Compound-specific carbon isotope analysis of volatile organic compounds in water using solid-phase microextraction technique[φ]

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Abstract

The compound-specific isotope analysis technique in conjunction with solid-phase microextraction using a Carboxen-polydimethylsiloxane fiber was tested and implemented for isotopes analysis of organic compounds aiming for environmental application in contaminated groundwater. $\delta^{13}C$ values of several chlorinated methanes and ethenes, toluene and chlorobenzene were determined using a gas chromatograph coupled to an isotope ratio mass spectrometer through a combustion interface. Direct and headspace solid-phase microextraction (D-SPME, HS-SPME) methods were tested in order to determine the optimum conditions to obtain reproducible $\delta^{13}C$ values at very low concentration (µg/L range) and, to elucidate the carbon isotopic effects associated with the competitive extraction. For D-SPME higher accuracy and precision of $\delta^{13}C$ results were obtained with no salted aqueous standards. Despite that the $\delta^{13}C$ of those compounds analyzed with both methods showed similar precision (< 0.5 ‰) and accuracy, the highest sensitivity was reached with HS-SPME. Furthermore, the $\delta^{13}C$ values of *cis*-1,2-dichloroethylene, chorinated methanes and aromatic compounds obtained using HS-SPME showed measurable deviations respect to the isotopic composition of pure phase compounds, however, these deviations are constant according to the analytical uncertainties, indicating that they are not affected by competitive extraction and, they could be corrected using standard correction technique based on internal calibrated standards.

Keywords: competitive extraction, organic contaminants, environmental isotopes, groundwater

1. Introduction

Volatile organic compounds (VOCs) are common contaminants found in groundwater. They are currently used in a wide variety of industries as degreasers, solvents or chemical intermediates, and are also part of gasoline and fuels. This study focussed on chlorinated methanes [dichloromethane (DCM), chloroform (CF), carbon tetrachloride (CT)], chlorinated ethenes [1,1-dichloroethylene (1,1-DCE), *cis*-1,2-dichloroethylene (cis-DCE), trichloroethylene (TCE), tetrachloroethylene (PCE)], toluene and chlorobenzene (MCB) (Table 1). All of them have a high toxicity, and the permissible level for drinking water ranges between 1 mg/L and 2 µg/L [1,2].

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These low limits require very sensitive analytical techniques for environmental studies in groundwater. Carbon isotope analysis by compound-specific isotope analysis (CSIA) using gas chromatography coupled to isotope ratio mass spectrometry through a combustion interface (GC-C-IRMS) has become a promising tool to trace the origin of VOCs, and for assessing degradation processes that control the fate of these compounds in groundwater [3,4]. Using headspace analysis, water samples with dissolved organic contaminants at concentrations of hundreds of μg/L are necessary to obtain reproducible $\delta^{13}C$ values [5-8]. In order to reach a lower limit of quantification, in the tens of μg/L range, Morrill et al. [9] use a dynamic headspace method. However, lowest method detection limits are achieved using pre-concentration methods like solid-phase microextraction (SPME) [6,7,10,11] and purge and trap [7,12,13] techniques.

(----------Table 1----------)

SPME was created and developed by Pawliszyn and coworkers [14,15]. Some advantages are: fast extraction, solvent free, easy to use, simply mechanism, portable and low cost. Another important feature is that it can be used to extract organic compounds from solid, liquid and gas matrices. This method uses a fine silica fiber coated with a thin layer of a selective coating to extract analytes by absorption or adsorption, directly from aqueous samples. The extraction can be done with the fiber immersed in the solution (direct SPME, D-SPME) or exposed to the headspace (HS-SPME). After the extraction, the fiber is placed in the injector of the GC and the compounds are thermally desorbed. The first coating developed was a liquid polymer of high viscosity, polydimethylsiloxane (PDMS) [16,17]. The extraction mechanism of this coating is the absorption. Nowadays, several coatings are available in order to improve the extraction efficiency. These coatings are made specifically to improve the extraction depending on the properties of the target compounds. For VOCs dissolved in water, the Carboxen (CAR)-PDMS coating has demonstrated higher extraction efficiency, in comparison with other coatings [18,19]. The main extraction mechanism of porous coatings is the adsorption, in contrast to the PDMS coating, and the amount of analyte extracted can be calculated using Langmuir isotherm equation [20]. Nevertheless, we cannot apply this equation to Carboxen-PDMS fibers, because the adsorption of the analytes on the Carboxen particles is not the only extraction mechanism. During the exposition of the fiber to the sample, the analytes also condense filling the microporosity. The capillary condensation gives to this coating an extra capacity of extraction, but takes a long time to reach the equilibrium. In HS-SPME of tetraethyllead from water, the amount extracted increased with increased extraction time even after 48 h [20]. A difficult for the use of this fiber is the low linearity observed at the calibration curves, in comparison with absorption fibers (i.e. PDMS). This low linearity is caused by the limited adsorption sites of the coating and the competition between the analytes [20]. Black and Fine [21] show that concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX), higher than 1 mg/L, hinder the quantification of methyl *tert*-butyl ether (MTBE) due to competition. Zwank et al. [7] studied the effect of competitive sorption of BTEX and MTBE by D-SPME, on the isotopic signature of MTBE, and found a fractionation of -1 ‰, with regard to the expected value, for BTEX concentrations ≥ 10 mg/L.

The goals of this study are to elucidate the carbon isotopic effects associated with the extraction of commonly found organic compounds by CAR-PDMS fibers from contaminated water samples and to determine the optimum conditions to obtain reproducible $\delta^{13}C$ values at very low concentration (μg/L range). There has been to our knowledge no systematic study about the fractionation effect associated to HS-SPME of VOCs, in multi-component aqueous standards, during compound specific carbon isotope analysis using the CAR-PDMS fiber. Microbial degradation produces carbon isotope fractionation of these compounds and an accumulation of ^{13}C in the remaining compound and an enrichment of ^{12}C in the degradation product are observed. High precision of

$\delta^{13}C$ values is necessary to assess accurately biodegradation of organic compounds using the stable carbon isotope approach. In aquifers contaminated with organic compounds, under specific range of redox conditions, biodegradation can be the most significant natural attenuation process.

