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Trace-level determination of 1,4-dioxane in water by isotopic dilution GC and GC-MS

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The volatile and polar solvent 1,4-dioxane has recently been reported as a contaminant of ground and surface waters, establishing the need to determine this substance in drinking water. This investigation established that 1,4-dioxane can be determined in water by various techniques including direct aqueous injection (DAI) gas chromatography (GC) and purge and trap GC–mass spectrometry (MS). Purge and trap GC-MS is limited by 1,4-dioxane's poor purge efficiency, resulting in detection limits up to 100 times greater than the efficiently purged volatile organic compounds. To attain the sensitivity required for drinking water monitoring, a method based on continuous liquid–liquid extraction with dichloromethane was developed. Isotope dilution was more accurate and reproducible than quantification with external standards, and the improvement in precision led to a lower method detection limit, 0.2 μg L^{-1}, using a quadrupole ion trap instrument in the electron ionization mode. Isotope dilution accuracy approached 100% in ppb determinations. Isotopic dilution quantification was also possible using a non-selective GC detector owing to the high efficiency of capillary GC columns that resolve the deuterium-labeled solvent from the natural isotopes.

Introduction

1,4-Dioxane is a common solvent found in many industrial waste streams and by-products. 1,4-Dioxane is also a constituent of landfill leachates and a contaminant of ground waters impacted by them.[1–3] 1,4-Dioxane is degraded slowly and is highly mobile in aquifer materials. 1,4-Dioxane travels 2.5 times further than tetrahydrofuran in migrating plumes[4] and has been found up to 10 km from point sources.[3] While no federal or state drinking water standards exist, the occurrence of 1,4-dioxane in current or future drinking water supplies is a concern owing to the compound's toxicity. Based on reproductive effects and classification as a B2 or probable human carcinogen, health authorities have established action levels or drinking water health advisories of 3 μg L^{-1}.

1,4-Dioxane has no dipole moment owing to its symmetry, but with two oxygen atoms it is hydrophilic and infinitely soluble in water. 1,4-Dioxane boils at 101 °C, typical of other volatile organic compounds (VOCs) determined in water by the purge and trap technique; xylene, for example, boils at 137 °C. 1,4-Dioxane, however, has a low purge efficiency,[5] accounting for its poor purge and trap GC-MS response.[5–7] This response may also be a function of trap performance (*e.g.*, trapping and desorption efficiency), which is optimal for the recovery of non-polar VOCs and minimal trapping of water.[8] 1,4-Dioxane also gives a poor response with headspace sample introduction.[9] The partition coefficients for 1,4-dioxane lead to low recoveries in single contact liquid–liquid extraction (LLE), and very large solvent-to-water ratios are needed to achieve acceptable 1,4-dioxane recoveries.[10]

Because of these limitations, analytical chemists have sought alternative techniques to improve the determination of 1,4-dioxane and other polar, water-soluble VOCs. A modified purge and trap apparatus relying on transport across a semipermeable membrane allowed the determination of 1,4-dioxane at concentrations below 100 μg L^{-1}.[8] The determination of 1,4-dioxane at ppb levels is possible using heated purge and trap GC-MS with salting out[6] or enrichment on charcoal followed by carbon disulfide–methanol desorption and GC-FID.[6] Kadokami *et al.* described a low ppb method for 1,4-dioxane and other hydrophilic compounds based on carbon adsorption followed by GC-MS analysis.[11] Azeotropic distillation (USEPA Method 5031, January 1995) or direct aqueous injection (USEPA Method 8260A, Revision 1, November 1992)[6] have been used to determine 1,4-dioxane in waste water. Azeotropic distillation recoveries are typically 10–40%, and direct aqueous injection gives GC-FID detection limits in the mg L^{-1} range.[6] 1,4-Dioxane has also been determined in aqueous media at sub-ppm concentrations using GC–FTIR after continuous LLE with a chlorofluorocarbon solvent.[12]

The purpose of this investigation was to develop practical and rugged methods useful for determination of 1,4-dioxane at low μg L^{-1} concentrations in drinking water supplies. Because of 1,4-dioxane's properties and the availability of a deuterated analogue, d_8-1,4-dioxane, we evaluated isotopic dilution. Purge and trap, LLE and SPE methods were examined for sample preparation and both GC-FID and GC-MS spectrometry were employed in quantitative analysis.

