

Accessory publication**A method for the simultaneous quantification of 23 C₁–C₉ trace aldehydes and ketones in seawater**

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Calculation of potential contamination or loss of carbonyl compounds

We modelled exchange between a seawater sample and any gas to which it was exposed (a headspace of laboratory or ambient air or ultra-high purity (UHP) argon) as follows:

A constant volume of water (V_W) is in contact with a constant volume of gas (V_G). Initially (time 0), the water contains a certain molar concentration (C_0) of a dissolved carbonyl compound, and the gas contains a certain partial pressure (P_0) of the same compound. The concentration and partial pressure change by ΔC and ΔP respectively, coming to an equilibrium concentration (C_{eq}) and equilibrium partial pressure (P_{eq}), which are related as described by Zhou and Mopper^[1] by

$$K^* = C_{eq}/P_{eq} \text{ (A1)}$$

The temperature-dependence of K^* can be described by

$$\log K^* = A + B/T \text{ (A2)}$$

where A and B are empirically fitted.^[1] We used $T = 21^\circ\text{C}$, the typical temperature in our laboratories. For glyoxal and methylglyoxal no temperature-dependence coefficients have been reported, so K^* for 25°C was used.

For a closed system, any number of moles n of compound lost from the seawater is gained by the gas (or vice versa), thus

$$\Delta n_W = -\Delta n_G \text{ (A3)}$$

Furthermore

$$\Delta n_w = \Delta C V_w \quad (\text{A4})$$

$$\Delta P V_G = \Delta n_G RT \quad (\text{A5})$$

Rearrangement and substitution gives

$$\Delta C = \frac{K^* P_0 - C_0}{\left(\frac{K^* RT V_w}{V_G} + 1 \right)} \quad (\text{A6})$$

from which $C_{eq} = \Delta C + C_0$ is readily calculated.

For a headspace of UHP argon, P_0 was assumed to be zero, and thus the percentage change (loss) in carbonyl compound concentration C in seawater depends only on the ratio of V_w to V_G . Therefore, results for any value of C_0 are shown; the percentage of each carbonyl compound lost to the headspace is independent of this (Table A1). The percentage change in C in seawater when air, containing carbonyl compounds at various mixing ratios, is introduced into the headspace is shown in Table A2.

For the calculations, we used a range of carbonyl compound concentrations in seawater reported in the literature.^[2–6] Carbonyl compound mixing ratios used for air were those reported for the Los Angeles basin by Grosjean et al.^[7] Since these mixing ratios came from a relatively polluted urban environment, we took them to be among the highest in air to which a seawater sample might be exposed. Furthermore, their reported maximum formaldehyde mixing ratio of 10 ppbv^[7] corresponds to the typical level measured in our laboratory air (V. Kanthasamy, McGill University, pers. comm., September 2009).

Table A1. Expected reduction in concentrations of carbonyl compounds in seawater on equilibration with a carbonyl-free headspace (UHP argon)

Compound	Volume (mL)		Percentage change in seawater concentration
	Seawater	Headspace	
Formaldehyde	20	20	0.00
Acetaldehyde	20	20	-0.24
Propanal	20	20	-0.31
Butanal	20	20	-0.44
Pentanal	20	20	-0.65
Hexanal	20	20	-0.94
Heptanal	20	20	-1.44
Octanal	20	20	-2.84
Nonanal	20	20	-8.03
Benzaldehyde	20	20	-0.10
Acetone	20	20	-0.11
Butanone	20	20	-0.21
Glyoxal	20	20	0.00
Methylglyoxal	20	20	0.00
Formaldehyde	20	100	0.00
Acetaldehyde	20	100	-1.21
Propanal	20	100	-1.52
Butanal	20	100	-2.16
Pentanal	20	100	-3.17
Hexanal	20	100	-4.51
Heptanal	20	100	-6.80
Octanal	20	100	-12.7
Nonanal	20	100	-30.4
Benzaldehyde	20	100	-0.51
Acetone	20	100	-0.57
Butanone	20	100	-1.03
Glyoxal	20	100	0.00
Methylglyoxal	20	100	0.00