2. Experimental

2.1. Material and methods

The isotopic analyses were performed in the laboratories of the *Serveis Cientificotècnics*, University of Barcelona, Barcelona, Spain. DCM, CF and toluene were obtained from Merck (Darmstadt, Germany); 1,1-DCE, cis-DCE, TCE, PCE and MCB from Aldrich (Milwaukee, WI, USA), and CT from Riedel-de Haën (Seelze, Germany). For the preparation of internal standards, the ^{13}C composition of pure phase of each compound was determined using an elemental analysis system coupled to IRMS (EA-IRMS). Volumes of 1 μL for toluene and MCB, and 2 μL for chlorinated methanes and ethenes were inserted into the EA-IRMS system using tin capsules for liquids. Subsequently, some repetitions were done with direct liquid injection and the results obtained were the same in the range of analytical uncertainty, confirming the results obtained with tin capsules.

Standard stock solutions of multi-component mixtures were prepared by dissolution of pure phase compounds in HPLC-grade methanol. For D-SPME tests, multi-component standard solutions were prepared dissolving a standard stock solution of PCE, TCE and cis-DCE, at the same concentration, in ultra pure water (Milli-Q) with a final volume of 100 mL. This method was also tested with salted standards. In this case, the standards were prepared in a 5 M NaCl solution. In both tests, aqueous standards of 50, 100 and 200 μg/L were used. The standard solutions for the HS-SPME tests were prepared using two different standard stock solutions, P10 and P10-C. Both contained all the compounds studied, however, in P10 these were dissolved at the same concentration and in P10-C, the concentrations were modified in order to obtain similar signal intensities in mass m/z 44 in the IRMS chromatogram. The final volume used was the same that in D-SPME. For D-SPME and HS-SPME, 100 mL glass vials with open screw cups and PTFE-coated silicone septums, were filled with the prepared solutions. A volume of 15.6 mL remained empty to avoid contact of the needle holding the SPME fiber with the aqueous phase. This volume was also used as a headspace for HS-SPME. Before the analysis, a 30 mm long PTFE-coated stir bar was added and during the extraction, the solution was stirred at 500 rpm, for D-SPME, and at 1100 rpm for HS-SPME.

Two manual sampler holders equipped with 75 μm CAR-PDMS fibers (Supelco, Bellefonte, PA, USA) were used to optimize the time of the process. Before the first use, each fiber was conditioned in the injector of the GC for 1 h at 300 ºC and, every time before to start the extractions they were placed in the injector for 45 min at 270 ºC. For D-SPME, extraction times of 25 and 40 min and desorption times of 5 and 25 min were used to compare the extraction efficiency. In case of HS-SPME, extraction and desorption times of 25 min were used.

2.2. Instrumentation

A Flash EA1112 elemental analyzer coupled to a Delta C isotope ratio mass spectrometer through a Conflo III interface (ThermoFinnigan, Bremen, Germany) was used for ^{13}C determination of pure phase compounds. The combustion and reduction furnaces temperature was 900º C and 680º C, respectively. The column was kept at 45º C. The GC-C-IRMS system consisted of an Agilent 6890 gas chromatograph (Palo Alto, CA, USA) equipped with a splitless injector, coupled to a Delta Plus isotope ratio mass spectrometer through a GC-Combustion III interface

(ThermoFinnigan). Helium was used as a carrier gas. Two fused-silica columns were used for separation. For D-SPME tests, the GC system was equipped with a BP-624 column (30 m × 0.32 mm, 1.8 μm stationary phase; SGE, Kiln Farm Milton Keynes, UK) and, for HS-SPME tests, the column used was a SPB-624 (60 m × 0.32 mm, 1.8 μm stationary phase; Supelco). The 30 m long column (column A) was changed because the standard solution analyzed with HS-SPME contained more analytes and partial overlaps were observed between cis-DCE, CF and CT. These compounds have a similar retention time and a 60 m long column (column B) was necessary to obtain a good baseline separation. For column A, the oven temperature program was kept at 35º C for 2 min, heated to 220º C at a rate of 8º C/min and finally held at 220º C for 2 min. The injector temperature was 270º C and the injection was in splitless mode (keeping the splitless valve closed for 0.7 min). For the second column used, column B, the oven temperature program was: 60º C (5 min) to 200º C (5 min) at a rate of 8º C/min. The injector was 270º C and the injection was in the split mode (split ratio of 5:1). The temperatures in the GC-C interface were 940º C and 600º C for the combustion and reduction furnaces respectively.

3. Results and discussion

3.1 *Determination of carbon isotope ratios of pure phase compounds*

The $^{13}C/^{12}C$ ratios are reported in the usual delta notation, $\delta^{13}C$, defined as $\delta^{13}C=((R_s/R_r)-1) \times 1000$ (‰) where R_s and R_r are the $^{13}C/^{12}C$ ratios of the sample and the international standard, respectively. $\delta^{13}C$ values of pure phase compounds obtained with EA-IRMS (Table 2), were corrected using three international standards (USGS 24, IAEA-CH-6 and IAEA-CH-7) [22] calibrated respect to the Vienna PeeDee Belemnite (VPDB) standard. This correction was obtained using a linear regression derived from the $\delta^{13}C$ determination of these reference materials, measured with the same instrumental settings.

In order to optimize the determination of the carbon isotope ratios of organic compounds with GC-C-IRMS, two extraction methods were tested, D-SPME and HS-SPME.

