

## Short Communication

# Enhanced resolution of organic compounds from sediments by isotopic gas chromatography–combustion–mass spectrometry

Eric Lichtfouse<sup>\*,☆</sup>, Katherine H. Freeman, James W. Collister and Dawn A. Merritt

*Biogeochemical Laboratories, Geology Building, Indiana University, Bloomington, IN 47405 (USA)*

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### ABSTRACT

The resolution of organic compounds from sediments is increased by  $^{13}\text{C}/^{12}\text{C}$  isotopic gas chromatography–combustion–mass spectrometry relative to gas chromatography with flame ionization detection. Impurities which elute close together with *n*-alkanes, phytane and a  $\text{C}_{32}$  hopanoid acid methyl ester are resolved with a valley increase of up to 100%. This phenomenon is probably due to fractionation during gas chromatographic elution and enhanced detection monitoring of the isotopic composition of the carbon dioxide produced by the combustion of the eluting substances.

### INTRODUCTION

The development of gas chromatography–combustion–mass spectrometry (GC–C–MS) allows the direct measurement of the  $^{13}\text{C}/^{12}\text{C}$  isotopic composition of individual organic substances eluting in GC [1]. This method has found interesting applications in molecular organic biogeochemistry such as the linking of sedimentary organic compounds with their biological sources [2] or with the atmospheric partial pressure of carbon dioxide at the time of deposition [3].

During the GC–C–MS analysis of complex organic mixtures from sediments including petroleum, it was observed that compounds assumed to be “pure” (one peak) by routine GC almost co-elute with unidentified compounds. We report here se-

lected examples of this phenomenon and discuss its origin and consequences.

### EXPERIMENTAL

Alkane fractions were obtained from methylene chloride extracts of Paris Basin sediments or petroleum by silver nitrate–silica gel thin-layer chromatography (TLC) with *n*-hexane as the eluent ( $R_F$  0.8–1). Acid fractions were obtained from extracts by potassium hydroxide–silica gel column chromatography, then derivatized with 15% boron trifluoride–methanol and purified by TLC using ethyl acetate–hexane (5%, v/v) as the eluent; monocarboxylic acid methyl ester fractions were obtained [4–6].

The GC–C–MS conditions (Delta S, Finnigan, Hewlett-Packard GC) were as follows: on-column injection; 50 m × 0.25 mm column; Ultra 1 phase (100% polymethylsiloxane, 0.5 μm); column head pressure, 20 p.s.i.; helium flow-rate, 1.5 ml/min; GC

\* Present address: Institut für Chemie, ICH-5, Postfach 1913, D-5170 Jülich, Germany.

temperature programme, 60–100°C (30°C/min), 100–320°C (4°C/min), hold 60 min at 320°C; combustion furnace temperature, 850°C; MS, electron ionization (3 kV), simultaneous Faraday cup detection at  $m/z$  44, 45 and 46, 0.25-s integration periods.

The basis of GC–C–MS has been described by Hayes and co-workers [1,2]. Briefly, after separation by GC, the eluting compounds, e.g. hydrocarbons, are burnt on copper(II)oxide at 850°C. The water is removed and the helium carrier stream en-

ters the ion source through a restrictor capillary (1 m  $\times$  0.11 mm I.D.). The isotopic compositions are calculated by comparison with co-injected standards ( $n$ -C<sub>16</sub><sup>2</sup>H<sub>34</sub>,  $n$ -C<sub>20</sub><sup>2</sup>H<sub>42</sub>,  $n$ -C<sub>24</sub><sup>2</sup>H<sub>50</sub> and  $n$ -C<sub>36</sub><sup>2</sup>H<sub>74</sub>) which elute before  $n$ -alkanes of the same carbon number (Fig. 1d).

