J]. Drug Testing and Analysis, 2022, 14(3): 505-513.

[16] SALOUROS H, SUTTON G J, HOWES J, HIBBERT D B, COLLINS M. Measurement of stable isotope ratios in methylamphetamine: a link to its precursor source[J]. Analytical Chemistry, 2013, 85(19): 9 400-9 408.

[17] BUCHANAN H A S, DAEID N N, KERR W J, CARTER J F, HILL J C. Role of five synthetic reaction conditions on the stable isotopic composition of 3, 4-methylenedioxymethamphetamine [J]. Analytical Chemistry, 2010, 82 (13): 5 484-5 489.

[18] BUCHANAN H A S, KERR W J, MEIER-AUGENSTEIN W, DAEID N N. Organic impurities, stable isotopes, or both: a comparison of instrumental and pattern recognition techniques for the profiling of 3,4-methylenedioxymethamphetamine[J]. Analytical Methods, 2011, 3 (10): 2 279-2 288.

[19] ZHANG D M, SUN W, YUAN Z P, JU H X, SHI X J, WANG C H. Origin differentiation of a heroin sample and its acetylating agent with ^{13}C isotope ratio mass spectrometry[J]. European Journal of Mass Spectrometry, 2005,11(3): 277-285.

[20] 孙伟,张大明,宋朝锦,汪聪慧. 同位素比值质谱法鉴别海洛因来源——1.海洛因水解制备吗啡的研究[J]. 中国司法鉴定,2003(2):21-24.
SUN Wei, ZHANG Daming, SONG Chaojin, WANG Conghui. Identifying iuicit heroin origins by isotope ratio mass spectrometry 1. Study on the preparation of morphine by hydrolysis of heroin[J]. Chinese Journal of Forensic Sciences, 2003(2): 21-24(in Chinese).

[21] 汪聪慧,孙伟,张大明,田玉杭,方家骏,王静竹,吴侔天,朱绍棠. 同位素比值质谱法鉴别缴获的海洛因来源——2.海洛因的碳同位素比值质谱法研究[J]. 中国司法鉴定,2003(4):19-22.
WANG Conghui, SUN Wei, ZHANG Daming, TIAN Yuhang, FANG Jiajun, WANG Jingzhu, WU Moutian, ZHU Shaotang. The origin differentiation of seized heroin using GC-C-IRMS Ⅱ-Study on the ^{13}C isotope ratio mass spectrometry of seized heroin[J]. Chinese Journal of Forensic Sciences, 2003(4): 19-22(in Chinese).

[22] MACKINNON G. Forensic anthropology current methods and practice[J]. Journal of Forensic and Legal Medicine, 2014, 27: 87-88.

[23] EHLERINGER J R, BOWEN G J, CHESSON L A, WEST A G, PODLESAK D W, CERLING T E. Hydrogen and oxygen isotope ratios in human hair are related to geography[J]. Proceedings of the National Academy of Sciences, 2008, 105(8): 2 788-2 793.

[24] 于子洋,梅宏成,朱军,杨瑞琴,胡灿,刘昌景,郭洪玲,王萍,郑继利,权养科,王桂强. 不同城市居民头发中碳、氮稳定同位素比值特征研究[J]. 质谱学报,2021,42(6):1 183-1 192.
YU Ziyang, MEI Hongcheng, ZHU Jun, YANG Ruiqin, HU Can, LIU Changjing, GUO Hongling, WANG Ping, ZHENG Jili, QUAN Yangke, WANG Guiqiang. Analysis on carbon and nitrogen stable isotope ratios of residents′ hair from different cities[J]. Journal of Chinese Mass Spectrometry Society, 2021, 42(6): 1 183-1 192(in Chinese).

[25] MUHAMMAD S A, FREW R D, HAYMAN A R. Forensic differentiation of diesel fuels using hydrocarbon isotope fingerprints[J]. Central European Geology, 2013, 56(1): 19-37.

[26] MUHAMMAD S A, HAYMAN A R, van HALE R V, FREW R D. Assessing carbon and hydrogen isotopic fractionation of diesel fueln-alkanes during progressive evaporation[J]. Journal of Forensic Sciences, 2015, 60: S56-S65.

[27] SCHWARTZ Z, AN Y, KONSTANTYNOVA K I, JACKSON G P. Analysis of household ignitable liquids and their post-combustion weathered residues using compound-specific gas chromatography-combustion-isotope ratio mass spectrometry[J]. Forensic Science International, 2013, 233(1/2/3): 365-373.