(----------Table 2----------)

3.2 *CSIA of multi-component aqueous standards by D-SPME*

Previous studies using the absorption fiber (100 μm PDMS) [6] and the same adsorption fiber used in this study [7] employed the fiber immersed method in salted solutions to enhance the sensitivity. Therefore, the first experiments in the present study were done with salted solutions. Relative high differences of signal intensities, in duplicate tests, were observed with a desorption time of 5 min (data not shown). For this reason, different desorption times were tested obtaining higher and better constrained intensities using a 25 min desorption time. Using an aqueous standard of 100 μg/L, average intensities below 150 mV and up to 300 mV were obtained for all the compounds with desorption times of 5 and 25 min respectively. Together with the analytes, an important amount of water is also extracted by the fiber [20]. Due to the lower volatility of the water, in comparison with the studied compounds, the fiber probably needs more than 5 min to dry completely in order to recover the total extraction capacity. Different extraction times, of 25 and 40 min, were also tested with aqueous standards, without salt, and concentrations of 25 and 50 μg/L. The signal intensity increased with the extraction time however, the relative average increase was higher for the standard of 25 μg/L. For this standard, a relative average increase of 122 ± 42 %, 144 ± 41 % and 141 % ± 38 % for cis-DCE, TCE and PCE respectively, was observed using 40 min extraction time in comparison with the average signal intensity obtained with 25 min extraction time. This increase

was probably related with the capillar condensation of the analytes. In agreement with results showed in previous studies [7], no significant isotope fractionation was observed comparing the $\delta^{13}C$ values of the pure standards with the values obtained with different extraction times.

Higher accuracy, based on the comparison with $\delta^{13}C$ values of pure phase compounds, and reproducibility of $\delta^{13}C$ values, were obtained with the aqueous standard solutions without salt (Fig. 1). No differences were observed for 25 and 40 minutes extraction times. Moreover, a significant average increase of intensity was detected for PCE and TCE, and less for cis-DCE (Fig. 1). The lower signal intensity for the salted solution is probably related to the fact that the salt ions were also adsorbed on the coating, limiting the adsorption sites available.

(---------Fig. 1----------)

3.3 *CSIA of multi-component aqueous standards by HS-SPME*

The HS-SPME method is more selective for volatile compounds than D-SPME, since the less or non volatile compounds remain in solution. Even though the amount of high volatile compounds in equilibrium in the headspace is lower than in the solution, their relative concentration is higher. Furthermore, fewer compounds compete for the adsorption sites of the coating. This selectivity enhances the extraction efficiency of VOCs in the case of complex aqueous samples with an important fraction of semi-volatile or non volatile organic compounds.

(---------Fig. 2----------)

Higher sensitivity was obtained with this method in comparison with D-SPME (Table 2), in spite of the tests of HS-SPME were done with a standard with more analytes than the used with D-SPME. The difference of sensitivity detected between these methods probably would be higher if the same standard had been used. Nevertheless, high variations of the amount of analyte extracted were observed for different compounds at the same initial concentration. Moreover, the calibration curves also exhibit very different linearity (Fig. 2). In this figure, the initial amount of each compound in the aqueous standard was expressed as nmol of carbon due to, at the same concentration, the compounds with more C also produce more CO_2 and the signal intensity in the IRMS chromatogram is higher than the signal intensity of the compounds with less C in their molecules. To obtain these calibration curves, several standards of different concentration were analyzed. These standards were prepared dissolving in deionized water the standard stock solution P10-C (Fig. 3). Then, the increase in the concentration of one compound in the standard, implies that the concentration of the rest of compounds also increase proportionally. Figure 2 shows that for chlorinated ethenes (Fig. 2a) and methanes (Fig. 2b), less chlorinated compounds exhibit lower sensitivity than high chlorinated compounds. At the same time in each group, except for 1,1-DCE, the signal intensity increase with the increase of Henry's constant (K_H) (Table 1). This relation is also valid for the selected aromatic compounds (Fig. 2c). Cho et al., [18] studied several factors that could affect analyte selectivity of CAR-PDMS fiber during HS-SPME. These authors observed that the peak area increases with the increase of the molecular weight and with the decrease of the vapour pressure (P^0). Black and Fine [21] also investigated the effect of the competition for the adsorption sites during the quantification of MTBE and *tert*-butyl alcohol (tBA), with the same fiber in aqueous mixtures containing BTEX and trimethylbenzenes (TMBs). They explained the decrease in MTBE and tBA as replacement of polar compounds by less polar compounds. In this study, the sensitivity of chlorinated ethenes (Fig. 2a) and methanes (Fig. 2b) also increase with the increase of molecular weight and, except for 1,1-DCE, with the decrease of P^0 (Table 1). Even though 1,1-DCE has the highest K_H of the studied ethenes, also has the highest

P^0 which difficult its adsorption on the fiber. In both groups, the differences of sensitivity also could be explained by differences in compound polarity. The signal intensity increases with the decrease of polarity (Table 1), as Black and Fine [21] indicated. For the selected aromatic compounds (Fig. 2c), the higher sensitivity of toluene only can be explained by K_H and polarity factors. If we compare the calibration curves between compounds of different groups, the analyte selectivity of the fiber still can be explained, except for 1,1-DCE and CT, by K_H. For the low sensitivity compounds (MCB, 1,1-DCE, cis-DCE, CT, CF and DCM) these relation is valid from a minimum amount of carbon in the aqueous standard of approximately 100 nmol. In this case, the relation with the other factors is not clear. However, the compounds which showed the calibration curves with highest linearity (PCE, TCE, toluene and MCB) are the compounds with lowest P^0.

