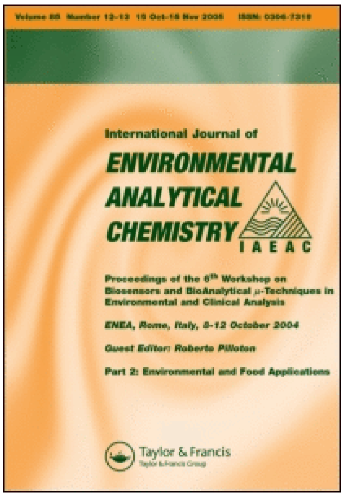

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ANALYSIS OF OXYGENATED SOLVENTS IN GROUNDWATER BY DYNAMIC THERMAL STRIPPING-GC-MSD

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Analysis of three oxygenated solvents (acetone, THF and 1,4-dioxane) in groundwater was conducted by dynamic thermal stripping 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 (13 vs. 150 μg/L for 1,4-dioxane). Using this method a plume of groundwater contaminated with 1,4-dioxane emanating from a former solvent disposal site was mapped. More than 10 years after disposal, concentrations of 1,4-dioxane greater than 3 mg/L were measured at points more than 300 m from the site.

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 7μg/L in drinking water will increase the risk of one excess cancer per million, assuming water consumption of 2 L/d by a 70 kg adult over a 70 year lifetime.[1]

Currently, 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 μg/L[2] A maximum permissible limit (MPL) of 66.5 μg/L for 1,4-dioxane was set by provincial regulatory authorities at the boundary of the Gloucester Landfill, i.e. the point of compliance.[3] Because this MPL 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 analyzed 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.[4]

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.[5] It also appears that dioxane does not degrade under anoxic conditions, which are the expected conditions beneath most hazardous waste/landfill sites.[6] 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 = 100µg/L).[2] These compounds are of much less concern from a health point of view and were found at lower concentrations than dioxane at this particular site.

Alternative analytical methods in the literature are scarce.[7-10] A detection limit of 5µg/L for dioxane was obtained using solvent extraction but with poor reproducibility (32% RSD).[7] Charcoal adsorption followed by CS_2 elution has also been used.[8] Other methods using purge and trap concentration gave essentially the same results as the EPA recommended method.[9,10] The proposed method combines dynamic thermal stripping at 60°C with subsequent off-line thermal desorption into a GC-MSD. It provides a lower detection limit than the conventional method and is suitable for the 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 former solvent disposal site at the Gloucester Landfill near Ottawa, Canada.

METHOD

A 10 mL aqueous sample was transferred by pipette from the sample vial to a sparge tube fitted with a septum port. One µL of a 10 mg/L solution of difluorobenzene (internal standard) in methanol was added with a syringe through a septum port of the tube. This sample was heated to 60°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 (6 mm by 20 cm (Envirochem)) 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 at a maximum temperature of 280°C in the external tube desorber of an Envirochem Unacon concentrator (Model 810) interfaced with a Hewlett-Packard GC-MSD (Model 5890/5970).

Table 1 Summary of analytical results

Design Conc. (µg/L)	*Acetone*		*THF*		*1,4-Dioxane*		*I.S. %RSD (n=4)*
	Conc. (µg/L)	*%RSD (n=4)*	*Conc. (µg/L)*	*%RSD (n=4)*	*Conc (µg/L)*	*%RSD (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

