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原著

토양중 Thiolane 농도 결정방법

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Determination of Thiolane Concentration from Soils by Purging Apparatus

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ABSTRACT

The unknown amount of thiolane retained on different soil matrix was characterized by employing an uniquely designed glass vessel, which was forced to purge the prepared slurry sample so that thiolane may diffuse into Tenax/charcoal tube. Thiolane can be recovered ranging from approximately 89 % at 1 ppm regardless of soil types, which was not consequently affected by potential biodegradation during sample preparation. For 5 ppm, thiolane is more recoverable up to 92 % for sand, whereas it was poorly recovered as low as 85 % for clay. It strongly suggests that controls should be considered when soil types varied in a concerned area. The technique was eventually capable of determination of thiolane for the samples taken from the site which led to be taken into consideration for proper site remediation.

Key words : Thiolane, Soil Contamination, Analysis

1. Introduction

Thiolane has been found from groundwater samples in LWTF (Liquid Waste Treatment Facility) located in Brisbane, Australia. It was reported that the sulfolane contained in Sulfinol waste sludge, which had been careless dumped, has been supposed to be converted into thiolane by the act of facultative bacteria for past 20 years. The facultative bacteria in soils can use sulfolane as electron acceptor and then reduced it into thiolane as demonstrated (Schrementi and Meganathan, 1986, 1987). Thiolane is widely used as a warning odorant for odourless natural gas and herbicides (Carlucci et al., 1984). It is appeared to be moderately toxic (Kirk-Othmer, 1983), but its strong smell is offensive to humans at very low concentrations (i.e. headache, vomiting, and nausea)(Moschandreas et al., 1982; Bradstreet et al., 1985; Schmidt and Meyer-Schmidt, 1985; Coy, 1987). The threshold value has been established as low as 0.5 ppb (Bradstreet et al., 1985). Thiolane has been assayed in gases (Moschandreas et al., 1982; Bradstreet et al., 1985; Coy, 1987; Parlman and Williams, 1979; Hoshika et al., 1987) and water (Schrementi and Meganathan, 1987; Waggott, 1981; Barber and Davis, 1985; . Yasuhara et al., 1992; Yasuhara et al., 1993a, 1993b; Rivasseau and Caude, 1995).

To our knowledge, there has been no effort on analysis of thiolane in the soil matrix even though (Lorprayoon and Condrate, 1983) has attempted to obtain infrared (IR) absorption spectral information of thiolane on clay suspension. This paper reports a simple, highly sensitive procedure to quantitate thiolane in soil using ultrasonic extraction combined with a direct purging procedure and subsequent GC-FID analysis in conjunction with Tenax/charcoal tube (50 : 50).

2. Materials and Methods

2.1 Apparatus

The novel aspect of this technique consists of purging thiolane from a slurry sample onto a Tenax/charcoal tube as presented in Thiolane is purged from soil slurry by maintaining a concentration gradient between the soil and added water. A driving force is maintained for the diffusion of thiolane from the solid phase to the liquid phase. A special glass vessel was thus

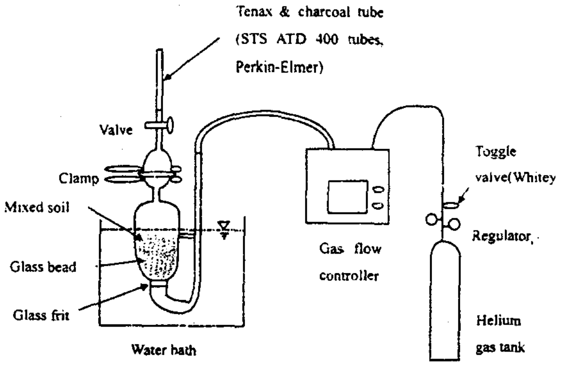

Fig. 1. Schematic of thiolane purging from soil slurry

Table 1. The Operating Condition of Gas Chromatography for Thiolane Quantification

Column	DB624 fused slica megabore column 30m x 0.53 mm i.d., 0.3μm film thickness	
Injection mode	Splitless	
Injection volume	2.0 μl	
Temperature	Initial temperature	60℃
	Initial time	2 minutes
	Program rate	10 ℃ per minute
	Final temperature	220 ℃
	Final time	2 minutes
	Detector temperature	350 ℃
	Carrier(Helium)	1.7 ml/min

designed to intimately mix the soil, liquid, and helium gas stream. The purge vessel was made of Pyrex glass. A 9 mm opening at the top allows introduction of the slurry sample. A fine glass frit (0.2 mm pore size) and glass beads (ie. 4 to 5 mm OD) were used to improve the mixing intensity at the slurry sample with the helium gas and therefore maximise the purging effect of thiolane on a Tenax/charcoal tube. The vessel accommodates 2 g of soil and 20 μl of MilliQ water which become soil slurry. It is connected to the (50 : 50) tube via a ball and socket joint.

The vessel is first equilibrated to a temperature of 40℃ (Kirk-Othmer, 1983). The vessel contents are then purged with helium at 40 μl/min ((0.2 μl/min) at 40℃ for 12 min using a Varian 3700 GC flow controller. The flow rate is regularly checked with a gas flow meter (Accu Rate 100 - J&W Scientific). Thiolane that is adsorbed onto the Tenax/charcoal was desorbed via an in-lined Perkin Elmer ATD 400 (oven temperature : 290℃ at 15 min, valve temperature : 220℃). Analyses were performed on a GC-FID (Perkin Elmer, AutoSystem GC) as shown in Table 1.