The C<sub>32</sub> hopanoid acid methyl ester from an extract of the Green River Formation (CO, USA) was identified by GC–MS ( $m/z$  191, 263, 369, 484) and compared with previously reported values [6,7]; the

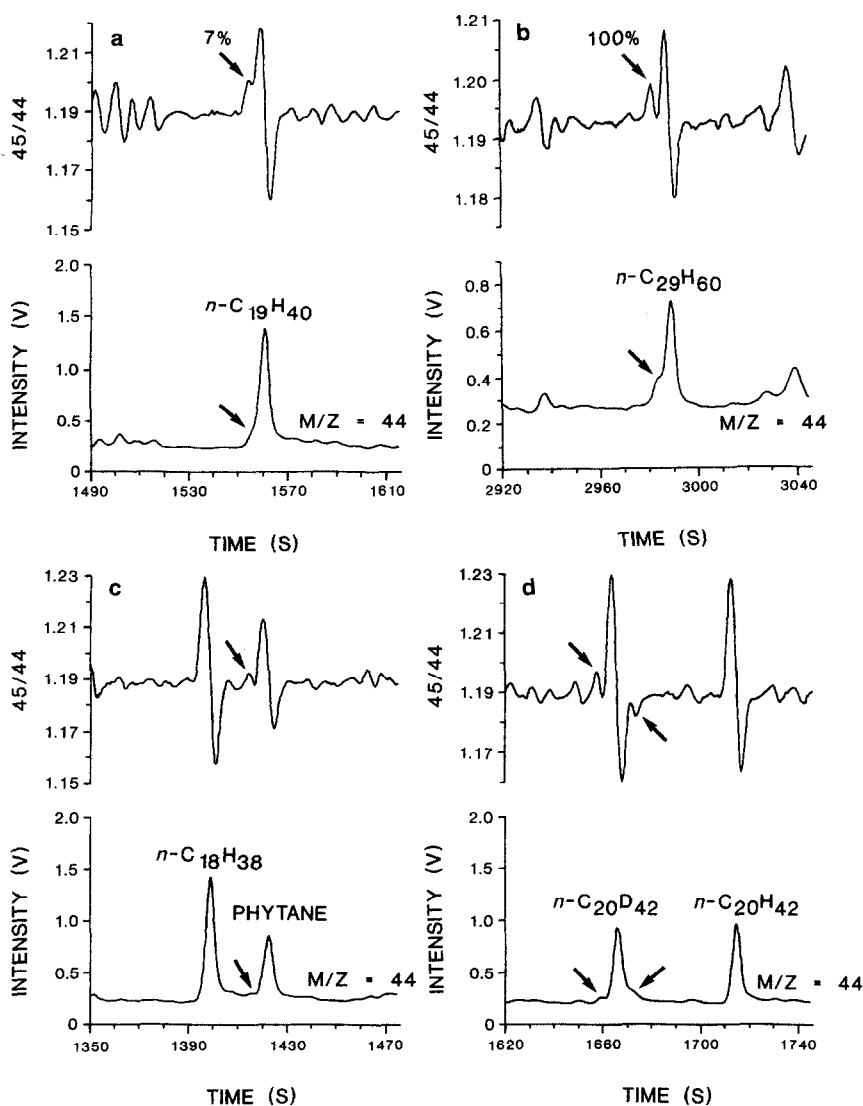


Fig. 1.  $m/z$  44 fragmentogram and 45/44 trace of sedimentary alkanes analysed by GC–C–MS. D = Deuterium.

unknown compound eluting before this ester was tentatively identified as a ring A methylated hopanoid acid methyl ester based on the presence of a 205 mass fragment and the occurrence of ring A methyl hopanoids in sediments [8] and bacteria [9–11]. These two hopanoids give one peak in GC with flame ionization detection (GC–FID) or in the total ion current trace in GC–MS, but the ring A methylated hopanoid acid methyl ester has a slightly shorter retention time, as shown by a comparison of the 191 and 205 ion currents.

## RESULTS

Sedimentary alkane fractions usually contain *n*-alkanes extending from C<sub>10</sub> to C<sub>40</sub>, pristane and phytane, as major compounds. Other compounds such as branched and/or cyclic alkanes are minor but numerous, especially in mature sediments, and they are often poorly resolved in GC–FID. The *m/z* 44 ion current trace (<sup>12</sup>C<sup>16</sup>O<sub>2</sub>) and the 45/44 isotopic trace of selected alkanes from Paris Basin sediments are shown on Fig. 1. The *m/z* 44 ion current is similar to the signal obtained by either GC–FID or conventional GC–MS with total ion current monitoring.

