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Short communication

Rapid determination of 1,4-dioxane in water by solid-phase extraction and gas chromatography–mass spectrometry

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Abstract

A highly sensitive and accurate gas chromatography–mass spectrometry method for rapidly quantitative analysis of dioxane in water samples is described. Dioxane in water sample was extracted by hexane–methylene chloride (80:20, v/v) then transferred to a C_{18} solid-phase extraction (SPE) cartridge and eluted by acetonitrile. An aliquot of this solution was analyzed by gas chromatography–mass spectrometry with electron impact ionization and selected ion monitoring (dioxane m/z 88) mode. The quantitative limit was set to be 0.05 $\mu\text{g}/\text{ml}$ with an injection volume of 2 μl and a sample volume of 1 ml. The isotopically labelled [$^2\text{H}_8$]dioxane (m/z 96) was used as internal standard. Analysis time is approximately 6 min. The results for various kinds of SPE cartridges in this method are also discussed. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Dioxane

1. Introduction

1,4-Dioxane is an anticipated carcinogen [1,2]. Since it is water soluble and has a boiling point of 101°C, dioxane can persist in water longer than other volatile organic compounds. 1,4-Dioxane is a common solvent and can be found in industrial waste and by-products (e.g., from the cosmetic industry [3–5]). Its monitoring in the environment is therefore of some concern.

Our laboratory has developed a method for testing dioxane in cosmetics [6] with high sensitivity (0.1 $\mu\text{g}/\text{g}$) by GC–MS. In this manuscript we adapt this

method for determining dioxane in water after isolation by solid-phase extraction (SPE). Although the purge-and-trap technique is used for extracting dioxane and other volatile organic compounds from water samples according to US Environmental Protection Agency (EPA) method 1624, it suffers from the problem of sample interferences. The use of the SPE technique provides a way to reduce sample interferences which results in an increase in the signal-to-noise ratio (S/N) and eventually lowers the detection limit. In our method, detection limits of at least 0.025 $\mu\text{g}/\text{ml}$ are obtainable with a 1 ml sample. The use of the isotopically labelled compound [$^2\text{H}_8$]dioxane (dioxane- d_8) as an internal standard ensures better accuracy and reproducibility. The sensitivity and reproducibility of our method are better than those of EPA method 1624 and literature

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results by GC [7,8], HPLC [9] and GC–MS [10] methods.

2. Experimental

2.1. Chemicals and materials

1,4-Dioxane, 99.9%, HPLC grade and 1,4-dioxane- d_8 , 98.5 at.% of 2H were purchased from Sigma (St. Louis, MO, USA). Dichloromethane, acetonitrile and hexane (HPLC grades) were purchased from EM Science (Gibbstown, NJ, USA). SPE cartridges C_{18} (18% carbon loading) were obtained from Applied Separations (Bethlehem, PA, USA).

2.2. Sample preparation

To 1 ml of water sample in a 15 ml glass test tube was added 50 μ l of internal standard solution (200 μ g/ml in water) and 6 ml hexane–dichloromethane (80:20, v/v) solution. The test tube was capped and vortexed for 15 min, and then centrifuged for 10 min at ambient temperature at 700 g. The organic layer was applied to a SPE C_{18} cartridge that was preconditioned prior to use by 1 ml of acetonitrile and 1 ml of extraction solution. The sample should be processed as slowly as possible without vacuum.

Dioxane was recovered by eluting with 0.5 ml acetonitrile two times. An aliquot (50 μ l) of the combined elution solution was transferred to a sample vial for analysis by GC–MS.

2.3. Method of analysis

Analysis was performed on an HP 5890 II gas chromatography with a high-resolution HP-5 column (25 m \times 0.20 mm I.D, 0.33 μ m film thickness) and HP 5989 MS engine equipped with a Model 7673 autosampler and a Model HP DOS G1034C MS ChemStation (Hewlett–Packard, Palo Alto, CA, USA).

Helium carrier gas flow-rate was about 1 ml/min at 25°C. Injector temperature was 130°C. The oven temperature programming started at an initial temperature of 40°C for 4 min, then was ramped at 10°C/min to 100°C. Injection volume was 2 μ l. Separation time was approximately 6 min. The mass spectrometer was set at the electron impact ionization (EI) and selected ion monitoring (SIM) acquisition mode: monitoring ions at m/z 88 and 96. The temperatures of source and quadrupoles were 150 and 100°C, respectively. The ionizing energy and electrical multiplier voltage were set at 70 eV and 2000 V, respectively.