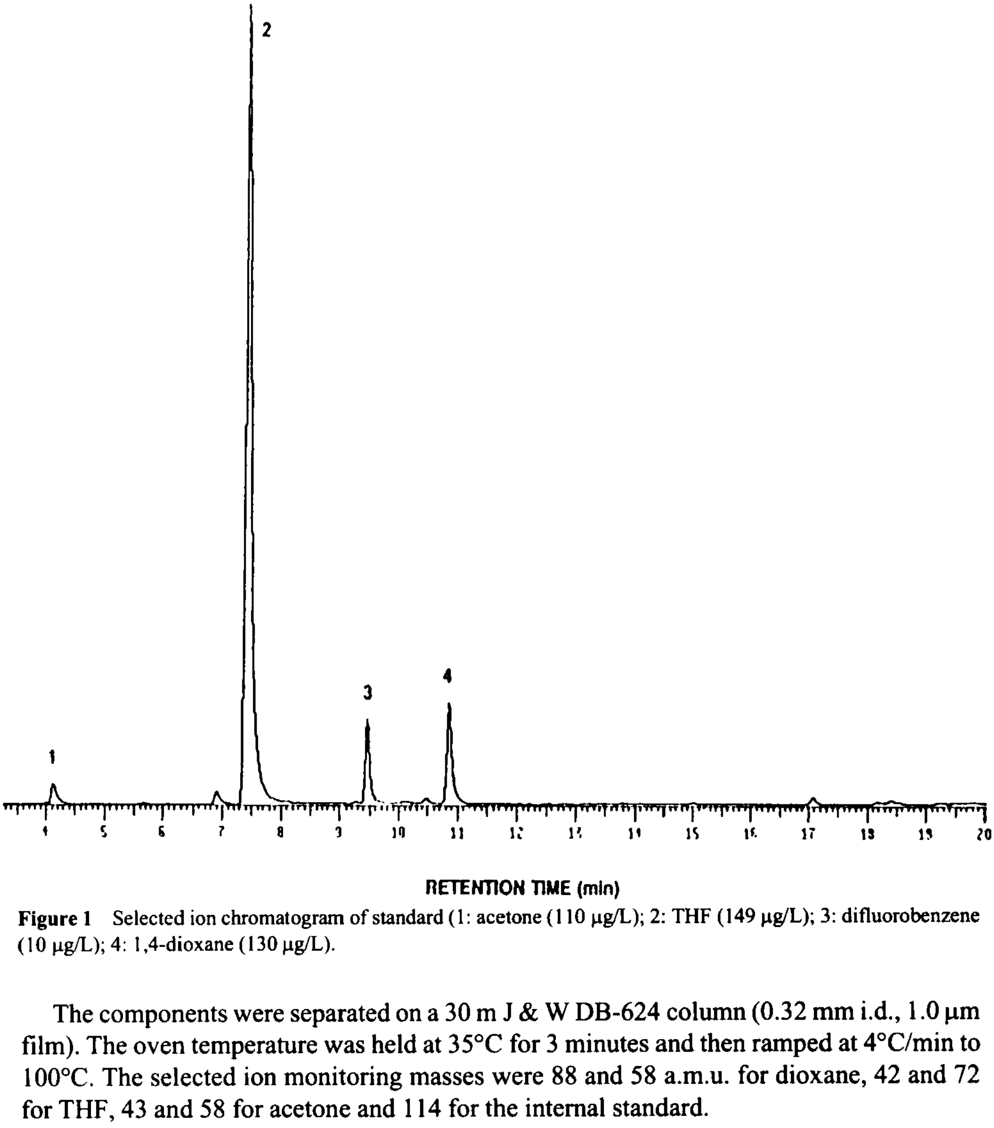

Figure 1 Selected ion chromatogram of standard (1: acetone (110 μg/L); 2: THF (149 μg/L); 3: difluorobenzene (10 μg/L); 4: 1,4-dioxane (130 μg/L).

The components were separated on a 30 m J & W DB-624 column (0.32 mm i.d., 1.0 μm film). The oven temperature 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 a.m.u. 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 40mL/min. The total analysis time per sample was about 60 minutes but the dynamic thermal stripping procedure was conducted while the previous sample was being analyzed allowing samples to be run every 35 minutes.