(---------Fig.3----------)

To test if the competition process produces an isotopic effect on C isotopes, aqueous standard solutions of selected compounds at different concentration were prepared with the standard stock solutions P10 and P10-C (Fig. 3). When an analyte has the same concentration in two aqueous standard solutions, one prepared with the stock solution P10 and the other with P10-C, the total concentration of VOCs in each standard will be different. The calibration curves of PCE and TCE (Fig. 4) did not show significant differences, despite the reduction of their molar fraction and the increase of VOCs concentration, in 147.0 %, in the standards P10-C compared to P10. This fact indicates that these compounds have a high affinity to the fiber. For the compounds with lower linearity, 1,1-DCE and cis-DCE, an average increase of the signal intensity was observed in the aqueous standards prepared with P10-C (Fig. 4), although it was in the range of analytical uncertainty. This increase only can be explained for the molar fraction reduction, in the standards P10-C, of those analytes with higher affinity. Chlorinated methanes, CT and CF, showed a significant increase of sensitivity with the aqueous standards prepared with P10-C (Fig. 5). For both compounds this increase was related to the increase of their molar fraction and the reduction of VOCs concentration in 50.6 % in these standards in comparison to P10. For the selected aromatic compounds, MCB showed a similar sensitivity for both standards despite the reduction of its molar fraction, and the increase of VOCs concentration in the standards P10-C (Fig. 5). Just as PCE or TCE, this compound also has a high affinity to the fiber. Finally, toluene showed lower linearity with the aqueous standards prepared with P10-C, for concentrations higher than 5 μg/L, because in these standards the VOCs concentration was much higher, 12.3 times, than in the standards P10 (Fig. 5). This low linearity probably indicates the saturation of the fiber. This comparison was not possible for DCM, since was not detected in the aqueous standards prepared with P10, for the range of concentration used in the tests. Regardless of the standard differences and, consequent observed signal intensity variations of several compounds due to the competition for the adsorption sites and fiber saturation, the $\delta^{13}C$ values for PCE, TCE, cis-DCE and 1,1-DCE analyzed in the aqueous standard solutions are in a good agreement, generally within ± 0.7 ‰, with the values obtained in the pure compounds (Fig. 4). The rest of the compounds showed a tendency toward depleted $\delta^{13}C$ values compared to the values of the pure compounds (Fig. 5).

(---------Fig.4----------)
(---------Fig.5----------)

The optimum intensity range to obtain accurate $\delta^{13}C$ value was evaluated analyzing several aqueous standards at different concentration prepared dissolving the standard stock solution P10-C in deionized water. The optimum intensity range was selected in order to obtain the highest reproducibility and the necessary concentrations to reach this intensity range are indicated on table 2. Both ranges are compound specific. A new cathode in the IRMS system was used in these tests.

The precision obtained was below 0.5 ‰, except for chlorinated methanes that was ≤ 0.7 ‰. All the compounds with high linearity (PCE, TCE, toluene and MCB) also have a high precision, below 0.5 ‰. Concerning accuracy, in relation to the EA-IRMS values, CT and CF exhibit the highest deviations (Table 2). This fractionation can be corrected because it was approximately constant in the selected intensity range, was not affected by competitive extraction and high precision of the isotope composition of the extracted compounds from the aqueous standards and pure phase compounds was reached. The results obtained validated the use of CAR-PDMS coating for CSIA, of the selected compounds in multi-component aqueous samples in the low concentration range observed in contaminated groundwater. However, further research is necessary to improve the results of chlorinated methanes.

(---------Fig 6.----------)

In order to relate the isotope deviation of each compound with the factors that control the extraction efficiency, the deviations are represented versus K_H/P^0 ($L \cdot mol^{-1}$) ratio (Fig. 6). The deviation was expressed as $\Delta\delta^{13}C_{f0} = \delta^{13}C_f - \delta^{13}C_0$, where $\delta^{13}C_f$ and $\delta^{13}C_0$ were the isotope composition of the extracted compound from the aqueous standard and pure phase compound, respectively. This figure shows that for ethenes and aromatic compounds, in each group the fractionation decrease with the increase of K_H/P^0 ratio. This relation was not observed for methanes. This fact means that the factors that control the extraction efficiency, also probably control the isotope fractionation between the compound in the aqueous solution, and the compound extracted by the fiber.

4. Conclusion

CAR-PDMS SPME fibers are a sensitive preconcentration method for CSIA of water samples contaminated with VOCs at very low concentration (μg/L range). The tests using the D-SPME method showed higher accuracy and precision of $\delta^{13}C$ results with no salted aqueous standards and with a desorption time of 25 min. Higher sensitivity was reached using HS-SPME, obtaining reproducible results from 10 to 20 μg /L for chlorinated ethenes, from 50 to 125 μg /L for chlorinated methanes and, from 4 to 10 μg /L for aromatic compounds. For both extraction techniques, D-SPME and HS-SPME, a precision below 0.5 ‰ was reached for all studied compounds, except for chlorinated methanes which was below 0.7 ‰ with HS-SPME. $\delta^{13}C$ values of chlorinated ethenes determined using D-SPME and PCE, TCE and 1,1-DCE using HS-SPME method, did not show a significant isotope fractionation comparing the results with the $\delta^{13}C$ values of the pure standards. Furthermore, an appreciable deviation was observed for cis-DCE, chorinated methanes and aromatic compounds using HS-SPME. However, these deviations are constant according to the analytical uncertainties in the selected intensity range, indicating that they are not affected by competitive extraction and, they could be corrected using standard correction techniques based on calibrated internal standards.