Experimental

Chemicals

Dioxane (99+%) and d_8-1,4-dioxane (99 atom% D) were obtained from Aldrich Chemical (St. Louis, MO, USA) and were used as received. Reagent water [1,4-dioxane-free at the method detection limit (MDL)] was prepared with a Barnstead (Dubuque, IA, USA) Nanopure Infinity reverse osmosis purifier with D50250, D50253 and D50252 cartridges.

Calibration and fortification solutions

Stock standard solutions were prepared in methanol at a concentration of 2 mg mL^{-1} and were diluted with methanol to 20 μg mL^{-1} to obtain the internal standard spike solution.

Gas chromatography

A Hewlett-Packard (Wilmington, DE, USA) Model 5890A gas chromatograph equipped with an autosampler, a packed port, a flame ionization detector and a Restek 105 m × 0.53 mm id, 3.0 μm film thickness Rtx 502.2 capillary column (Supelco, Bellefonte, PA, USA) was used. The operating conditions were as follows: inlet, 250 °C; detector, 300 °C; isothermal oven temperature, 90 or 100 °C, head pressure, ~12 psi; and injection volume, 1 μL (water) and 2 μL (methylene chloride). With a 100 °C oven the typical retention times for d_8-1,4-dioxane and 1,4-dioxane were 13.78 and 14.01 min, respectively. A Spectra-Physics (San Jose, CA, USA) Winner computerized data system was used for data acquisition and processing and quantification was based on peak area.

Gas chromatography–mass spectrometry

A Varian (Sugarland, TX, USA) Saturn Model 2000 GC-MS system was used for analysis of methylene chloride extracts. The instrument was equipped with a Varian 3400 CX gas chromatograph, a Varian Model 1078 large volume injector (1 or 5 μL injection volume) and a J&W Scientific (Rancho Cordova, CA, USA) 30 m × 0.25 mm id, 0.25 μm film thickness, DB-5MS capillary column. The mass spectrometer trap was Silchrom treated and the mass spectrometer was operated as follows: multiplier, 1400–1450 V; axial modulation amplitude, 3.3 V; EM gain, 10^5; trap temperature, 200 °C; manifold temperature, 40 °C; transfer line temperature, 300 °C; and mode, electron ionization. For increased sensitivity a limited mass scan range of 85–100 u was used with a scan rate of 1 s^{-1}. Automatic gain control was set at 22 100 and the segment factor for the 45–100 u range was 150%. The injector temperature was 250 °C and the GC column was held at 35 °C for 5 min before programming at a high rate to 320 °C to elute any high boilers. The filament and multiplier delay was 4.2 min and typical retention times for d_8-1,4-dioxane and 1,4-dioxane were 4.68 and 4.74 min, respectively.

Purge and trap GC-MS

Purge and trap GC-MS was carried out with an Extrel ELQ 400 quadrupole instrument interfaced to a Tekmar Precept II autosampler, a Tekmar 3000 purge and trap inlet and a Varian 3400 chromatograph. The gas chromatograph used a Supelco 75 m × 0.75 mm id, 1.5 μm film thickness VOCOL column (Supelco) and a jet separator. For optimal sensitivity the mass spectrometer was operated in selected ion monitoring (SIM) mode on molecular ions of both 1,4-dioxane (*m/z* 88) and d_8-1,4-dioxane (*m/z* 96). Purge and trap sample introduction used a 25 mL sample volume with an 11 min purge time and 30 mL min^{-1} purge flow rate. The purge vessel was maintained at 30 °C with supplemental heating to improve reproducibility.[5] A Supelco three-part trap with Tenax GC, coconut charcoal and OV-1 on Chromosorb W was used.

Continuous LLE

An LLE extraction apparatus using a hydrophobic membrane and allowing the use of substantially reduced solvent volumes and shorter extraction times (relative to conventional Hershberg–Wolfe type extractors) was used. A Corning (NY, USA) Model 3915 extractor was operated according to the manufacturer's recommendations. Water samples (1 L) were dechlorinated by addition of 1 mL of 5% sodium sulfite and extracted with 100 mL of methylene chloride for 6 h. The condenser was cooled (6 °C) and the extraction solvent was heated (85 °C) with circulating water. The sample was concentrated to ~2 mL in the extraction apparatus and further concentrated to 1.0 mL in a nitrogen evaporator before analysis.

