# ANALYSIS OF OXYGENATED SOLVENTS IN GROUNDWATER BY DYNAMIC THERMAL STRIPPING-GC-MSD

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ABSTRACT

Α plume Óf groundwater contaminated with 1,4-dioxane, tetrahydrofuran and acetone emanating from a solvent disposal site was Analysis was conducted with dynamic thermal stripping mapped. followed by thermal desorption into a GC-MSD with monitoring of selected ions. This method has a significantly better practical quantitation limit than the current EPA method (10 vs. 150 µg/L for 1,4-dioxane). Ten years after disposal, concentrations of 1,4-dioxane greater than 3 mg/L were measured at points more than 300 m from the site.

RÉSUMÉ

On a déterminé l'emplacement d'un panache d'eaux souterraines contaminées par du 1,4-dioxane, du tétrahydrofurane et de l'acétone, s'écoulant à partir d'un site d'élimination de solvants. L'analyse a été réalisée par extraction thermique dynamique, puis par désorption thermique dans un chromatographe couplé à un spectromètre de masse qui contrôlait certains ions. Cette méthode possède une limite de dosage beaucoup plus faible que celle de la méthode couramment employée par l'EPA (10 µg/L en comparaison de 150 µg/L pour le 1,4-dioxane). On a mesuré, dix ans après l'élimination, des concentrations de 1,4-dioxane supérieures à 3 mg/L en des points situés à plus de 300 mètres du site. The disposal by DOE of laboratory wastes consisting mostly of organic solvents, at a waste disposal site on crown property managed by Transport Canada at Gloucester, Ontario has resulted in the contamination of the underlying aquifer. A wide variety of volatile compounds were identified and quantitated in samples from the aquifer. The compound of greatest concern is 1,4-dioxane because of its toxicity and mobility as it is now present at very high concentrations beyond the boundaries of the property. A new, more precise and sensitive method was used to analyse these latest samples.

### PERSPECTIVE-GESTION

L'élimination par le Ministère de l'Environnement de déchets de laboratoire, constitués principalement de solvants organiques, au site d'élimination de déchets situé sur une propriété de la Couronne à Gloucester (Ontario) a provoqué la contamination de la formation aquifère sous-jacente. Nous avons identifié et dosé une grande variété de composés volatils dans des échantillons prélevés dans cette formation aquifère. Le 1,4-dioxane est le composé qui nous inquiète le plus en raison de sa toxicité et de sa mobilité; en effet, il est présent en concentrations élevées à l'extérieur des limites de la propriété. Nous avons utilisé une nouvelle méthode plus précise et plus sensible pour analyser ces échantillons.

## INTRODUCTION

The presence of 1,4-dioxane (dioxane) in groundwater is of concern because it has been classified as a potential human carcinogen (1). Because of its carcinogenic potential, long-term and lifetime Health Advisories have not been issued. However, the USEPA has estimated that a concentration of 7  $\mu$ g/L in drinking water will increase the risk by one excess cancer per million, assuming water consumption of 2 L/d by a 70 kg adult over a 70 year lifetime (1).

There is a lack of appropriate analytical methods to detect such low levels in water. The USEPA recommended method using purge and trap concentration achieves a practical quantitation limit (PQL) of 150  $\mu$ g/L (2). A maximum permissible limit (MPL) of 66.5  $\mu$ g/L for 1,4-dioxane was set by provincial regulatory authorities at the boundary of the Gloucester Landfill, i.e. the point of compliance (10). Because this MPL value was less than half of the USEPA PQL, it was necessary to develop a more sensitive analytical method. Concentrations of greater than 3 mg/L were determined at monitoring points off-site. Since dioxane is not a priority pollutant it is rarely analysed for at hazardous waste sites and it has not been included in federal or state surveys of drinking water (1). However, it is widely used in the resin and paint industries and is found in many landfills (3).

The need for an awareness of this problem arises because of this compound's mobility. With a log octanol-water partition coefficient  $(K_{OW})$  of -0.27, dioxane is essentially unretarded in the subsurface (4). It also appears that dioxane does not degrade under anoxic

conditions, which are the expected conditions beneath most hazardous waste/landfill sites (5). Two other compounds, tetrahydrofuran (THF) and acetone, were also examined during this study because of their high aqueous solubilities and similar analytical problems (acetone PQL=100  $\mu$ g/L (2)).