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Figures

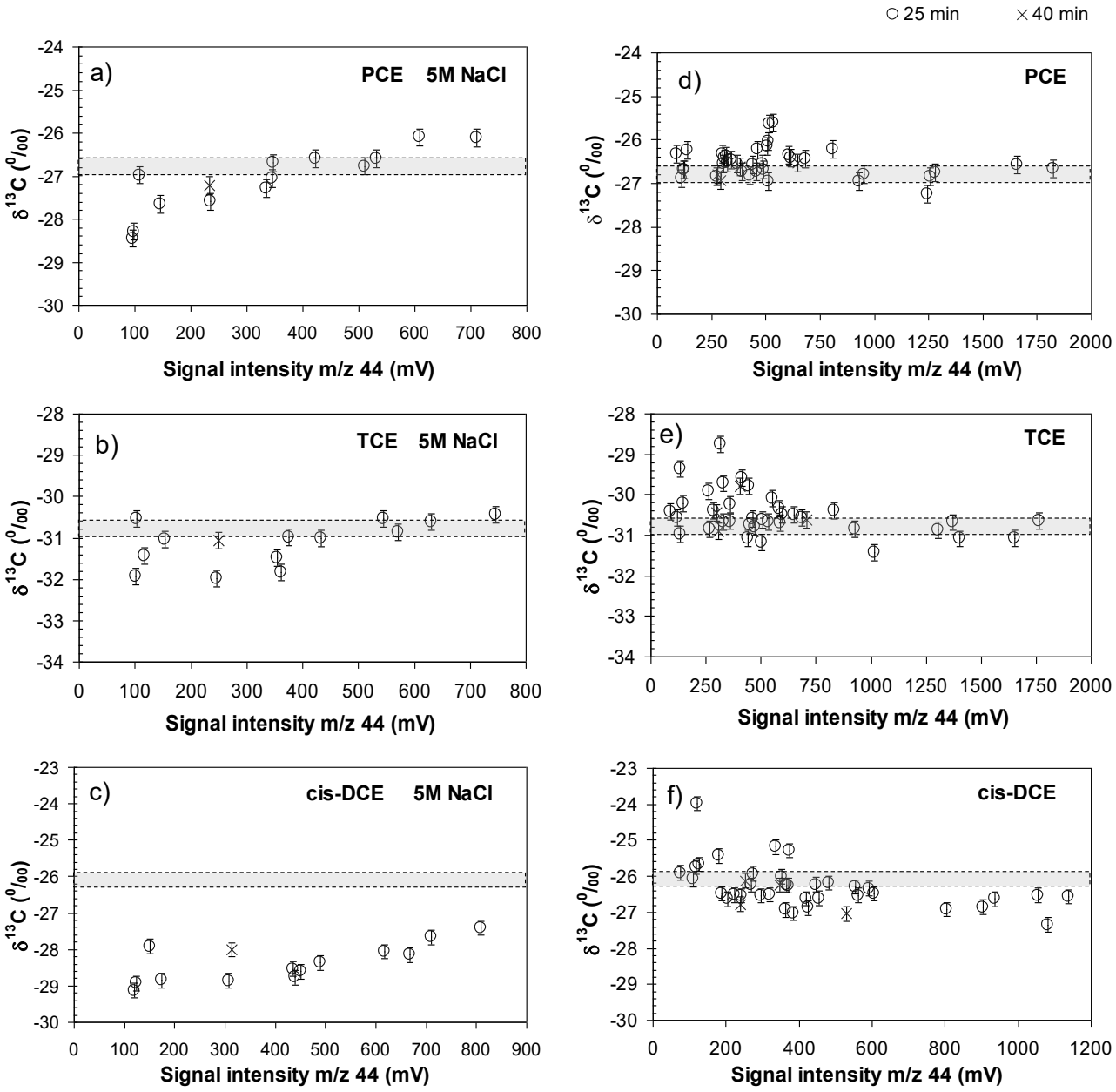


Fig. 1. $\delta^{13}C$ values for aqueous standard solution of PCE, TCE and cis-DCE, salted (a-c) and without salt (d-f), for different signal intensities (m/z 44) and adsorption times of 25 and 40 min. The analyses were performed using the GC column A. The error bars correspond to a ± 0.2 ‰. The horizontal bar corresponds to the isotopic signature (± 0.2 ‰) of the pure phase compound analyzed with the EA-IRMS.