Results and discussion

Purge and trap mass spectrometry

The 70 eV electron ionization mass spectral ions from 1,4-dioxane include the molecular ion (*m/z* 88, base peak) and fragment ions, *m/z* 58 (95%, $[M - CH_2O]^+$), *m/z* 86 (20%, $[M - 2H]^+$) and *m/z* 43. The perdeuterated molecule has corresponding ions at *m/z* 96 (M^+), 92 ($[M - 2D]^+$), 64 ($[M - CD_2O]^+$) and 46. d_8-1,4-Dioxane and 1,4-dioxane are resolved by the 75 m × 0.75 mm id VOCOL column with typical retention times of 10.35 and 10.48 min, respectively. Although there was only about 50% chromatographic resolution of the peaks (R_S = 0.86), there was no interference as the molecular ions displaced 8 u were monitored. The chromatographic peaks were symmetrical (Fig. 1).

Using a 25 mL purge volume and SIM, 1,4-dioxane was calibrated over the range 10–5000 μg L^{-1}. In SIM at concentrations below 5 μg L^{-1} the signal was not distinguishable from noise. The instrument was linear over the calibration range with a 16% response factor relative standard deviation (RSD). Use of the labeled internal standard improved the linearity and gave a 13% response factor RSD. Both calibration curves were roughly comparable as the response factor at each concentration varied in the same pattern. In the mass scanning mode the instrument detection limit was *ca.* 50 μg L^{-1}.

MDLs were determined using no internal standard or fluorobenzene (8 μg L^{-1}) or d_8-1,4-dioxane (400 μg L^{-1}) as an internal standard (IS); fluorobenzene was detected in the *m/z* 96 channel. Fluorobenzene, unlike 1,4-dioxane, is efficiently purged and is a recommended IS for the determination of purgeable compounds in water. In both cases laboratory reagent water (boiled to remove trace VOC contamination) was spiked with 1,4-dioxane at 100 μg L^{-1}. The experimental detection limits were *ca.* 10 μg L^{-1} in each case (Table 1). Both the accuracy and MDL are improved on using the deuterated analogue as the IS, but not fluorobenzene. The deuterated compound has identical physico-chemical properties and is better able to compensate for run-to-run variations in purging, trapping and desorption. This is particularly important for polar compounds where recoveries are more variable.[10,13]

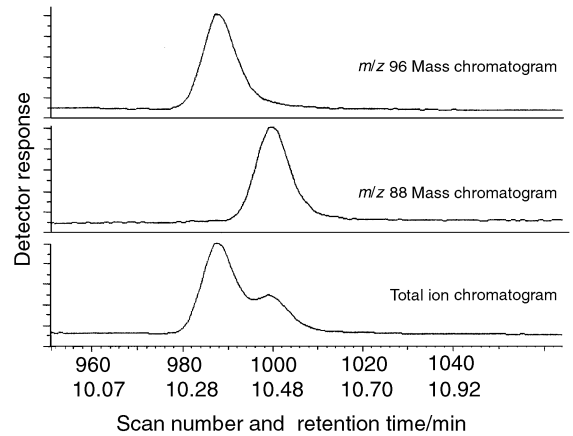

Fig. 1 Purge and trap GC-MS using a quadrupole instrument with a 75 m × 0.75 mm id VOCOL column. A 25 mL sample containing 100 μg L^{-1} each of 1,4-dioxane and its deuterated IS was used.

There is a substantial difference in purge and trap sensitivity between 1,4-dioxane and readily purged VOCs, the conventional or optimal purge and trap analytes. For these compounds the quadrupole mass spectrometer, even in the mass scanning mode, has a linear dynamic response at concentrations above 0.1–0.5 μg L^{-1}. MDLs for the optimal analytes (*e.g.*, trihalomethanes (THMs), benzene, toluene, ethylbenzene and xylene (BTEX), halogenated solvents) vary between 0.06 and 0.6 μg L^{-1} on the same instrument with an MDL spike concentration of 0.5 μg L^{-1}.

In summary, purge and trap analysis with or without isotopic dilution is useful for the determination of 1,4-dioxane, but owing to the poor purge efficiency the practical detection limits are well above those routinely achieved for efficiently purged volatiles, *ca.* 10–100 times higher even when SIM is compared with mass scanning. Purge and trap may therefore be useful in waste water monitoring, but not for the determination of 1,4-dioxane in natural water and drinking water supplies.

