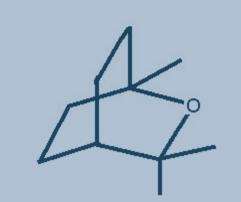
T.J. Benbow*
R.D. Frew
A.R. Hayman

Department of Chemistry, University of Otago Dunedin New Zealand

*Corresponding Author: tbenbow@chemistry.otago.ac.nz



EXPERIMENTAL. Three SPE cartridges and

extraction efficiency and isotopic fractionation

(ACM) and spiked natural water samples.

Artificial Contaminant Mixture: The ACM

alkane), benzothiazole (thioazole), dibutyl

This mixture was added directly to SPE

six eluting solvents were tested to determine the

with respect to an artificial contaminant mixture

consisted of: eucalyptol (terpene), dodecane (n-

phthalate (phthalate), and naphthalene (PAH).

cartridges or dissolved in Milli-Q to form an

artificial contaminant solution (ACS) with the

following concentrations: eucalyptol = 30 ug/L,

benzothiazole = 30 ug/L, and dibutyl phthalate

dodecane = 10 ug/L, naphthalene = 20 ug/L,

= 10 ug/L. No fractionation occurred when

Solid Phase Extraction: SPE cartridges used

included Strata-C18E and Strata-X cartridges

(Phenomenex), and Isolute ENV+ cartridges

(Biotage). Cartridges were conditioned with

with the desired solvent, dried over ashed

sodium sulphate (1 g), and reduced to 1 mL.

Spiked Natural Water Samples: Natural water

samples (potable water, urban river water,

coastal ocean water, and landfill leachate)

GC-IRMS Analysis: Isotope ratios were

Delta plus XP IRMS (Thermo, Bremen,

GC through a split/splitless injector and

0.22 mm i.d., 0.25 µm film).

with 5 uL of ACM.

samples.

were poisoned with sodium azide and spiked

measured using a Trace Ultra GC coupled to a

Germany). Samples were introduced to the

separated using a BP-225 GC column (25 m,

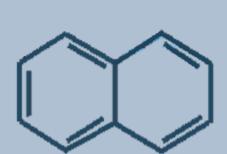
isotopic standard ACM was analysed every 6

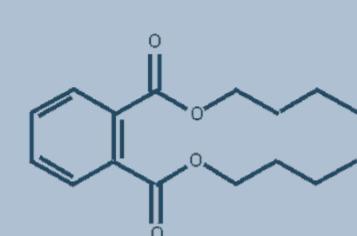
In addition to CO₂ working gas pulses, an

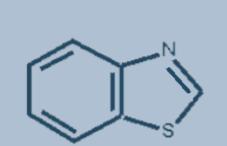
methanol, equilibrated with distilled water; the

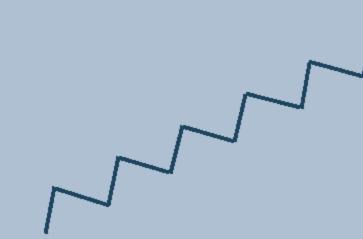
sample was loaded at a rate of 5 ml/min, eluted

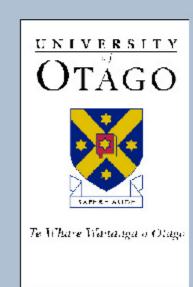
compounds were dissolved in Milli-Q.















Compound Specific Carbon and Hydrogen Isotope Fractionation during Solid Phase Extraction

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 (%)	Naphthalaene (%)	Benzothiazole (%)	Dibutyl phthalate (%)
High Volume S	Sample (50 mL)				
C18E Strata-X ENV+	97(3) 108 (12) 100 (9)	89 (3) 88 (3) 86 (6)	98 (4) 107 (10) 104 (3)	101 (2) 107 (7) 110 (2)	102 (3) 98 (1) 105 (9)
Low Volume S	ample (1 mL)				
C18E Strata-X ENV+	95 (2) 95 (2) 83 (5)	107 (2) 104 (3) 94 (4)	97 (1) 97 (3) 88 (4)	97 (3) 98 (1) 92 (5)	81 (15) 90 (7) 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.

		Tracebu bio									
SPE Cartridge	Eluting Solvent	Compound Fractionation (‰ vs VSMOW and VPDB for Hydrogen and Carbon respectively)									
		Eucalyptol		Dodecane		Naphthalene		Benzothiazole Dibutyl Phthalate			
		$\delta^2 H$	δ ¹³ C	$\delta^2 H$	δ^{13} C	$\delta^2 H$	δ ¹³ C	$\delta^2 H$	δ ¹³ C	$\delta^2 H$	13C
C18E	Dichloromethane	3.2	0.06	-6.7	0.03	-1.4	0.02	-2.7	-0.02	-1.2	(0 δ
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	Co 6-
C18E	Methanol	91.3	-	-87.9	_	-5.3	-	n.d.	-	n.d.	- 60
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.	0 -
Strata-X	Methanol/Acetonitrile (1:1)	-183.7	-	n.d.	-	n.d.	-	n.d.	-	n.d.	0 05
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.

