

Measurement of 1,4-dioxane in surface water by headspace GC-MS

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(Received October 15, 2013; Revised January 20, 2014; Accepted January 20, 2014)

GC-MS에 의한 지표수에서 1,4-Dioxane의 측정

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(2013. 10. 15. 접수, 2014. 1. 20. 수정, 2014. 1. 20. 승인)

Abstract: 1,4-Dioxane was classified as a Group 2B carcinogen by the International Agency for Research on Cancer. The compound was measured in surface water with a headspace gas chromatographic mass spectrometric detection. A 5 mL water sample was placed in a 10 mL headspace vial and saturated with NaCl, and the solution was spiked with 1,4-dioxane-d8 as an internal standard and sealed with a cap. Water samples were collected from twenty-two basins of Gum-River on June and September 2012, respectively. As a result, 1,4-dioxane was detected in the concentration range of 0.49-43.0 µg/L (mean 2.0 µg/L) in the frequency of about 30% in surface water samples.

요약: 1,4-dioxane은 국제 암연구소에서 2B의 발암물질로 분류하고 있는 물질이다. 지표수 중에 1,4-dioxane을 headspace gas chromatographic mass spectrometry에 의해 측정하였다. 시료 5 mL를 10 mL 헤드스페이스 vial에서 넣고 NaCl로 포화시킨 후 내부표준물질로 1,4-dioxane-d8 첨가한 후 90 °C에서 30분간 가열하였다. 위의 방법을 사용하여 금강 22 개 지점에서 2012년 6월과 9월 시료 채취하여 분석한 결과 0.49-43.0 µg/L (평균 2.0 µg/L)의 범위로 약 30%의 빈도로 검출되었다.

Key words: 1,4-Dioxane, surface water, headspace extraction, gas chromatography-mass spectrometry

1. Introduction

1,4-Dioxane is used as a solvent for a variety of

practical applications as well as in the laboratory¹⁻⁴ and a contaminant of some ingredients used in the manufacture of personal care products and cosmetics.⁵ Acute (short-term) inhalation exposure to high levels

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of 1,4-dioxane has caused vertigo, drowsiness, headache, anorexia and irritation of the eyes, nose, throat, and lungs in humans.⁶ It may also irritate the skin.⁶ Damage to the liver and kidneys has been observed in rats chronically (long-term) exposed in their drinking water. In three epidemiologic studies on workers exposed to 1,4-dioxane, the observed number of cancer cases did not differ from the expected cancer deaths. Tumors have been observed in orally exposed animals

The International Agency for Research on Cancer classified 1,4-dioxane as a Group 2B carcinogen : *possibly carcinogenic to humans* because it is a known carcinogen in other animals⁷ and the U.S. environmental protection agency (US EPA) classified it as a probable human carcinogen.⁸ World Health Organization suggested 50 µg/L as the maximum contaminant level.⁹ 1,4-Dioxane is often found in many water sources: industrial waste water, stream water and ground water. The monitoring is required to establish new water quality criteria.

A wide range of analytical techniques has been developed to monitor the contaminant at trace levels in environmental samples. Most of these procedures are based on determining 1,4-dioxane by using a gas chromatography-flame ionization detector (GC-FID)¹⁰⁻¹² and gas chromatography-mass spectrometry (GC-MS).¹³⁻¹⁹ Recently, a specific and highly sensitive headspace solid phase microextraction (SPME)²⁰⁻²³ and a isotopic dilution headspace (IDHS)²⁴ GC-MS were developed for the determination of 1,4-dioxane in water.

The aim of this paper was to measure trace 1,4-dioxane in surface water using IDHS GC-MS and to provide basic data to establish new surface water quality criteria.

2. Experimental

2.1. Chemicals and reagents

1,4-Dioxane, 1,4-dioxane-d8, sodium chloride, acetone and methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Water was purified by milli-Q equipment (Millipore Corp., Milford,

MA, USA).

2.2. Water sampling and extraction procedure

Surface water samples were collected from 16 basins in the Gum River without headspace in 40 mL VOC bottles containing 1 drop of 2 M HCl. The sampling sites were selected to uniformly represent all streams of the River. All samples were collected in duplicate, and 5 mL water were placed in a 10 mL headspace vial containing 2 g NaCl. 50 µL of 1,4-dioxane-d8 solution (1.0 mg/L in milli-Q water) as an internal standard was added in the sample as soon as possible, and then the vial was sealed with a cap. The sample vial was placed in a heating block for 30 min at 90 °C.

