

Compound Specific Carbon and Hydrogen Isotope Fractionation during Solid Phase Extraction

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BACKGROUND. As the range of applications for compound specific isotope analysis (CSIA) increases, it is important investigators have a rapid and robust method for sample preparation. Traditional preparation methods require laborious wet chemical work-up, highly specialised apparatus or result in significant isotope fractionation. To resolve this problem, a rapid and reproducibly solid phase extraction (SPE) method has been developed for the isolation of semi-volatile organic compounds from aqueous systems prior to CSIA.

RESULTS.

1. Artificial Contaminant Solution

| | Eucalyptol (%) | Dodecane (%) | Naphthalene (%) | Benzothiazole (%) | Dibutyl phthalate (%) |
|-----------------------------------|----------------|--------------|-----------------|-------------------|-----------------------|
| <i>High Volume Sample (50 mL)</i> | | | | | |
| C18E | 97(3) | 89(3) | 98(4) | 101(2) | 102(3) |
| Strata-X | 108(12) | 88(3) | 107(10) | 107(7) | 98(1) |
| ENV+ | 100(9) | 86(6) | 104(3) | 110(2) | 105(9) |
| <i>Low Volume Sample (1 mL)</i> | | | | | |
| C18E | 95(2) | 107(2) | 97(1) | 97(3) | 81(15) |
| Strata-X | 95(2) | 104(3) | 97(3) | 98(1) | 90(7) |
| ENV+ | 83(5) | 94(4) | 88(4) | 92(5) | 99(16) |

Table 1. The ACS extraction efficiency for each ACS compounds when extracted using 3 different SPE cartridges (% extracted relative to solvent extraction). Cartridges were loaded with 1 mL and 50 mL of the ACS solution. Values in brackets = %SD, n=3.

| SPE Cartridge | Eluting Solvent | Compound Fractionation (‰ vs VSMOW and VPDB for Hydrogen and Carbon respectively) | | | | | | | | | |
|---------------|------------------------------|---|-----------------------|--------------------|-----------------------|--------------------|-----------------------|--------------------|-----------------------|--------------------|-----------------------|
| | | Eucalyptol | | Dodecane | | Naphthalene | | Benzothiazole | | Dibutyl Phthalate | |
| | | $\delta^2\text{H}$ | $\delta^{13}\text{C}$ | $\delta^2\text{H}$ | $\delta^{13}\text{C}$ | $\delta^2\text{H}$ | $\delta^{13}\text{C}$ | $\delta^2\text{H}$ | $\delta^{13}\text{C}$ | $\delta^2\text{H}$ | $\delta^{13}\text{C}$ |
| C18E | Dichloromethane | 3.2 | 0.06 | -6.7 | 0.03 | -1.4 | 0.02 | -2.7 | -0.02 | -1.2 | 0.08 |
| C18E | Ethyl Acetate | 2.4 | -0.01 | 1.3 | -0.77 | -7.5 | 0.61 | -0.8 | 1.12 | 2.3 | 0.4 |
| C18E | Ethyl Acetate/Methanol (4:1) | 7.9 | 0.03 | 58.1 | 0.21 | 27 | 0.54 | 9.9 | 0.73 | 31.7 | 0.39 |
| C18E | Acetonitrile | -244.8 | - | -127.7 | - | -91.4 | - | -137.7 | - | -76.6 | - |
| C18E | Methanol | 91.3 | - | -87.9 | - | -5.3 | - | n.d. | - | n.d. | - |
| C18E | Methanol/Acetonitrile (1:1) | -196.6 | - | -142.7 | - | n.d. | - | n.d. | - | -63.2 | - |
| Strata-X | Dichloromethane | 4.8 | 0.07 | -5.7 | -0.03 | -0.6 | 0.02 | -0.4 | 0.12 | -1.9 | 0.04 |
| Strata-X | Ethyl Acetate | 15 | 0.27 | -2.9 | -0.55 | 45.5 | 1.83 | 7.5 | 1.05 | 0.3 | 0.54 |
| Strata-X | Ethyl Acetate/Methanol (4:1) | 18 | 0.06 | 92.1 | -0.01 | -18 | 0.27 | 7.9 | 0.71 | 32 | 0.37 |
| Strata-X | Methanol | 53.9 | - | -86.7 | - | -88.4 | - | n.d. | - | n.d. | - |
| Strata-X | Methanol/Acetonitrile (1:1) | -183.7 | - | n.d. | - | n.d. | - | n.d. | - | n.d. | - |
| ENV+ | Dichloromethane | 5.1 | 0.09 | -5.5 | 0.09 | -3.1 | 0.04 | -1.1 | 0.61 | -1.2 | 0.06 |
| ENV+ | Ethyl Acetate/Methanol (4:1) | 8.7 | 0.01 | 68 | 0.28 | -12.9 | 0.11 | 14.3 | 1.19 | 29.6 | -0.02 |