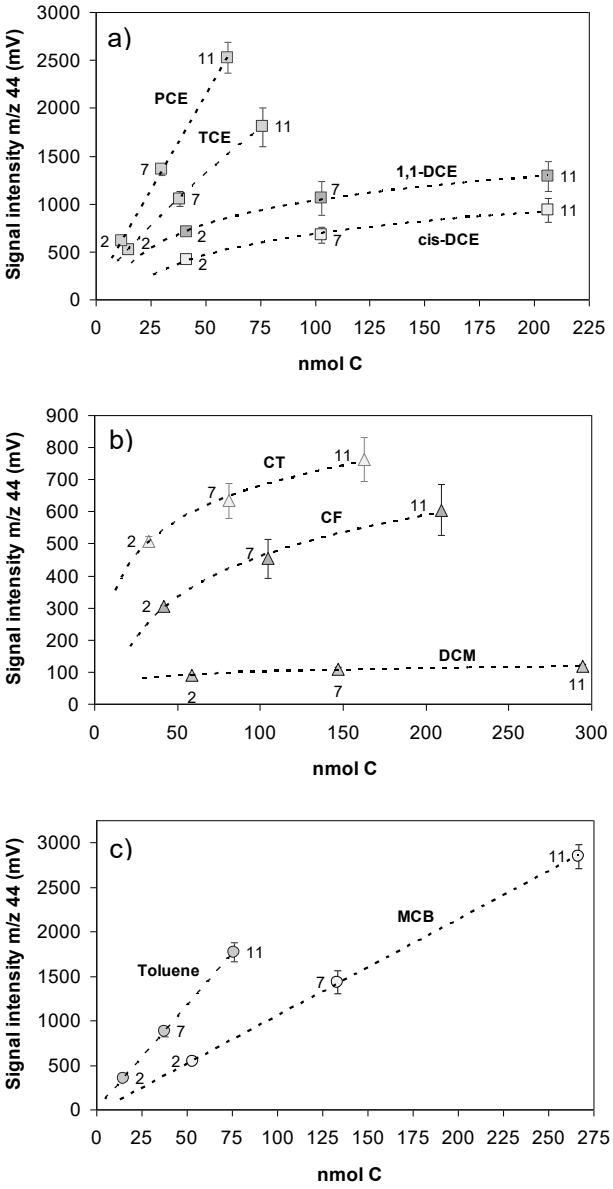
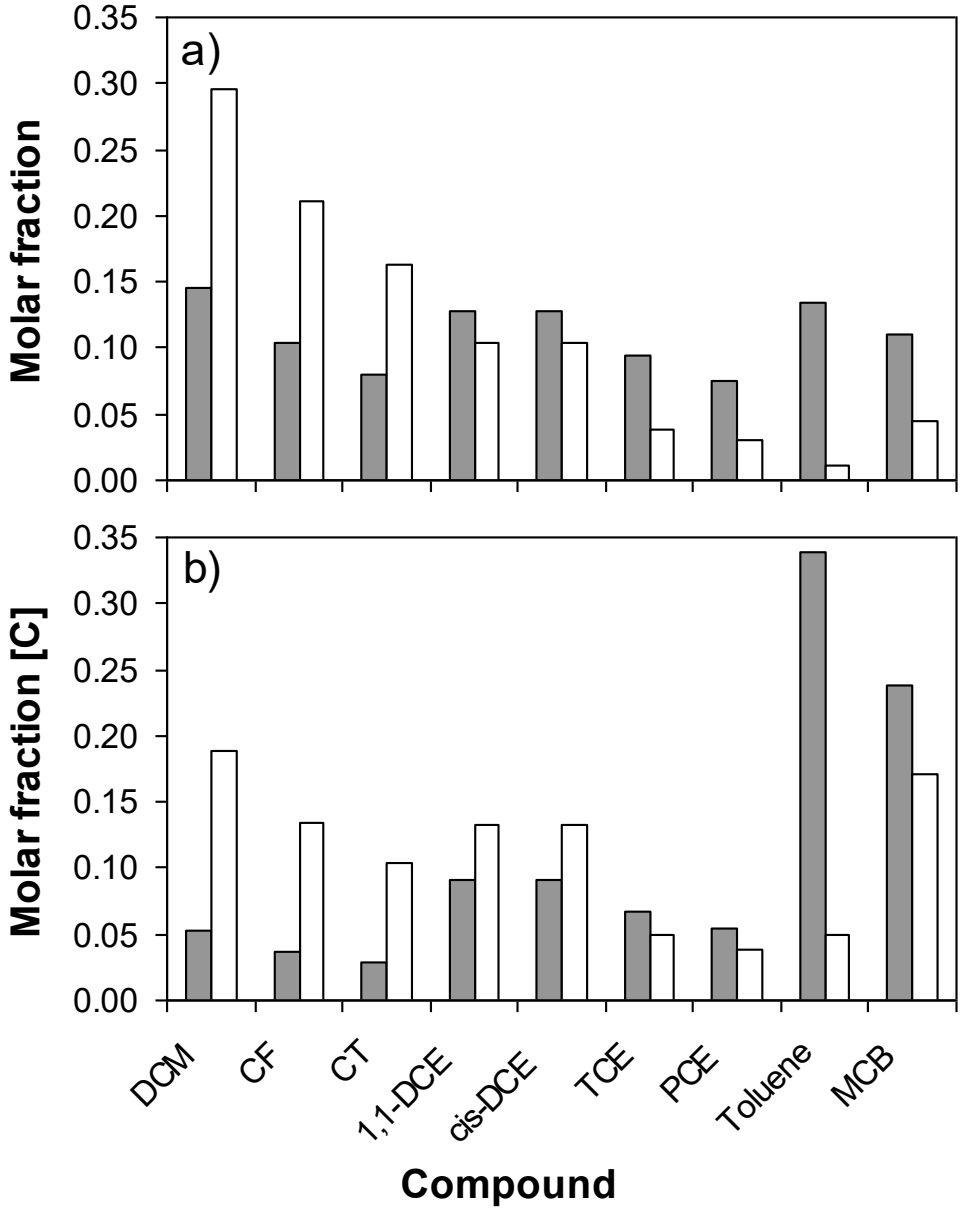


Fig. 2. Calibration curves of aqueous standard solutions prepared with the standard stock solution P10-C and analyzed with the GC column B and new cathode. (a), (b) and (c) show the calibration curves of chlorinated ethenes, chlorinated methanes and aromatic compounds respectively. The error bars correspond to the standard deviation for a number of repetitions indicated next to the symbol.



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415 **Fig 3.** (a) Molar fraction and (b) carbon molar fraction of each compound in the standards prepared
416 with the stock solutions P10, grey columns, and P10-C, white columns.
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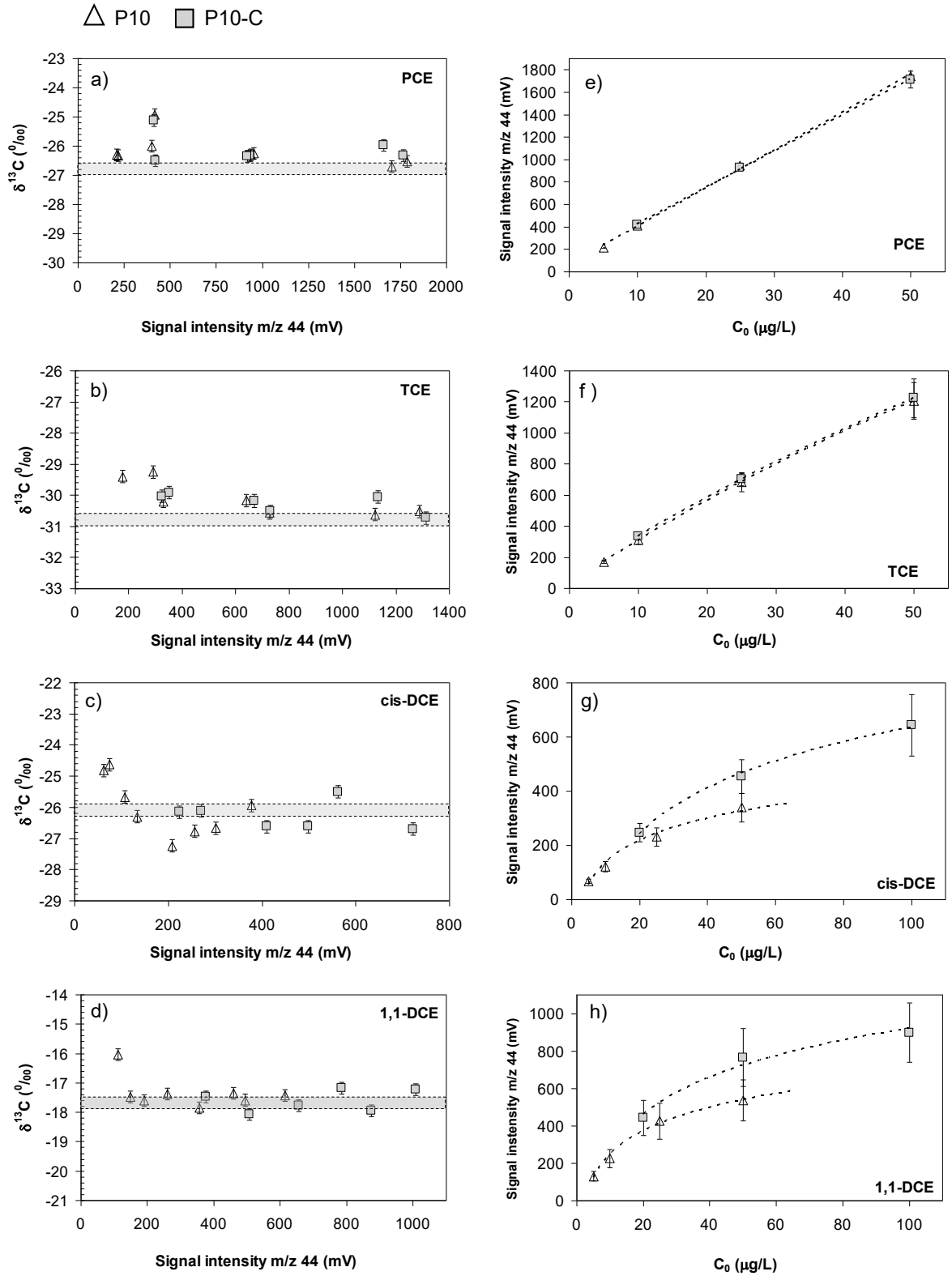