Direct aqueous injection gas chromatography

GC with direct aqueous injection (DAI) and flame ionization detection (FID) was useful for the determination of 1,4-dioxane at low ppm concentrations. The injection volume was limited to *ca*. 1 μL because of the tendency to extinguish the hydrogen flame with larger volumes. A 105 m megabore column (0.53 mm id) and direct injection with a packed column inlet was used. The chromatographic peaks were symmetrical, and under isothermal conditions with a 90 °C column temperature, near baseline resolution of 1,4-dioxane and its deuterated analogue was possible (R_S = 1.2), as seen in Fig. 2. It is important to note that resolution of the compounds is critical in isotope dilution GC, but not essential with mass spectrometry, where specificity is greatly improved.

The DAI GC response was linear and the instrument detection limit was *ca*. 2 μg mL^{-1}. The linearity using either external or isotope dilution calibration was acceptable as seen in Table 2. Over several decades of concentration the calibration curves again were comparable (Fig. 3). Moreover, because analyte recovery is not an issue in DAI, there is less need for isotopic dilution analysis than in methods relying on other sample preparation or introduction techniques.

Table 1 Purge and trap MDLs for 1,4-dioxane

	Internal standard		
Parameter	d_8-1,4-Dioxane	Fluorobenzene	None
No. of replicates	8	8	8
Recovery (%)	87	80	78
RSD (%)	3.3	5.5	4.5
MDL/μ L^{-1}	8.6	13	11

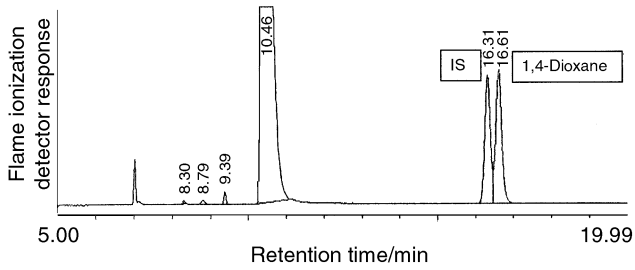

Fig. 2 Direct aqueous injection FID gas chromatogram using a 105 m × 0.53 mm id megabore capillary column. Chromatographic resolution of many compounds from their deuterated analogs is possible using efficient capillary columns (unpublished results) allowing isotope dilution quantification by GC.

Solvent extraction

Single contact LLE with methyl *tert*-butyl ether (MTBE) was investigated as a means of enriching 1,4-dioxane residues to improve detection limits. Water (100 mL) was combined with 25 g of sodium sulfate and 5 mL of MTBE and the two phase system was agitated vigorously for 2 min in a separating funnel. Addition of the salt was required for phase separation.

The extraction efficiency was 5% for each of the compounds when spiked in reagent water at 1.0 mg L^{-1}. Quantification based on the compound ratios had acceptable accuracy with a recovery of 120%. A further advantage of organic solvent extraction is that larger injection volumes (*e.g.*, 5 μL) can be used, although larger injection volumes were accompanied by some band broadening and reduced resolution of the analyte and the IS. Overall, the 20 : 1 concentration factor was nullified by the low extraction efficiency; the increased injection volume lowered the detection limits slightly but with a decrease in resolution. Isotope dilution was critical for accuracy in this method.

Continuous liquid–liquid extraction

Determination of 1,4-dioxane at trace levels requires a combination of efficient extraction, enrichment in the final sample extract and sensitive quantification. Continuous LLE using the methylene chloride soluble membrane extractor afforded 1,4-dioxane extraction efficiencies between 70 and 75% (GC-MS analysis) after cycling for 6 h. Moreover, a 1 L sample and a 1 mL final extract volume corresponding to a 1000-fold concentration factor significantly improved the overall method sensitivity.

Table 2 Direct aqueous injection GC-FID calibration

	Response factor RSD (%)	
	Range 2–500 μg mL^{-1}	Range 20–500 μg mL^{-1}
External calibration	15%	4.4%
Isotope dilution	13%	1.9%