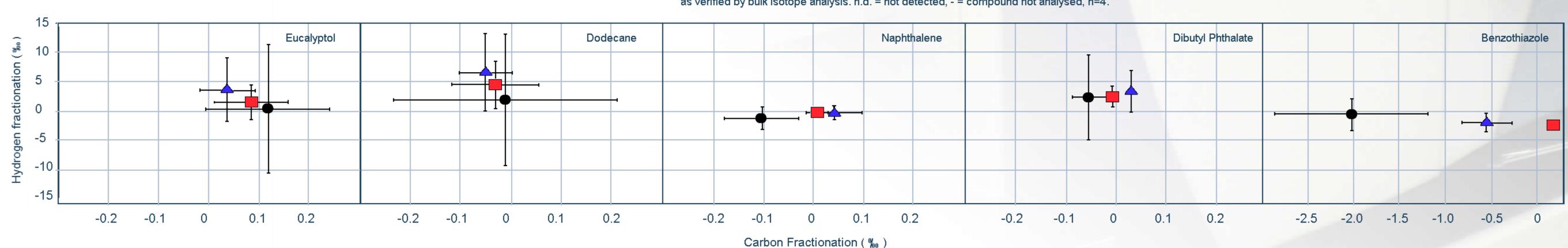


Figure 1. Hydrogen and carbon fractionation (‰) of ACM compounds when eluted with dichloromethane from Strata-X cartridges (circles), ENV+ cartridges (squares) and C18-E cartridges (triangles). Error bars are 1σ, n=3.

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

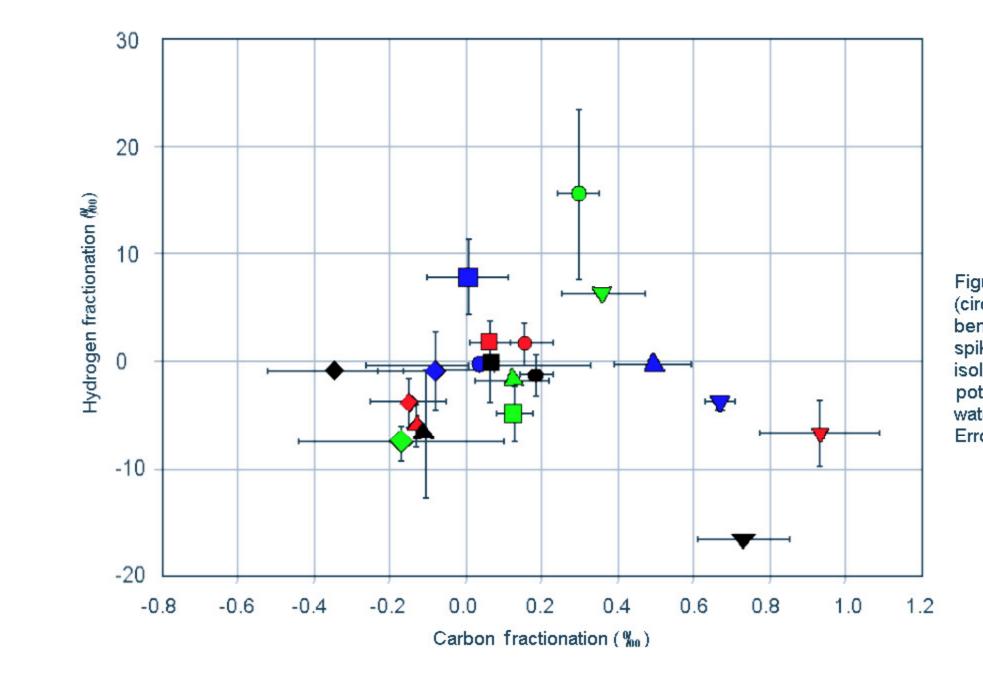
	Eucalyptol (%)	Dodecane (%)	Naphthalaene (%)	Benzothiazole (%)	Dibutyl phthalate (%)	
Potable Water	104 (3)	16 (4)	91 (3)	108 (4)	88 (4)	
River Water	99 (2)	15 (1)	88 (3)	104 (3)	91 (5)	
Sea Water	99 (19)	22 (8)	75 (28)	107 (17)	79 (24)	
Landfill Leachate	69 (18)	24 (5)	59 (16)	80 (20)	69 (14)	

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.



(circles), dodecane (inverted triangle), naphthalene (square), benzothiazole (diamond), and dibutyl phthalate (triangle) when spiked into NaN₃ 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.