A pure compound with a Gaussian isotopic distribution gives a positive or negative peak or both on the 45/44 trace, depending on its <sup>13</sup>C/<sup>12</sup>C isotopic composition relative to the baseline [12]. For example, *n*-C<sub>20</sub>H<sub>42</sub> gives a positive peak followed by a negative peak corresponding to the <sup>13</sup>C-enriched and <sup>13</sup>C-depleted isotopic compositions of the carbon dioxide produced, respectively, relative to the baseline (Fig. 1). The inflections of the 45/44 trace allow the improved resolution of closely eluting components. For example, the peak representing *n*-C<sub>19</sub>H<sub>40</sub> in the *m/z* 44 trace is regular in shape, except for its slightly enlarged base. A second component is clearly distinguished in the 45/44 trace with a valley of 7%. Similarly, an increase of about 100% valley is observed for *n*-C<sub>29</sub>H<sub>60</sub>. Such close elutions have been detected for *n*-alkanes, phytane and polydeuterated standards in petroleum and shale of various maturities, ages and locations. Two negative peaks were observed on the 45/44 trace of a C<sub>32</sub> hopanoid acid methyl ester (Fig. 2).

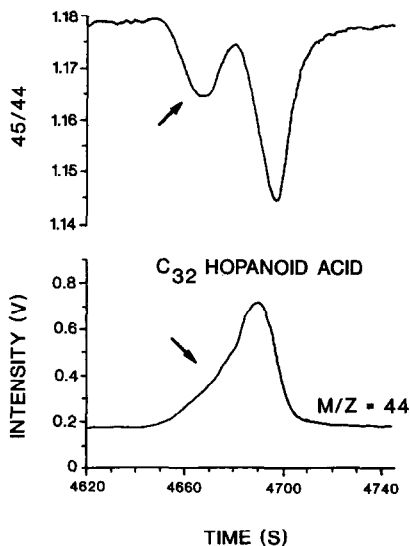


Fig. 2. *m/z* 44 fragmentogram and 45/44 trace of a sedimentary C<sub>32</sub> hopanoid acid methyl ester analysed by GC–MS.

## DISCUSSION

Strong <sup>13</sup>C/<sup>12</sup>C isotopic fractionation has been observed previously in eluting methane or carbon dioxide in GC on various phases; the front portion of the effluent was enriched in <sup>13</sup>C [13]. This is due to an inverse isotope effect associated with the interaction of the eluent with the stationary phase [14]. The same behaviour is apparent on 45/44 traces, which show that the <sup>13</sup>C enriched carbon dioxide elutes first (Fig. 1). Therefore the resolution increase for various compounds (compared with GC–FID or GC–MS with total ion current monitoring) probably results from the chromatographic fractionation and enhanced sensitivity of GC–MS to the variations of the <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> ratio with increasing time. The 45/44 trace of a C<sub>32</sub> hopanoid acid methyl ester shows that even peaks which are only negative can be better resolved (Fig. 2), excluding a possible artificial effect of the baseline level.

Alkanes fractions from sediments usually contain *n*-alkanes as major compounds and minor but numerous branched and/or cyclic alkanes. Unresolved GC areas are therefore common and the compounds which elute close together could be struc-

turally different compounds, isomers, or compounds with the same configuration but a different isotopic composition.

Enhanced resolution by isotopic GC-C-MS will be useful when dealing with complex mixtures. The isotopic ratios of compounds eluting close together cannot be measured accurately if the isotopic compositions of the co-eluting substances are unknown. Accordingly, in organic geochemistry, simpler fractions are needed for isotopic studies, provided that there is no isotopic fractionation during previous separations. These observations also strengthen the conclusion that one GC-FID peak is not a definitive proof of purity.

#### CONCLUSIONS

A significant increase in resolution has been observed by isotopic GC-C-MS relative to GC-FID or GC-MS with total ion current monitoring. This phenomenon is probably due to the fractionation of eluents during GC and the enhanced sensitivity of GC-C-MS to  $^{13}\text{CO}_2/^{12}\text{CO}_2$  variations. Such enhanced resolution will be useful in studies of complex mixtures.

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