Table A2. Expected equilibrium concentrations of carbonyl compounds in seawater for various starting concentrations of these compounds in seawater and in air to which it is exposed

Assumptions for initial seawater and air carbonyl concentrations are based on the references listed

Compound	Initial concentration in seawater (nM)	Initial mixing ratio in air (ppbv) ^[7]	Volume (mL)		Equilibrium concentration in seawater (nM)	Percentage change in seawater concentration
			Seawater	Air (headspace)		
Formaldehyde	3.88 ^[6]	10 ^A	20	20	4.3	11
	3.88 ^[6]	10	20	100	6.0	53
	15 ^[2]	10	20	20	10.4	4.1
	15 ^[2]	10	20	100	12.1	21
Acetaldehyde	1.38 ^[6]	8.0 ^A	20	20	1.7	24
	1.38 ^[6]	8.0	20	100	3.0	117
	7.0 ^[8]	8.0	20	20	7.3	4.5
	7.0 ^[8]	8.0	20	100	8.6	22
Acetone	3.0 ^[6]	6.0 ^A	20	20	3.2	8.1
	3.0 ^[6]	6.0	20	100	4.2	41
	17.6 ^[5]	6.0	20	20	17.8	1.3
	17.6 ^[5]	6.0	20	100	18.7	6.5
Glyoxal	0.28 ^[6]	3.8 ^A	20	20	0.44	56
	0.28 ^[6]	3.8	20	100	1.1	280
	5.0 ^[2]	3.8	20	20	5.1	3.5
	5.0 ^[2]	3.8	20	100	5.8	16
Propanal	0.4 ^[6]	0.79	20	20	0.43	7.9
	0.4 ^[6]	0.79	20	100	0.55	39
	2.0 ^[8]	0.79	20	20	2.0	1.3
	2.0 ^[8]	0.79	20	100	2.1	6.5
Methylglyoxal	0.2 ^[6]	2.3 ^A	20	20	0.30	48
	0.2 ^[6]	2.3	20	100	0.68	240
Butanal	0.2 ^[6]	0.71	20	20	0.23	14
	0.2 ^[6]	0.71	20	100	0.34	70
Butanone	0.5 ^B	8.0 ^A	20	20	0.83	66
	0.5	8.0	20	100	2.1	330

Compound	Initial concentration in seawater (nM)	Initial mixing ratio in air (ppbv) ^[7]	Volume (mL)		Equilibrium concentration in seawater (nM)	Percentage change in seawater concentration
			Seawater	Air (headspace)		
Pentanal	0.11 ^[6]	0.41	20	20	0.13	15
	0.11 ^[6]	0.41	20	100	0.19	72
Hexanal	0.05 ^[6]	1.2 ^A	20	20	0.10	98
	0.05 ^[6]	1.2	20	100	0.28	470
Heptanal	0.05 ^[6]	0.64	20	20	0.08	51
	0.05 ^[6]	0.64	20	100	0.17	240
Octanal	0.05 ^[6]	0.53	20	20	0.07	40
	0.05 ^[6]	0.53	20	100	0.14	180
Nonanal	0.09 ^[6]	1.09	20	20	0.12	38
	0.09 ^[6]	1.09	20	100	0.22	140
Benzaldehyde	0.5 ^B	0.6	20	20	0.52	4.9
	0.5	0.6	20	100	0.62	24

^AMaximum mixing ratio reported by Grosjean et al.^[7]; other listed mixing ratios reported by these authors are averages.

^BEstimate.

Fractional factorial experiment to consider factor interactions

A 2^{4-1} half-factorial experiment^[9] was conducted on derivatisation and SPME conditions to evaluate the influence of four parameters simultaneously – SPME fibre type (sorbent), pH, SPME sorption time, and sample volume. The experiment was undertaken to consider the possibility that key factors may interact to influence optimum conditions. Maximum (+) and minimum (–) values for each parameter were:

- Fibre type (A): 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) (+) v. 100 μm polydimethylsiloxane (PDMS) (–)
- pH (B): pH 4.7 (+) v. pH 2.2 (–)
- sorption time (C): 30 min (+) v. 15 min (–)
- sample volume (D): 20 mL (+) v. 10 mL (–)

Each set of conditions was run in duplicate to provide an intrinsic error estimate over the entire experimental domain. The factor table (Table A3) shows that the design allowed for the evaluation of main factor effects and two-factor interactions, but not higher-level factor interactions. Furthermore, two-factor interactions involving sample volume were aliased with other two-factor interactions; this was on the expectation that sample volume would interact negligibly with the other three factors screened, since previous experiments had suggested a minimal effect of sample volume. Results were plotted using Statgraphics Centurion XVI software (StatPoint Technologies, Warrenton, VA).