Table 2. Hydrogen and carbon fractionation (‰) for ACM compounds when isolated using a variety of SPE absorbent and eluting solvent combinations. Fractionation is the deviation from expected isotopic value as verified by bulk isotope analysis. n.d. = not detected, - = compound not analysed, n=4.

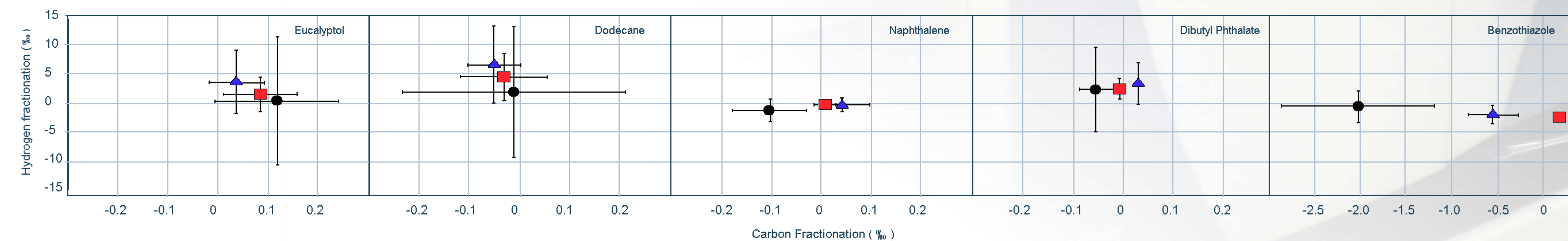


Figure 1. Hydrogen and carbon fractionation (‰) of ACM compounds when eluted with dichloromethane from Strata-X cartridges (circles), ENV+ cartridges (squares) and C18-E cartridges (triangles). Error bars are 1σ, n=3.

Artificial contaminants were extracted efficiently using all SPE cartridges but significant fractionation was observed when compounds were eluted with polar solvents (e.g. methanol, acetonitrile and ethyl acetate). No significant fractionation was detected when compounds were eluted from the SPE cartridges with dichloromethane (except benzothiazole isolated on Strata-X).

2. Spiked Natural Water Samples

| | Eucalyptol (%) | Dodecane (%) | Naphthalene (%) | Benzothiazole (%) | Dibutyl phthalate (%) |
|-------------------|----------------|--------------|-----------------|-------------------|-----------------------|
| Potable Water | 104(3) | 16(4) | 91(3) | 108(4) | 88(4) |
| River Water | 99(2) | 15(1) | 88(3) | 104(3) | 91(5) |
| Sea Water | 99(19) | 22(8) | 75(28) | 107(17) | 79(24) |
| Landfill Leachate | 69(18) | 24(5) | 59(16) | 80(20) | 69(14) |

Table 3. Extraction efficiency (%) of ACM compounds from poisoned natural water samples using ENV+ cartridges and dichloromethane. Values in brackets = %SD, n = 3.

The extraction efficiency for spiked leachate, and dodecane from all water samples, was poor. This may be due to the formation of colloids, microbial degradation or competitive absorption at the SPE surface. For most compounds, isotopic fractionation was closely related to the extraction efficiency (data not shown). Apart from dodecane, which exhibited large fractionation, results were within 2 S.D. of accepted values i.e. minimal fractionation was observed.