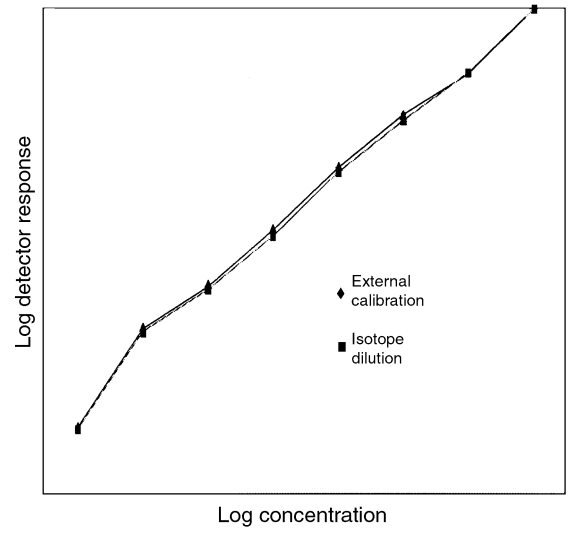

Fig. 3 Direct aqueous injection GC-FID calibration curves demonstrating the isotope dilution technique with deuterated compounds in GC. For DAI there was no specific advantage to using isotope dilution because sample preparation (or extraction) was not involved.

Ion trap mass spectrometry

The resolution of d_8- and d_0-1,4-dioxane was approximately baseline (R_S = 1.36) using splitless injection, a 0.25 mm id capillary column and a 35 °C oven temperature. Absence of tailing contributed to resolution of the compounds (Fig. 4). A typical low concentration standard using the conditions specified was *ca*. 1 ng injected. Calibration by either absolute response or isotope dilution was highly linear and was optimal with the lower injection volume (Table 3).

Analyses of the methylene chloride extracts obtained were performed using both GC-MS and GC-FID. The GC-FID system described previously used direct injection (2 μL of methylene chloride) and the 105 m megabore capillary column operated isothermally. The ion trap mass spectrometer used splitless sample injection with 1 or 5 μL injection volumes and a 30 m × 0.25 mm id DB-5MS capillary column. The mass spectrometer was specifically tuned to improve the sensitivity to 1,4-dioxane with a reduced scan range (85–100 u), an automatic gain control setting of 22 100 and a large segment factor (150%) for the 45–100 u scan portion.

With a 5 μL sample the mass spectrometer gave a linear response between *ca.* 0.1 and 10 μg mL^{-1} and the low standard had an abundant signal; the response factor RSD was 18% for the range (Fig. 5). Isotopic dilution was of no particular benefit in improving linearity, but the method accuracy was substantially improved as described below.

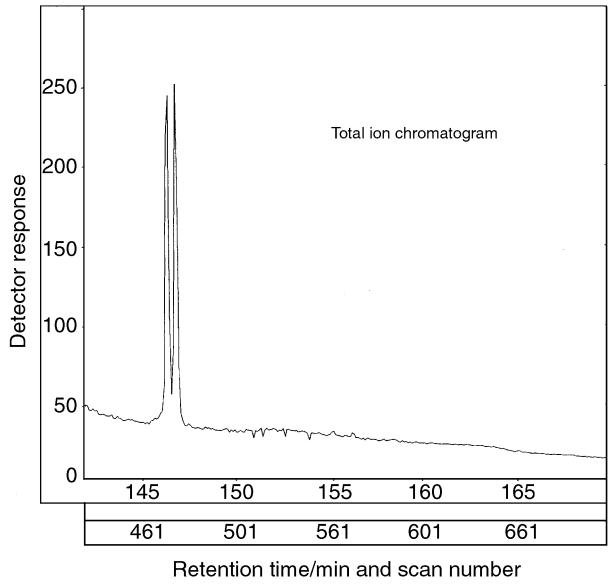

Fig. 4 Quadrupole ion trap total ion chromatogram (scan range *m/z* 85–100) for 10 μg mL^{-1} each of d_8-1,4-dioxane and 1,4-dioxane.

Table 3 Linearity for 1,4-dioxane using splitless injection and ion trap MS

Calibration range/ μg mL^{-1}	Linearity (response factor RSD, %)	
	Absolute response	Response relative to IS
	1 μL injection volume—	
2–25	9.7	7.9
10–25	3.5	4.8
	5 μL injection volume—	
0.1–10	18	19
1–10	13	14

Comparative instrument detection limits in CI-MS-MS operation

Although it was not the intention of this work to examine the quadrupole ion trap's special ion preparation methods or explore its optimal sensitivity, a limited comparative study was conducted. In the methanol chemical ionization (CI) mode the MH^+ of 1,4-dioxane (*m/z* 89) was the base peak. The most abundant product ion generated by collision induced dissociation (CID) appeared at *m/z* 45. The corresponding precursor and product ions for the deuterated internal standard were detected at *m/z* 97 and 49. Methanol CI-MS-MS allowed substantially improved detection limits with a linear dynamic response in the low ppb range. For example, a signal-to-noise of >120 was found for a 10 pg μL^{-1} 1,4-dioxane standard. In this mode of operation, therefore, and as we have observed with other water contaminants such as *N,N*-dimethylnitrosamine (NDMA), low ppt detection limits for 1,4-dioxane are expected using a similar sample workup. Appropriate precautions regarding the purity of reagents, cleanliness of glassware, *etc*., are needed for reliable ppt measurements. Consistent with the requirements of this study, the electron ionization quadrupole ion trap MS method was used exclusively.