Fig. 4. (a-d) $\delta^{13}C$ of PCE, TCE, cis-DCE and 1,1-DCE respectively, in two aqueous standard solutions prepared with the standard stock solutions P10 and P10-C, for different signal intensities (m/z 44). The horizontal bar corresponds to the isotopic signature (± 0.2 ‰) of the pure phase compound analyzed with the EA-IRMS. (e-h) show the calibration curves of these compounds in the same standards. The analyses were performed using the GC column B.

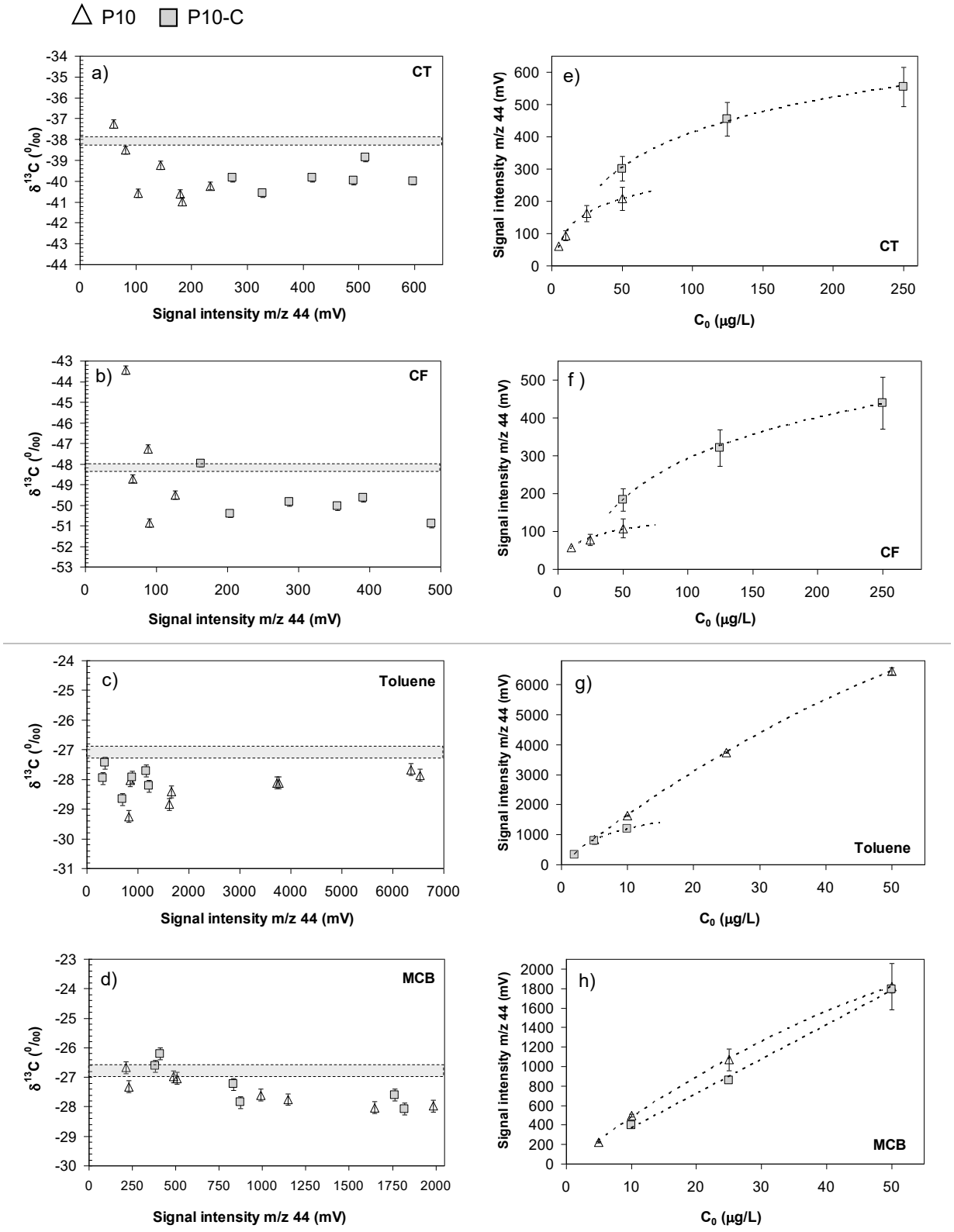

Fig. 5. (a-d) $\delta^{13}C$ of CT, CF, toluene and MCB respectively, in two aqueous standard solutions prepared with the standard stock solutions P10 and P10-C, for different signal intensities (m/z 44). The horizontal bar corresponds to the isotopic signature (± 0.2 ‰) of the pure phase compound analyzed with the EA-IRMS. (e-h) show the calibration curves of these compounds in the same standards. The analyses were performed using the GC column B.