2.3. Gas chromatography-mass spectrometry

An Agilent 6890/5973 N instrument and a Combipal Autosampler (Agilent, USA), which allows automated HS injections, were used. All mass spectra were obtained with an Agilent 6891/5973N instrument. The ion source was operated in the electron ionization mode (EI; 70 eV, 230 °C) and full-scan mass spectra (m/z 40-800) were recorded for analyte identification. An HP-InnoWax capillary column (40 m × 0.25 mm I.D. × 0.25 µm film thickness) was used. Samples were injected in the splitless mode. The flow rate of helium as a carrier gas was 1.0 mL/min. The injector temperature was set at 210 °C. The oven temperature programs were as follows: an initial temperature of 35 °C (held for 3 min) increased to the final temperature of 220 °C at 8 °C/min. Head space conditions of 1,4-dioxane are as described in *Table 1*. The ions selected by SIM were m/z 88, 58 and 57 for 1,4-

Table 1. Head space conditions of 1,4-dioxane

Parameter	Condition
Incubation temp (°C)	90
Extraction time (min)	30
Syringe temp (°C)	95
Agitator speed (rpm)	600
Fill speed (µL/s)	200
Injection volume (µL)	700
Flush time (min)	5

dioxane and m/z 96, 64 and 62 for 1,4-dioxane-d8 (internal standard).

2.4. Calibration and quantification

Calibration curves for 1,4-dioxane were established by extraction after adding 0.5, 2.0, 5.0, 20, 50, 100 and 250 ng of the standard and 50 ng of the internal standard (1,4-dioxane-d8) to 5.0 mL of water. The ratios of the peak area of the standard to that of the internal standard were used in the quantification of the compounds.

3. Results and Discussion

3.1. Method validation

For the GC separation of 1,4-dioxane, the use of the semi-polar stationary phase was found to be efficient. Chromatograms are shown in *Fig. 1*. As can be seen from the figure, the peaks of 1,4-dioxane and the internal standard are symmetrical and separation of the analytes from the background compounds in the water samples was good. The retention time of 1,4-dioxane was 8.19 min. There were no extraneous peaks observed in a chromatogram of spiked water in the near of the retention time of 1,4-dioxane.

The method was validated for linearity, the limit of detection (LOD), the limit of quantification (LOQ), precision and accuracy.

Calibration curves of the 1,4-dioxane were constructed by extraction of the spiked water samples. Examination of the typical standard curve by computing a regression line of peak area ratios for the 1,4-dioxane to the internal standard on concentrations using a least-squares fit demonstrated a linear relationship with correlation coefficients of 0.9997. The line of best fit for 1,4-dioxane is $y = 0.0952x +$

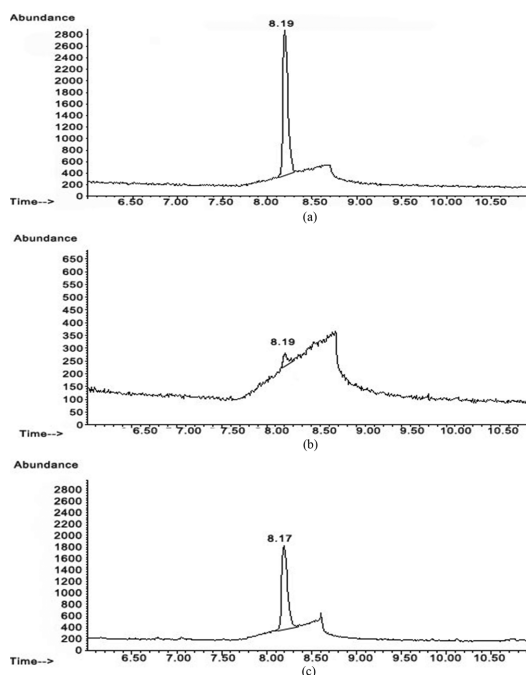


Fig. 1. GC-MS chromatogram from (a) a spiked ultra-pure water sample at 10 µg/L and a river water sample (1,4-dioxane was detected in concentration of 0.1 µg/L (b) and 1,4-dioxane-d8 was spiked at 10.0 µg/L (c)).

0.0134 over a range of 0.1-50 µg/L, where x is the analyte concentration (µg/L) and y is the peak area ratio of the analyte to the internal standard.

We have defined and calculated as following: LOD and LOQ were defined by 3.14 and 10 times the standard deviation for replicate determinations ($n=7$) from samples spiked at the concentration of 0.01 µg/L in stream water, in which the analyte was not detected. The LOD in this study was 0.02 µg/L and the LOQ was 0.07 µg/L using a 5.0 mL sample.

The accuracy can be assessed by determining the recovery in spiked samples: Intra-day accuracy was evaluated using five spiked samples at concentrations

Table 2. Intraday and interday laboratory precision and accuracy results for the analysis of 1,4-dioxane in water ($n=5$)

Spiked Conc.(µg/L)	Intraday measured value			Interday measured value		
	Mean ± SD (µg/L)	Accuracy (%)	Precision (%)	Mean ± SD (µg/L)	Accuracy (%)	Precision (%)
10.0	9.7±0.45	97.4	4.6	9.8 ± 0.56	98.0	5.7
50.0	49.6±1.8	99.2	3.7	48.0 ± 2.0	96.1	4.2

of 10.0 and 50.0 $\mu\text{g/L}$ for 1,4-dioxane. The inter-day accuracy was determined using sample recovery on three different days. The accuracy was in the range of approximately 96 to 99%, and the precision of the assay was less than 6%, as shown in *Table 2*.