Method detection limits

Laboratory reagent water (distilled and charcoal filtered) was fortified with the IS (25 μg L^{-1}) and 1,4-dioxane (10 μg L^{-1}) and eight samples were analyzed. The instrument gave a linear response between 2 and 25 μg mL^{-1} for standards dissolved in methylene chloride using either external or internal standard calibration with a <10% response factor RSD over the range. MDLs were slighly lower using isotope dilution as seen in Table 4. Internal standard quantification was more accurate since the average 71% extraction efficiency was corrected.

When using the flame ionization detector, calibration over the range 0.1–5 μg mL^{-1} was superior with external standards because dioxane and the internal standard were not completely resolved. Nevertheless, multipoint calibration was satisfactory (response factor RSD <30%) when the ratio of analyte to IS was between 0.1 and 10. At high or low analyte-to-IS ratios the GC data system sometimes missed the minor component, although a shoulder was evident. In such cases manual baseline

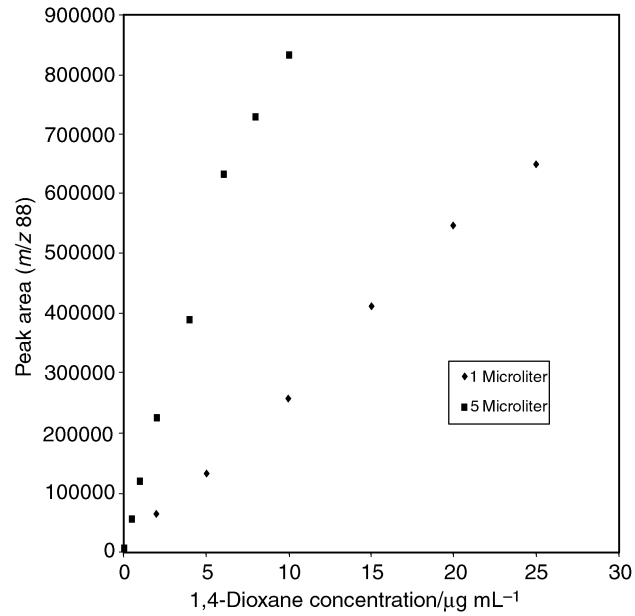

Fig. 5 1,4-Dioxane calibration curves for quadrupole ion trap GC-MS in the electron ionization mode for two injection volumes.

Table 4 1,4-Dioxane MDLs for the continuous LLE method

	Ion Trap GC-MS					
	Low injection volume		High injection volume		Gas chromatography	
Parameter	External calibration	Isotope dilution	External calibration	Isotope dilution	External calibration	Isotope dilution
No. of replicates	8	8	8	8	8	8
Spike level/μg L^{-1}	10	10	0.5	0.5	10	10
Accuracy (% recovery)	71	100	74	78	88	101
MDL/μg L^{-1}	1.5	1.1	0.14	0.16	3.1	0.72

Table 5 Stability of 1,4-dioxane and its deuterated analogue in water samples

	1,4-Dioxane/μg L^{-1}		d_8-1,4-Dioxane/μg L^{-1}	
Sample	Initial	14 d, 4 °C	Initial	14 d, 4 °C
Surface water	1.6 ± 0.20	2.1 ± 0.16	5.8 ± 1.2	8.4 ± 0.71
Tap water (1.9 mg L^{-1} total chlorine)	1.8 ± 0.35	2.3 ± 0.0064	6.1 ± 1.0	8.9 ± 0.24
Dechlorinated tap water	2.2 ± 0.22	2.3 ± 0.24	8.4 ± 0.43	8.3 ± 0.25

assigment was used. In the FID MDL study similar trends were seen, *i.e.*, both accuracy and precision were substantially improved using the isotope dilution technique (Table 4). Use of the labeled IS lowered the detection limit by a factor of four, most likely by compensating for injection imprecision.

