

CORRELATION OF FORENSIC SAMPLES OF MOTOR OILS USING ISOTOPES, LIKELIHOOD RATIOS AND BIOMARKERS: A NEW TOOL FOR RECONSTRUCTION OF TRAFFIC ACCIDENTS

Jorge E. SPANGENBERG¹, Georges PIERRINI², Christophe CHAMPOD³ and Franco TARONI³

1. Institute of Mineralogy and Geochemistry, University of Lausanne, 1015 Lausanne, Switzerland

2. Institute of Criminal Research, French Gendarmerie, 93111 Rosny sous Bois, France

3. Institute of Forensic Sciences, University of Lausanne, 1015 Lausanne, Switzerland

Isotope and molecular organic geochemistry have played an important role in the development of forensic methodologies for the identification of oil spills in the marine environment (Kaplan *et al.*, 1997). Here we explore a similar analytical approach for fingerprinting motor oil spills from traffic accidents. In most car crashes, aliquots from motor oil spills can be recovered from the road or highway surface, and compared with the crankcase oil from the involved or suspected vehicles. Oil/oil correlations of these samples provide a scientific framework for the identification of the involved vehicles, the reconstruction of the traffic accident, and help the tracing of the occupants of the vehicles.

In this study, motor oil samples were obtained from the crankcase of 7 vehicles with gasoline engine and 3 vehicles with diesel engine immediately after oil change (distance, $d = 0$ km) and after a known driven distance ($d = x$ km) (Table 1). The first set of 10 samples at $d = 0$ km, represent the recovered samples at the oil-spill site (hereafter refer to as r-oils) and the samples at $d = x$ km correspond to control samples of oil taken from the crankcase of the involved or suspected vehicles (hereafter refer to as c-oils). A sample from motor oil purchased in a local gas station was used to test for eventual analytical shifts. The oil samples were passed through an activated copper column to remove elemental sulphur and separated into three fractions (saturated, aromatic and NOS compounds) using liquid chromatography. The bulk sulfur-free oils and the three oil fractions were analyzed for $\delta^{13}\text{C}$ by EA-IRMS, and the saturated fraction by GC-MSD. All analyses were done in triplicate.

The variation of the $\delta^{13}\text{C}$ values of fraction within the r-oils follows generally the conventional trend recognised in crude oil and bitumens, increasing in the following order: $\delta^{13}\text{C}_{\text{sat}} < \delta^{13}\text{C}_{\text{aro}} < \delta^{13}\text{C}_{\text{NOS}}$, with $\delta^{13}\text{C}_{\text{sat}}$ up to 6.7‰ more negative than $\delta^{13}\text{C}_{\text{NOS}}$ (Table 1). This is not the case for all the c-oils, with the difference $\delta^{13}\text{C}_{\text{sat}} - \delta^{13}\text{C}_{\text{NOS}}$ between -0.9 to 0.9‰. The bulk, aromatic and NOS fractions of the c-oils are depleted in ^{13}C by up to 2.6‰ compared to the r-oils (Table 1). The saturated hydrocarbons of the c-oils are enriched in ^{13}C by up to 1.2‰ compared to the r-oils. This is the normal isotopic shift observed during cracking of hydrocarbons, which involve the release of ^{13}C -depleted moieties. The NOS fractions display the most important isotopic shift (by up to 2.6‰), indicating preferential loss of ^{12}C -rich moieties, most probably from thermally more labile oil or additives fractions (e.g., preservatives, antioxidants).

A multivariate statistical analysis of the isotopic data, based on the principle of likelihood ratio (LR, Aitken and Taroni, 2004) was applied to compute the probability ratios of the hypotheses H_p "the c-oil and r-oil come from the same crankcase" and H_d "the c-oil and r-oil come from different crankcases". The LR values were calculated from a measurements matrix composed from $m = 11$ cases (10 r and c oils and 1 test oil), $p = 5$ variables ($\delta^{13}C_{\text{bulk}}$, $\delta^{13}C_{\text{sat}}$, $\delta^{13}C_{\text{aro}}$, $\delta^{13}C_{\text{sat}}/\delta^{13}C_{\text{bulk}}$ and $\delta^{13}C_{\text{aro}}/\delta^{13}C_{\text{bulk}}$), and $n = 3$ replicates (Pierrini, 2005). LR values > 1 support hypothesis H_p and LR < 1 support hypothesis H_d . In all cases when c-oils and r-oils come from the crankcase of the same vehicle (H_p is true), the LR values are > 1 . For the other cases where c-oils and r-oils come from different bulk sources (H_d is true) the LR values are generally < 1 . However there are 15 wrong "positive" tests from 111 c-r pairs, with LR > 1 for true H_d . This would represent 13.5% of misleading evidence for the court. The distribution of the hopanes (m/z 191) and steranes (m/z 217), and the molecular parameters give further constraints for c-oil/r-oil correlation. The molecular parameters (e.g., hydrocarbons concentration ratios) of the c-oils compared favourably with the r-oils, suggesting that little thermal maturation took place after a relatively short use of the vehicle engine. Further work is needed to validate the proposed approach, by using real forensic scenes covering different cases of traffic accidents.

Vehicle (engine) ¹	$\delta^{13}C_{\text{bulk-r}}$ (‰)	Distance, km (days) ²	$\Delta^{13}C_{\text{bulk, c-r}}$ (‰)	$\Delta^{13}C_{\text{sat, c-r}}$ (‰)	$\Delta^{13}C_{\text{aro, c-r}}$ (‰)	$\Delta^{13}C_{\text{NOS, c-r}}$ (‰)
1 (G)	-27.12	2758 (58)	-0.39	1.14	-1.07	-1.82
2 (G)	-27.99	2800 (60)	-0.41	1.24	-0.57	-2.59
3 (G)	-26.81	286 (93)	-0.47	0.78	-0.88	na
4 (G)	-32.49	11139 (93)	-0.56	0.74	-0.42	na
5 (G)	-27.45	2669 (69)	-0.33	0.55	-0.45	-0.7
6 (G)	-28.09	3325 (65)	-0.33	0.95	-0.74	-0.54
7 (D)	-28.14	1703 (65)	-0.51	1.06	-0.39	0.14
8 (D)	-27.44	1308 (63)	-0.08	0.53	0.21	-0.45
9 (D)	-27.42	8859 (97)	0.02	0.9	-1.36	-0.79
10 (G)	-28.62	1000 (1)	-0.23	0.17	-0.49	-0.82

Table 1. Average $\delta^{13}C_{\text{bulk}}$ values of recovered car oil samples (r-oils) and $\Delta^{13}C$ values for hydrocarbon fractions of control (c) and recovered (r) samples.¹ G = gasoline engine; D = diesel engine; ² distance driven and days between sampling of r and c-oils.

REFERENCES

- Aitken C., and Taroni F. (2004) *Statistics and the evaluation of evidence for forensic scientists*. Chichester, John Wiley & Sons, 509 pp.
- Kaplan I.R., Galperin Y., Lu S.-T. and Lee R.P. (1997) Forensic environmental geochemistry: differentiation of fuel-types, their sources and release time. *Organic Geochemistry* **27**: 289-317.
- Pierrini G. (2005) *La spectrométrie de masse isotopique en sciences forensiques*. MSc thesis in Forensic Sciences, Université de Lausanne, 85 pp.