The experimental space was restricted by certain considerations such as the impracticality of long extraction times and the difficulty of maintaining basic pHs reproducibly. Fig. A1 illustrates the effect of the four simultaneously tested factors (coded (+) and (–); see Table A3), and their interactions, on the peak area response for selected carbonyl PFB oximes (Fig. A1a–e) as well as for the total PFB oxime peak area (Fig. A1f). The effect of factors on peak areas was calculated as the mean difference between the response when the factor was coded (+) v. when it was coded (–),^[9] and is normalised to the standard error due to all factors, calculated from all duplicate measurements (d.f. = 8). Sorption time (C) was always a significant factor, with the 30 min sorption always giving a greater response. For most PFB oximes as well as for the total oxime peak area, the fibre (sorbent) choice (A) and sorption time had the greatest effect on response, with the 65- μm PDMS/DVB fibre giving the greater response, as found previously. However, for C₅–C₉ aliphatic aldehydes (Fig. A1c), the effect of fibre choice did not show up as significant in

this experiment. This suggests that for these oximes, the effect of sorbent choice only becomes important at optimal pH (compare Fig. 1, for which a pH of 3.7 was used). No general trend was evident between the two pH values used, although pH 4.6 gave a greater response than pH 2.2 for a greater number of oximes. As noted previously (Fig. 3), the overall optimal pH lies between these two pHs and the effect of pH appears to be non-linear, and is therefore not well studied through a 2-level factorial experiment. The interaction between fibre choice (A) and pH (B) was rarely significant at pHs of 2.2 or 4.6, except for acetaldehyde, methylglyoxal and 2,4-pentanedione.

Although preliminary experiments suggested that sample volume (D) had little effect, the current experiment found a greater peak area response for a 20-mL sample volume than a 10-mL sample volume for higher molecular-weight (>C₅) aliphatic aldehydes (e.g. Fig. 4c). This indicated that a greater sample volume is preferable, which is also commensurate with minimising the vial headspace. The greater peak area when a 20-mL sample volume was used could be due the loss of higher molecular weight aldehydes to the headspace (Table A1) present with 10 mL of sample.

The experiment aliased two-factor effects which included sample volume with other two-factor effects (e.g. Fig. A1a: AC + BD). However, for any oximes for which sample volume significantly affected peak area response, no two-factor effect including sample volume was found to be significant. Overall, no two-factor interactions were detected which were antagonistic to the main effects, suggesting that our individual optimisation experiments were not missing any optima arising from two-factor interactions.

Table A3. Factor table for half-factorial evaluation of SPME conditions

Sample	Fibre type (A)	pH (B)	Factor or factor combination			Sample volume (D = ABC)	
			Sorption time (C)	Fibre pH AB	Fibre time AC		pH time BC
1	PDMS/DVB (+)	4.6 (+)	30 min (+)	+	+	+	+
2	PDMS/DVB (+)	4.6 (+)	15 min (-)	+	-	-	-
3	PDMS/DVB (+)	2 (-)	30 min (+)	-	+	-	-
4	PDMS/DVB (+)	2 (-)	15 min (-)	-	-	+	+
5	PDMS (-)	4.6 (+)	30 min (+)	-	-	+	-
6	PDMS (-)	4.6 (+)	15 min (-)	-	+	-	+
7	PDMS (-)	2 (-)	30 min (+)	+	+	-	+
8	PDMS (-)	2 (-)	15 min (-)	+	-	+	-