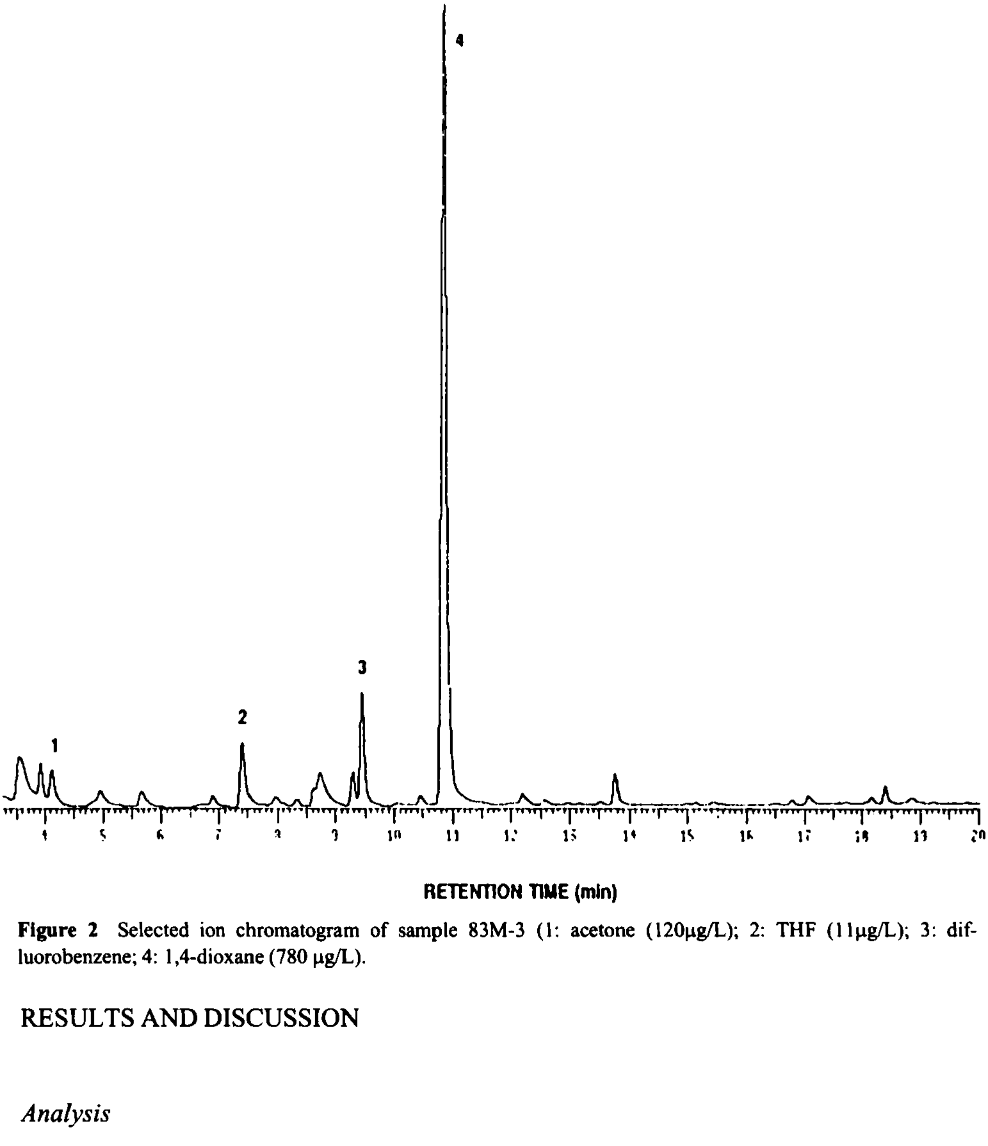

Figure 2 Selected ion chromatogram of sample 83M-3 (1: acetone (120μg/L); 2: THF (11μg/L); 3: difluorobenzene; 4: 1,4-dioxane (780 μg/L).

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.

It was found that increasing the sparging temperature did not improve stripping efficiency and required a longer drying period. Practical quantitation limits of 13, 3 and 55 μg/L were achieved for dioxane, THF and acetone respectively. These PQLs are routinely achievable detection limits with relatively good certainty that any reported value is reliable within prescribed limits. The method is linear over a range of 10 to 500 μg/L for dioxane ($r^2 = 0.9988$).

The linear ranges are considerably smaller for THF and acetone, being about 5 to 100 µg/L and 50 to 250 µg/L, respectively.

Aqueous standards were unstable, lasting less than 72 hours before noticeable losses occurred. However, the groundwater samples which were collected in standard 40 mL vials (EPA Method 624) with no headspace and stored in the dark at 5-10°C were stable for up to 3 months. Replicate samples were stored and then analyzed at different times after sampling and did not degrade within this period.

A selected ion chromatogram of a standard analyzed by the described method is presented in Figure 1. A selected ion chromatogram of a typical sample, 83M-3, is also presented (Figure 2). This particular sample was one of the few that contained all three oxygenated solvents.

GROUNDWATER QUALITY MONITORING

The Gloucester Landfill site has been described in detail elsewhere.[5,6,11,12] A wide assortment of organic solvents and other laboratory wastes were disposed of in unlined trenches overlying a sand and gravel aquifer. These disposals took place between 1969 and 1978. The plume of contaminated groundwater from this site (Special Waste Compound, Figure 3) 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.