[28] BEZEMER K D B, KOEBERG M, van der HEIJDEN A E D M, van DRIEL C A, BLAGA C, BRUINSMA J, van ASTEN A C. The potential of isotope ratio mass spectrometry (IRMS) and gas chromatography-IRMS analysis of triacetone

triperoxide in forensic explosives investigations [J]. Journal of Forensic Sciences, 2016, 61(5): 1 198-1 207.

[29] HOWA J D, LOTT M J, EHLERINGER J R. Observations and sources of carbon and nitrogen isotope ratio variation of pentaerythritol tetranitrate (PETN)[J]. Forensic Science International, 2014, 244: 152-157.

[30] CHESSON L A, HOWA J D, LOTT M J, EHLERINGER J R. Development of a methodological framework for applying isotope ratio mass spectrometry to explosive components[J]. Forensic Chemistry, 2016, 2: 9-14.

[31] HOWA J D, LOTT M J, CHESSON L A, EHLERINGER J R. Isolation of components of plastic explosives for isotope ratio mass spectrometry[J]. Forensic Chemistry, 2016, 1: 6-12.

[32] HOWA J D, LOTT M J, CHESSON L A, EHLERINGER J R. Carbon and nitrogen isotope ratios of factory-produced RDX and HMX[J]. Forensic Science International, 2014, 240: 80-87.

[33] HOWA J D, LOTT M J, EHLERINGER J R. Isolation and stable nitrogen isotope analysis of ammonium ions in ammonium nitrate prills using sodium tetraphenylborate[J]. Rapid Communications in Mass Spectrometry, 2014, 28(13): 1 530-1 534.

[34] BRUST H, KOEBERG M, van der HEIJDEN A, WIARDA W, MUGLER I, SHRADER M, VIVO-TRUYOLS G, SCHOENMAKERS P, van ASTEN A. Isotopic and elemental profiling of ammonium nitrate in forensic explosives investigations[J]. Forensic Science International, 2015, 248: 101-112.

[35] PYE K, BLOTT S J, CROFT D J, CARTER J F. Forensic comparison of soil samples: assessment of small-scale spatial variability in elemental composition, carbon and nitrogen isotope ratios, colour, and particle size distribution[J]. Forensic Science International, 2006,163(1/2): 59-80.

[36] DAÉID N N, MEIER-AUGENSTEIN W, KEMP H F. Investigating the provenance of un-dyed spun cotton fibre using multi-isotope profiles and chemometric analysis[J]. Rapid Communications in Mass Spectrometry, 2011, 25(13): 1 812-1 816.

[37] MEIER-AUGENSTEIN W, KEMP H F, SCHENK E R, ALMIRALL J R. Discrimination of unprocessed cotton on the basis of geographic origin using multi-element stable isotope signatures[J]. Rapid Communications in Mass Spectrometry, 2014, 28(5): 545-552.

[38] JONES K, BENSON S, ROUX C. The forensic analysis of office paper using carbon isotope ratio mass spectrometry-Part 1: understanding the background population and homogeneity of paper for the comparison and discrimination of samples [J]. Forensic Science International, 2013, 231 (1/2/3): 354-363.

[39] JONES K, BENSON S, ROUX C. The forensic analysis of office paper using carbon isotope ratio mass spectrometry-Part 2: method development, validation and sample handling[J]. Forensic Science International, 2013, 231(1/2/3): 364-374.

[40] JONES K, BENSON S, ROUX C. The forensic analysis of office paper using carbon isotope ratio mass spectrometry-Part 3: characterizing the source materials and the effect of production and usage on the $\delta^{13}C$ values of paper[J]. Forensic Science International, 2013, 233(1/2/3): 355-364.

[41] JONES K, BENSON S, ROUX C. The forensic analysis of office paper using oxygen isotope ratio mass spectrometry. Part 1: understanding the background population and homogeneity of paper for the comparison and discrimination of samples[J]. Forensic Science International, 2016, 262: 97-107.

[42] JONES K, BENSON S, ROUX C. The forensic analysis of office paper using oxygen isotope ratio mass spectrometry. Part 2: characterising the source materials and the effect of production and usage on the $\delta^{18}O$ values of cellulose and paper [J]. Forensic Science International, 2016, 268: 151-158.

[43] REIDY L J, MEIER-AUGENSTEIN W, KALIN R M. ^{13}C-Isotope ratio mass spectrometry as a potential tool for the forensic analysis of white architectural paint: a preliminary study[J]. Rapid Communications in Mass Spectrometry, 2005, 19(13): 1 899-1 905.

[44] FARMER N, MEIER-AUGENSTEIN W, LUCY D. Stable isotope analysis of white paints and likelihood ratios[J]. Science & Justice, 2009, 49 (2): 114-119.

(收稿日期:2022-03-06;修回日期:2022-05-01)