Table 1

(A) Intra-assay precision^a and accuracy^b from quality control samples for dioxane in water

Sample	Theoretical concentration (μ g/ml)	Concentration found (mean \pm S.D.; $n=5$) (μ g/ml)	R.S.D. (%)	% Theoretical value
QC _L	1.0	1.02 \pm 0.117	11.5	101.6
QC _M	10.0	9.68 \pm 0.72	7.4	96.8
QC _H	75.0	71.4 \pm 6.19	8.67	95.3

(B) Inter-assay precision^a and reproducibility^b from quality control samples for dioxane in water

Time	Sample	Nominal concentration (μ g/ml)	Concentration found (mean \pm S.D.; $n=5$) (μ g/ml)	R.S.D. (%)
Second day	Q _M	10.0	10.8 \pm 0.41	3.74
Seventh day	Q _M	10.0	9.45 \pm 0.31	3.21

^a Precision is reflected by R.S.D..

^b Accuracy/reproducibility is reflected by theoretical value%.

3. Results and discussion

3.1. Summary of results

Dioxane was determined at six concentrations: 0.05, 0.5, 5.0, 25.0, 50.0 and 100.0 $\mu\text{g/ml}$ (mg/ml). The concentration of internal standard dioxane- d_8 was 10.0 $\mu\text{g/ml}$. Quality control (QC) samples were run in duplicate at three different concentration levels: $\text{QC}_L=1.0$, $\text{QC}_M=10.0$, $\text{QC}_H=75.0$ $\mu\text{g/ml}$. The quantitative analysis was based on the ratio of peak height of the analyte to that of internal standard.

The calibration curve was nonlinear in the low concentration range (0.05–1.0 $\mu\text{g/ml}$) and linear

when concentration was high (>1 $\mu\text{g/ml}$). The calculation and regression of the standard curve was performed using nonlinear regression giving a good fit for the whole calibration range (0.05–100 $\mu\text{g/ml}$). The accuracy of intra-assay and reproducibility of inter-assay are better than 10% and listed in Table 1.

3.2. SPE and recovery

Hexane and methylene chloride efficiently extract dioxane from water samples, but their molecular masses (M_r 84 and M_r 85, respectively) are too close to that of dioxane for MS detection. Dioxane is miscible with lower-molecular-mass acetonitrile

Table 2
Experimental data for various solid phase extraction cartridges

(A) The extraction recoveries of dioxane by different SPE cartridges

Sorbent	Structure	Producer company	Recovery $\eta_{\text{SPE}}\%$
C_{18} 18% Octadecyl	$-\text{Si}-\text{C}_{18}\text{H}_{37}$	Spe-ed (Applied Separations)	88.3 $n=7$
C_{18} Octadecyl	$-\text{Si}-\text{C}_{18}\text{H}_{37}$	Analytichem International	79.4 $n=6$
C_8 Octyl	$-\text{Si}-\text{C}_8\text{H}_{17}$	J.T. Baker	76.7 $n=6$
C_2 Ethyl	$-\text{Si}-\text{C}_2\text{H}_5$	Varian	76.5 $n=6$
SI Silica	$-\text{Si}-\text{OH}$	Analytichem International	87.8 $n=6$
2OH Diol	$-\text{Si}-\text{C}_3\text{H}_6-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2$ OH OH	Varian	93.5 $n=7$
NH_2 -Aminopropyl	$-\text{Si}-\text{C}_3\text{H}_6-\text{NH}_2$	Varian	18.4 $n=7$

(B) Precision and reproducibility for testing dioxane in water by different SPE cartridges

SPE cartridge	Nominal concentration QA ($\mu\text{g/ml}$)	Concentration found (mean \pm S.D.) ($\mu\text{g/ml}$)	R.D.	% Theoretical value	n
C_{18} Octadecyl	10	10.96 \pm 0.49	4.51	109	6
C_8 Octyl	10	10.9 \pm 0.67	6.06	110	6
C_2 Ethyl	10	11.0 \pm 0.37	3.37	109	6
SI Silica	10	10.7 \pm 0.58	5.45	107	6
2OH Diol	10	9.94 \pm 0.58	5.84	99.4	6
NH_2 -Aminopropyl	10	9.65 \pm 0.17	1.76	96.5	6

causing few solvent interferences in detection. The dioxane extracted from water by hexane and methylene chloride was transferred to an SPE cartridge and eluted from the cartridge by acetonitrile.

According to our experiments: C_2 , C_8 , C_{18} (non-polar extraction) and NH_2 , $SiOH$, diol 2-OH (polar extraction) SPE columns are suitable for the extraction of dioxane. The recovery of dioxane from water samples by these cartridges are listed in Table 2A. The recovery was calculated by the ratio of peak height of the same standard sample with and without SPE to that of internal standard without extraction in both cases. It should be pointed out that these recoveries listed in Table 2 do not include liquid-liquid extraction recovery that was found to be 70–85%. In our case the total recovery is in the range 60–75%.