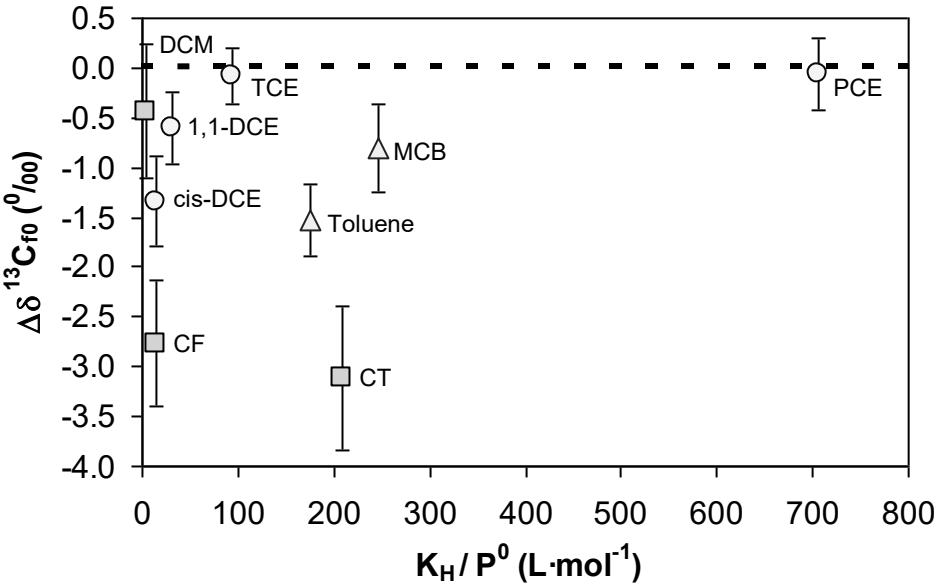

Fig. 6. Isotopic deviation versus K_H/P^0 (L mol^{-1}) ratio. The dashed line indicates no deviation respect to the isotopic signature of the pure phase compound.

Tables

Table 1. Physical and chemical properties determined at 25º C except the polarity.

Compound	Molecular weight (g/mol)	Polarity, $\varepsilon_r/\varepsilon_{r\,w}$ [f,b]	P^0 (kPa) [d]	K_H (kPa L mol^{-1}) [e]
DCM	84.9	0.11 (24.9º C)	55.3 [a]	215 [a]
CF	119.4	0.06 (20.1º C)	25.9 [a]	363 [a]
CT	153.8	0.03 (20.1º C)	14.5 [a]	3019 [a]
1,1-DCE	97.0	0.06 (20.1º C)	80.4 [a]	2584 [a]
cis-DCE	97.0	0.11 (25.1º C)	27.3 [a]	379 [a]
TCE	131.4	0.04 (28.4º C)	10.0 [a]	949 [a]
PCE	165.8	0.03 (30.1º C)	2.5 [a]	1763 [a]
Toluene	92.1	0.03 (23.2º C)	3.9 [c]	685 [c]
MCB	112.6	0.07 (20.1º C)	1.6 [a]	395 [a]

[a] Pankow and Cherry [23]. [b] CRC [24]. [c] Schwarzenbach et al., [25]. [d] Vapour pressure. [e] Henry's constant. [f] Relative dielectric constant at indicated temperature in relation to the water dielectric constant at 20.1º C = 80.1

Table 2. $\delta^{13}C$ for the optimum intensity (m/z 44) range together with the isotopic signature of the pure phase compounds.

Compound	EA-IRMS		dSPME / GC-C-IRMS				hSPME / GC-C-IRMS			
	$\delta^{13}C$ (‰)	n	Optimum concentration range (μg/ L)	Optimum intensity range (mV)	$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰) 5M NaCl (n=13) [a]	Optimum concentration range (μg/ L)	Optimum intensity range (mV)	$\delta^{13}C$ (‰)	n
PCE	-26.8 ± 0.2	10	100 - 200	550 - 1825	-26.6 ± 0.3 (n=14)	-27.1 ± 0.7	10 - 50	597 - 2855	-26.9 ± 0.3	29
TCE	-30.8 ± 0.2	11	100 - 200	450 - 1764	-30.7 ± 0.3 (n=21)	-31.1 ± 0.6	10 - 50	512 - 2239	-30.9 ± 0.2	23
cis-DCE	-26.1 ± 0.2	10	50 - 200	185 - 1137	-26.3 ± 0.4 (n=34)	-28.4 ± 0.5	20 - 100	406 - 1266	-27.4 ± 0.4	29
1,1-DCE	-17.7 ± 0.2	8	nd	nd	nd	nd	20 - 100	689 - 1587	-18.3 ± 0.3	29
CT	-38.1 ± 0.2	10	nd	nd	nd	nd	50 - 250	496 - 925	-41.2 ± 0.7	29
CF	-48.2 ± 0.2	10	nd	nd	nd	nd	100 - 250	324 - 782	-51.0 ± 0.6	27
DCM	-40.0 ± 0.3	12	nd	nd	nd	nd	125 - 250	107 -132	-40.4 ± 0.6	19
Toluene	-27.1 ± 0.2	10	nd	nd	nd	nd	4 - 10	693 - 1965	-28.6 ± 0.3	27
MCB	-26.8 ± 0.2	9	nd	nd	nd	nd	10 - 50	533 - 3152	-27.6 ± 0.4	29

[a] For salted aqueous standards the optimum intensity and concentration ranges were not determined. nd. No determined.