3.2. Water analysis

We analyzed the target compound in 44 surface water samples. 1,4-Dioxane was detected in a concentration range of 0.49-43.0 $\mu\text{g/L}$ in 13 samples of the 44 surface water samples collected from Gum-River, Korea. In 1st survey (in June, 2012), 1,4-dioxane was detected in a concentration range of 0.61-43.0 $\mu\text{g/L}$ (mean=2.2 $\mu\text{g/L}$) in 3 samples of the 22 surface water samples. Otherwise, in 2nd survey (in September, 2012), 1,4-dioxane was detected in a concentration range of 0.49-7.8 $\mu\text{g/L}$ (mean=1.7 $\mu\text{g/L}$) in 10 samples of the 22 surface water samples.

4. Conclusions

We measured the target compound in 44 surface water samples. 1,4-Dioxane was detected in a concentration range of 0.49-43.0 $\mu\text{g/L}$ in 13 samples of the 44 surface water samples collected from Gum-River. Maximum concentration of 1,4-dioxane detected in surface showed lower than Korea drinking water guideline.²⁵ The concentrations of 1,4-dioxane in environmental water were comparable to those present in other countries. 1,4-dioxane at the level of 1 $\mu\text{g/L}$ has been detected in many locations in the US. In the state of New Hampshire alone in 2010 it had been found at 67 sites, ranging in concentration from 2 $\mu\text{g/L}$ to over 11,000 $\mu\text{g/L}$.²⁶ Although the production of 1,4-dioxane in Korea is decreasing, its existence in river water calls for identifying its origin. 1,4-Dioxane can be discharged as a by-product in the industry of stabilizer, inks and adhesives.

References

- G. G. Hawley and R. J. S. Lewis, *Hawley's Condensed Chemical Dictionary*, John Wiley & Sons Inc., New York, USA, 2001.
- K. S. Surprenant, Dioxane. In *Ullmann's Encyclopedia of Industrial Chemistry* (p. 543), Wiley-VCH Verlag, Weinheim, Germany, 2002.
- IARC, 1,4-Dioxane. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, Lyon, France, 1999.
- Merck and C. Inc, *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*. Whitehouse Station, 2001.
- R. E. Black, F. J. Hurley and D. C. Havery, *J AOAC*, **84**(3), 666-670 (2001).
- E. J. Calabrese and E.M. Kenyon. *Air Toxics and Risk Assessment*. Lewis Publishers, Chelsea, MI, 1991.
- United States Department of Health and Human Services' National Toxicology Program. Eleventh Report on Carcinogens. <http://ntp-server.niehs.nih.gov/ntp/roc/eleventh/profiles/s080diox.pdf>. Accessed 2013-9-30.
- US EPA, EPA 749-F-95-010, OPPT Chemical Fact Sheets 1,4-Dioxane, <http://www.epa.gov/opptintr/chemfact/dioxa-fs.txt>. Accessed 2013-9-30.
- WHO, Rolling Revision of the WHO Guidelines for drinking water quality, 1,4-dioxane in Drinking Water Summary Statement, 2000.
- USEPA, Method 5030, Cincinnati, OH 45268, USA, 1986.
- USEPA, Method 5035, Cincinnati, OH 45268, USA, 1996.
- USEPA, Method 8015C, Cincinnati, OH 45268, USA, 2007.
- Y. M. Park, H. Pyo and S. J. Park, *Anal Chim. Acta*, **548**, 109-115 (2005).
- W. M. Draper, J. S. Dhoot and J. W. Remoy, *The Analyst*, **125**(8), 1403-1408 (2000).
- C. Isaacson, T. K. Mohr and J. A. Field, *Environ. Sci. & Technol.*, **40**(23), 7305-7311 (2006).
- D. Song and S. Zhang, *J. Chromatogr. A*, **787**, 283-287 (1997).
- M. Yano, T. Kawamoto and N. Makihata, *Bunseki Kagaku*, **54**(9), 917-922 (2005).
- P. E. Grimmett and J. W. Munch, *J. Chromatogr. Sci.*, **47**(1), 31-39 (2009).
- USEPA, Method 8260B, Cincinnati, OH 45268, USA, (1996).
- S. Nakamura and S. Daishima, *Anal. Chim. Acta*, **548**,

- 79-85 (2005).
21. R. E. Shirey and C. M. Linton, *J. Chromatogr. Sci.*, **44**(7), 444-450 (2006).
 22. S. Nakamura and S. Daishima, *Japan analyst*, **62**(3), 215-222 (2013).
 23. S. S. H. Davarani, L. Masoomi and M. H. Banitaba, *Chromatographia*, **75**(7/8), 371-377 (2012).
 24. H. S. Shin and H. H. Lim, *Chromatographia*, **73**(11/12), 1233-1236 (2011).
 25. The Environmental Minister of Korea, Drinking Water guideline, 2012.
 26. USEPA, 1, 4-Dioxane Fact Sheet: Support Document, *OPPT Chemical Fact Sheets*. Accessed 2013-9-30.