3.3. Detection limit and SPE

The detection limit of dioxane depends on instrument limitations and the level of sample interference. Since the molecular ion of dioxane is low (88), ions from interfering compounds are possible and limit the detection limit for dioxane. SPE may exclude some interferences from the sample prior to GC-MS analysis. The detection limit can reach 5 ng/ml with a 5 ml sample, significantly better than that of EPA method 1624 (10 ng/ml with 5 ml sample). There is still room for lowering the detection limit by raising the EM voltage because S/N is high. The quantification limit of our method is 0.05 $\mu\text{g/ml}$ with a 1 ml sample.

The use of isotopically labelled dioxane- d_8 as an internal standard in our method has overcome the

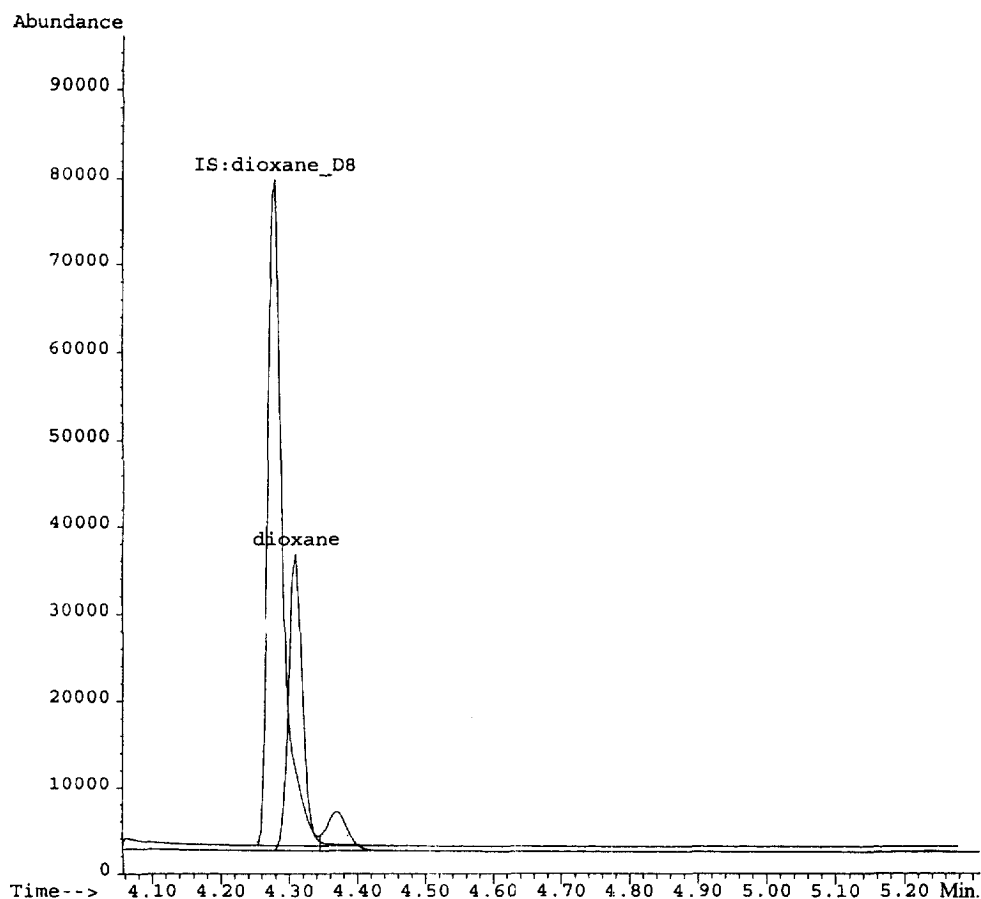


Fig. 1. GC-MS chromatogram of a water sample. The dioxane was found at 4.8 $\mu\text{g/ml}$.

major shortcomings of the low accuracy and reproducibility as well as high variability in the recovery [9] by GC–MS. Since dioxane- d_8 has identical chemical properties of dioxane, whatever changes in experimental conditions, the peak height of both dioxane and dioxane- d_8 change in the same way and the ratio remains the same [6]. The results showed that the accuracy of intra-assay and reproducibility of inter-assay of our method are better than 10% (Table 1). Even by the different SPE columns with different recoveries (η_{SPE} from 18.4 to 93.5), the precision and reproducibility are kept within 10%. (Table 2B). The data listed in Tables 1 and 2 showed that the results of our method are highly reliable and reproducible.

Fig. 1 is a GC–MS of a water sample. The concentration of dioxane was 4.8 $\mu\text{g}/\text{ml}$. The retention time of dioxane and dioxane- d_8 were 4.31 and 4.28 min, respectively. The small peak in the chromatogram is a sample impurity.

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