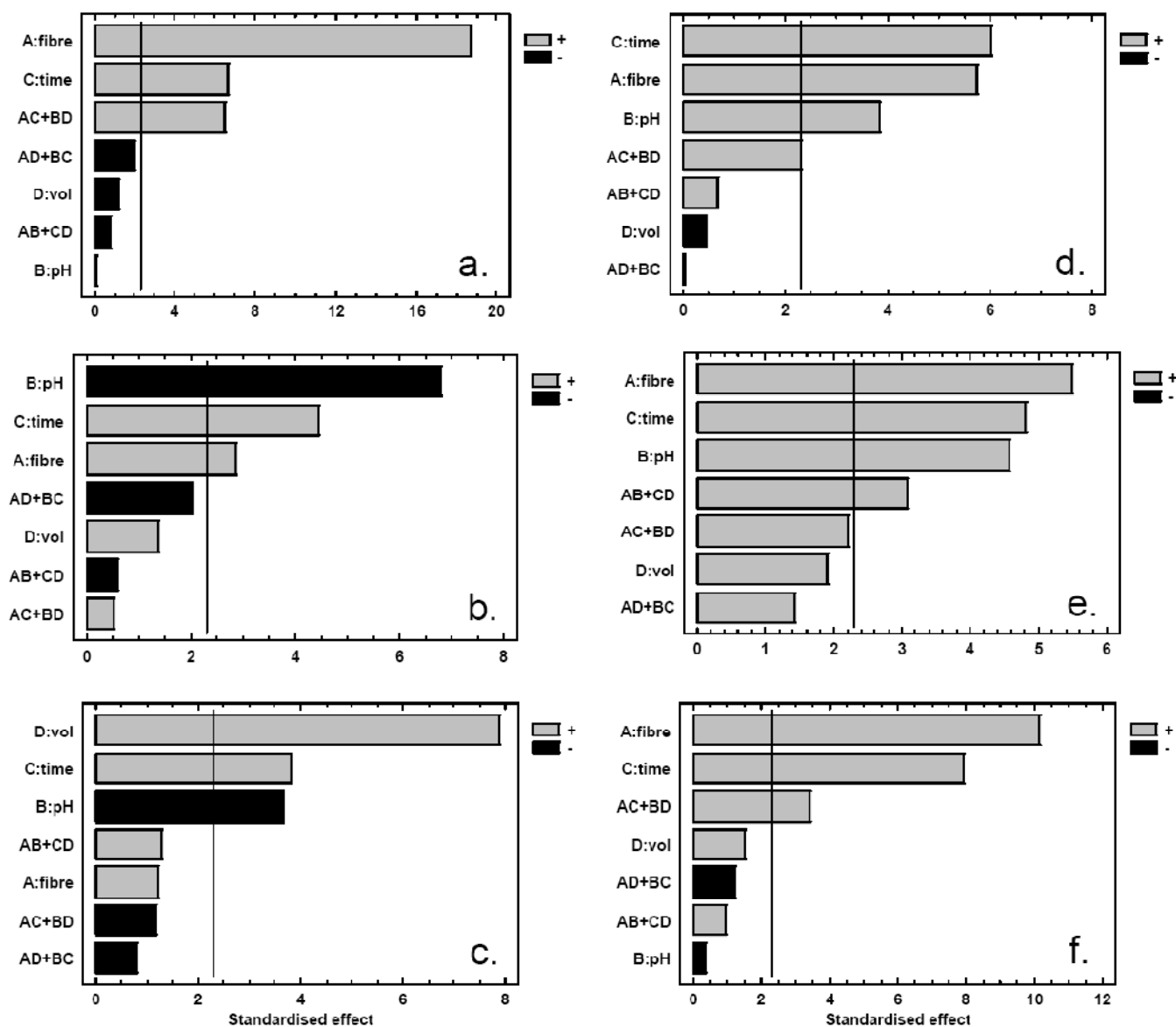


Fig. A1. Pareto plots for four simultaneously tested factors, at 2 levels, affecting peak area response for selected carbonyl PFB oximes: (a) formaldehyde; (b) propanal; (c) hexanal; (d) acetone; (e) methylglyoxal; and (f) total of all PFB oximes. Effect on peak areas is calculated as the mean difference between the response when the factor is coded (+) v. (-) (see also Table 1) and is normalised to the standard error across effects. Vertical lines represent a significant effect at $P < 0.05$.

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