Preservation and stability of 1,4-dioxane in water

Preservation and storage stability were investigated in a limited study. 1,4-Dioxane (2.0 μg L^{-1}) and its deuterated analogue (10 μg L^{-1}) were added to surface water from a Northern California lake and tapwater containing 1.9 mg L^{-1} total chlorine. Water samples (three replicates for each treatment) were adjusted to pH < 2 by addition of 1 : 1 HCl and analyzed immediately and after storage for 14 d at 4 °C. The chlorine-containing tap water was also dechlorinated by addition of 50 mg L^{-1} of sodium sulfite. There was no statistically significant change in the concentration of dioxane or d_8-dioxane associated with any of the treatments (Table 5). These data indicate that 1,4-dioxane is stable under typical preservation conditions used in drinking water compliance monitoring (*e.g.*, refrigeration, acidification, dechlorination). Additionally, there was no indication that 1,4-dioxane was susceptable to oxidation with chlorine (or chloramine) at the dosages encountered in drinking water disinfection.

Ground water samples

Ground waters from well fields adjacent to contaminated sites or from known contaminant plumes in California were analyzed using the continuous LLE isotope dilution GC-MS procedure. Nine sample batches were analyzed over a 6 month period and the accumulated quality control data demonstrated that the method was rugged and provided reliable information on drinking water quality. Fifteen blanks including laboratory reagent water and travel blanks were analyzed and had no detectable residue. Laboratory fortified blanks spiked at 5 or 10 μg L^{-1} were analyzed with a 1,4-dioxane recovery of 97 ± 11% ($n = 11$).

The majority of ground water samples from sites with suspected contamination were free of contamination (for the early sample batches the laboratory reporting limit was 5 μg L^{-1} but was changed to 1 μg L^{-1} after the injection volume was increased). Overall, 21% of the samples in this limited survey (13 out of 62) had detectable 1,4-dioxane, which ranged in concentration from 1.1 to 18 μg L^{-1}. Ground water sample No. C2630 containing 1.1 μg L^{-1} 1,4-dioxane is shown in Fig. 6.

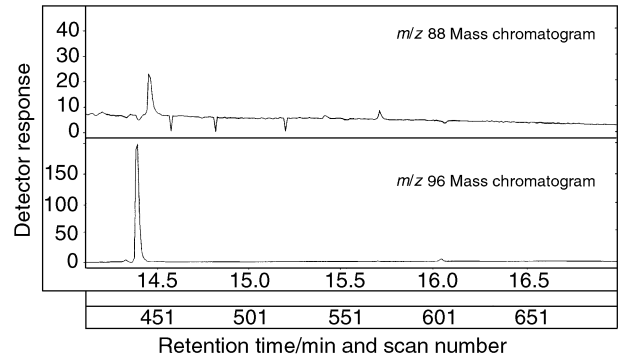

Fig. 6 Ground water sample No. C2630 containing 1.1 μg L^{-1} of 1,4-dioxane (upper trace) and 10 μg L^{-1} of d_8-1,4-dioxane (lower trace). The 1,4-dioxane level detected in the sample was *ca.* 5 times the MDL and just above the laboratory reporting limit.

The analytical method was also used in a preliminary study to evaluate the efficacy of treatment processes including advanced oxidation and granular activated carbon (GAC), techniques which appeared to be partially or completely effective at removing 1,4-dioxane from contaminated water.

Conclusion

1,4-Dioxane is determined reliably in water by various techniques including direct aqueous injection, purge and trap GC-MS and GC-MS analysis of continuous LLE extracts. The useful analytical range of each technique varies from about 1 mg L^{-1} (DAI) to as little as 0.2 μg L^{-1} (LLE). Methanol CI-MS-MS offered the potential of detection limits three orders of magnitude lower than the electron ionization MS ion trap method developed. Conventional purge and trap GC-MS is strictly limited by 1,4-dioxane's poor purge efficiency with detection limits about 100 times higher than for efficiently

purged volatile organic compounds. The use of internal standards, especially isotope-labeled compounds, can improve the analysis precision leading to lower statistical detection limits (*e.g.*, MDLs). The most substantial benefit of isotopic dilution regardless of the sample preparation or introduction technique, however, is improved accuracy, which in the current study approached 100%. Isotope dilution is not limited to mass spectrometric methods, but is also possible using non-selective gas chromatograph detectors owing to the high resolving power of capillary GC columns that separate deuterium-labeled compounds from their native analogues.

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