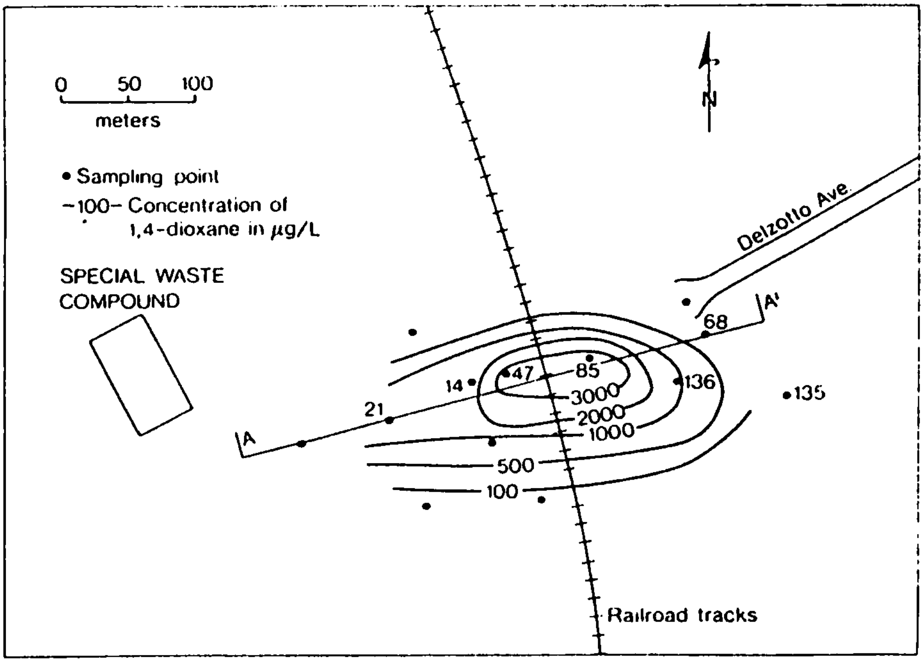

Figure 3 Plan view of 1,4-dioxane plume at the Gloucester Landfill near Ottawa, Ontario.

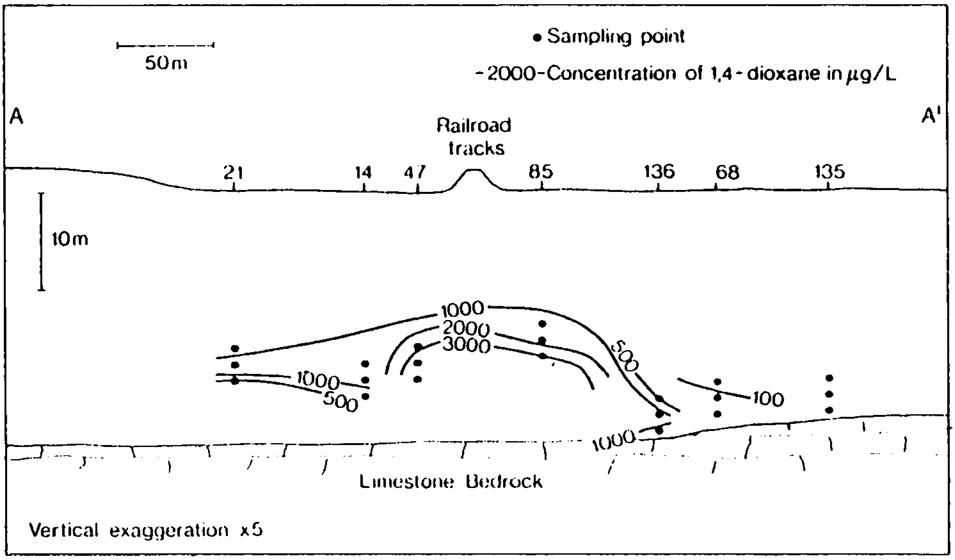

Figure 4 Cross-section of 1,4-dioxane plume through A-A'.

The groundwater samples were obtained using a peristaltic pump to remove water from a selection of points in multilevel samplers at the site.[5,6] The samples were taken in 40 mL VOA vials with no headspace and stored at 5-10°C until analysis.

During September of 1989, 33 groundwater samples were taken and analyzed by this thermal stripping procedure. From the analytical results the plume of 1,4-dioxane was mapped and is presented in plan view (Figure 3) and cross-section (Figure 4). The contours in plan view are based upon the maximum concentration in each multilever sampler. Only the dioxane plume is shown since concentrations of THF and acetone were much lower and contamination was not nearly as areally extensive. The seven numbered multilevels on Figure 3 were used to prepare the cross-section in Figure 4. Note that five of the seven points are projected on to the cross-section A-A'.

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