Alternative analytical methods in the literature are scarce (6-9). A detection limit of 5 µg/L for dioxane was obtained using solvent extraction but with poor reproducibility (32 % RSD) (6). Charcoal adsorption followed by CS<sub>2</sub> elution has also been used (7). Other methods using purge and trap concentration gave essentially the same results as the EPA recommended method (8,9). The proposed method is a purge and trap procedure conducted at elevated temperatures. It provides a better detection limit than the conventional method and is suitable for analysis of THF and acetone as well as dioxane. Using this method it was possible to define a plume of these very mobile chemicals originating from a solvent disposal site.

## METHOD

A 10 mL aqueous sample was added to a sparge tube along with an internal standard (difluorobenzene). This sample was heated to  $60^{\circ}$ C in the oven of a Dynamic Thermal Stripper (Envirochem, Kemblesville, PA). It was then purged with nitrogen at 35 mL/min for 10 minutes. The compounds were trapped on quartz sorbent tubes packed with 0.25 g Carbotrap and 0.30 g Carbotrap "C" (Supelco Canada, Oakville, ON), which were maintained at a temperature of 55°C during purging. These tubes were then dried with nitrogen at 50-60 mL/min for 5 minutes. The analytes were then thermally desorbed for 5 minutes (maximum temperature of 280°C) in the external tube desorber

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of an Envirochem Unacon concentrator (Model 810) interfaced with a Hewlett Packard GC-MSD (Model 5890/5970).

The components were separated on a 30 m J & W DB-624 column (0.32 mm I.D., 1.0  $\mu$ m film). The oven temparature was held at 35°C for 3 minutes and then ramped at 4°C/min to 100°C. The selected ion monitoring masses were 88 and 58 amu for dioxane, 42 and 72 for THF, 43 and 58 for acetone and 114 for the internal standard.

Between samples the sorbent tubes were purified by heating rapidly to 300°C while passing nitrogen through at 40 mL/min. Total time per sample was 60 minutes but the dynamic thermal stripping procedure was conducted while the previous sample was being analysed allowing samples to be run every 35 minutes.

**RESULTS AND DISCUSSION** 

### Analysis

Standards were run in quadruplicate for the three compounds at four different fortification levels (Table 1). Relative standard deviations were lowest for 1,4-dioxane, averaging 12% for the four different levels.

DESIGN	ACETONE		THF		1,4-DIOXANE		I.S.
CONC.	CONC.	%RSD	CONC.	%RSD	CONC.	%RSD	%RSD
(µg/L)	(µg/L)	(n=4)	(µg/L)	(n=4)	(µg/L)	(n=4)	(n=4)
25	23.2	51	32.6	43	24.7	9	9
50	46.4	20	65.2	16	49.4	3	20
100	92.8	31	130.4	10	98.8	21	22
500	464	45	652	40	494	15	10

Table 1. Summary of analytical results

It was found that increasing the sparging temperature did little to improve efficiency and required a longer drying period. Aqueous standards were unstable, lasting less than 72 hours before noticeable losses occurred. Practical detection limits of 10, 2 and 10  $\mu$ g/L at a signal to noise ratio of 2 were achieved for dioxane, THF and acetone, respectively. The method is linear over a range of 10 to 500  $\mu$ g/L for dioxane ( $r^2 = 0.9988$ ). The linear range is 10 to 100  $\mu$ g/L for both THF and acetone.

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## Ground Water Quality Monitoring

The site has been described in detail elsewhere (4,5,11,12). A wide assortment of organic solvents and other laboratory wastes were disposed of in unlined trenches overlying a sand and gravel aquifer. The plume of contaminated groundwater from this site (Special Waste Compound, Fig. 1) has now crossed the property boundary (railroad tracks). Dioxane is the organic contaminant that has migrated the farthest because of its high aqueous solubility and therefore low retardation. The plume of dioxane as mapped from results of the analysis of 33 groundwater samples by this thermal stripping procedure is shown in plan view (Figure 1(A)) and cross-section (Figure 1(B)). Contours in plan view are based on the maximum concentration in each multilevel sampler.

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Figure 1(A) Plan view of 1,4-dioxane plume at the Gloucester Landfill near Ottawa, Ontario

Figure 1(B) Cross-section of 1,4-dioxane plume.





FIGURE 2