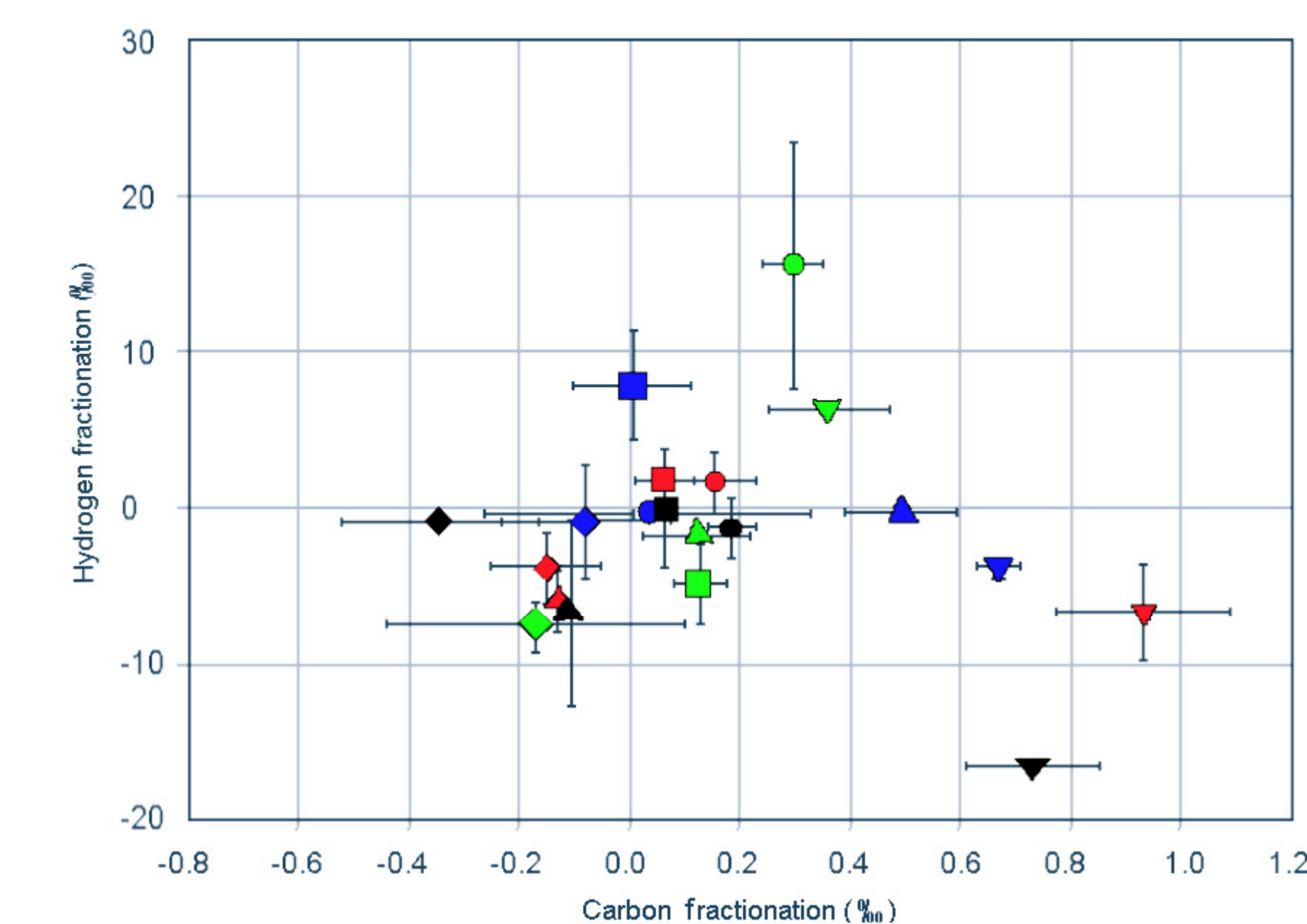


Figure 2. Hydrogen and carbon fractionation (‰) of eucalyptol (circles), dodecane (inverted triangle), naphthalene (square), benzothiazole (diamond), and dibutyl phthalate (triangle) when spiked into NaN_3 poisoned natural water samples prior to ENV+ isolation and elution with dichloromethane. Black symbols = potable water; red symbols = river water; blue symbols = sea water; and green symbols = landfill leachate. Error bars are 1σ, n=3.

CONCLUSIONS.

- Fractionation was controlled by i) the eluting solvent, ii) the SPE absorbant, and iii) the extraction efficiency.
- The least fractionation (hydrogen and carbon) was observed when compounds were eluted with dichloromethane.
- ENV+ cartridges caused the least fractionation (hydrogen and carbon), and displayed the greatest reproducibility.