2.2 Reagents

Thiolane (AR) is purchased from Aldrich Chemicals. 1,4-Dioxane (AR), purchased from BDH Chemicals, was used as an internal standard. 1,4-Dioxane was chosen because it has a similar density and boiling point with thiolane (Table 2).

Table 2. Comparison of Physical Properties of Thiolane and 1,4-Dioxane

	Density (g/ml)	Boiling point (℃)
Thiolane	0.96 to 1.0 (18℃)	100 to 102
1,4-Dioxane	1.032 to 10.034 (20℃)	119

2.3 Soil Sampling

Soil samples were collected from different depths along 11 locations in the study area using a split spoon sampler (75cm Lx7.5cm I.D.). The soil was immediately placed into a stainless steel tube (5cm x 3.5cm I.D.), filled to capacity and sealed off with parafilm. The tubes were placed in an iced box until arrival at the analytical laboratory. The soil that was actually placed into the purging vessel for analysis was taken from the middle of the stainless steel tube.

Subsequently, it was slid by stainless steel rod into the vessel on Sartorius 2007MP balance. Two grams of sample was weighed out and then 20μl of volatilized milli Q water with helium containing 1,4-Dioxane of internal standard was added into the vessel, and then was closed immediately the valve of the joint. The internal standard was made with the 20μl of milli Q water as 50 (l of 400 ppm 1,4-Dioxane. The internal standard then had a concentration of 1 ppm in the slurry.

2.4 Breakthrough Test and Calibration Curve Preparation

In order to ensure that no thiolane broke through the Tenax/charcoal tube, a purging trial was set up with two Tenax/charcoal tubes in series. The peak of thiolane of 5ppm and internal standard of 1ppm was only detected in the first tube and therefore a Tenax/charcoal tube was adopted in the purging process.

Two grams of soil (i.e. clay and sand) was weighed into the purging vessel. The weight was recorded to the nearest 0.001g. Immediately after weighing soil samples for purging preparation, 20g of the sample was weighed in a tared crucible and then the percent dry weight of the soil samples was determined by drying overnight at 105℃ and subsequent cooling in the desiccator overnight. Then, 0.5μl of thiolane at different concentrations and 50(l of 200ppm of 1,4-Dioxane were added into the purging vessel. A control was prepared in the same manner including autoclaving soil at 121℃ and 1 atm for 1 hr on three consecutive days using Tomy ES 315 high pressure steam steriliser and subsequent adding of $HgCl_2$ to be 1000 ppm (Davis, 1994). The samples were vigorously shaken and left at 18℃ in an incubator for 1 day. The control was checked to see if there was any biodegradation of thiolane and internal standard while the samples are incubated. The sample was then treated in an ultrasonic water bath (Transsonic TP 690, frequency 50~60Hz, Germany) for 20 min to break up agglomerated soil clods. Subsequently, the vessels were equilibrated in water bath at 40℃ for 15 mins. (Carlucci et al., 1984). The 60/80 mesh Tenax/charcoal tubes is slid on the top of the vessel. The valve to helium gas cylinder was then opened to commence purging.

3. Results and Discussion

3.1 Controls

At Table 3 the results were summarized from three experiments in order to quantify thiolane : 1) in liquid phase only, 2) in slurries, containing both salt and water; and 3) in autoclaved slurry samples.

The recovery observed in this study was 6% higher than that achieved by headspace purging methods normally used on water samples (84(2%) (Carlucci et al., 1984). This result indicates that the proposed method was quite accurate for determining thiolane concentrations from clay and sand samples. Results from the biological control indicated that there was no biological degradation during the incubation and purging procedures.

3.2 Chromatogram of Peaks

Thiolane and 1,4-Dioxane of soil sample are eluted in (3.8 minutes) and (4.3 minutes) as shown in Figures 2.

3.3 Field Study

Table 4 shows results of adsorbed thiolane concentrations for soil samples collected from the study area. The measured concentrations ranged from more than 254 (g-thiolane/kg-dry soil to undetectable levels (method detection limit : 10 (g-thiolane/kg-dry soil) which indicated that the proposed method can be used to delineate a spatial

Table 3. Characterization of Methods Development

#$C_{thiolane}/C_{1,4\text{-}Dioxane}$	*$A_{thiolane}/A_{1,4\text{-}Dioxane}$				
	1) STD without soil	2) STD with soil		3) control	
		clay	Sand	clay	Sand
1	0.526	0.475	0.456	0.475	0.465
	0.527	0.457	0.472	0.475	0.468
	0.526	0.468	0.467	0.467	0.471
	0.527	0.474	0.471	0.476	0.469
	0.526	0.460	0.469	0.468	0.474
Recovery (%)		89	89	90	89
5	2.339	1.989	2.127	1.935	2.124
	2.278	1.950	2.125	1.975	2.159
	2.305	1.974	2.127	1.982	2.103
	2.322	1.974	2.126	1.971	2.121
	2.328	1.979	2.126	1.963	2.122
Recovery (%)		85	92	85	92

* A : Peak area, # C : Concentration

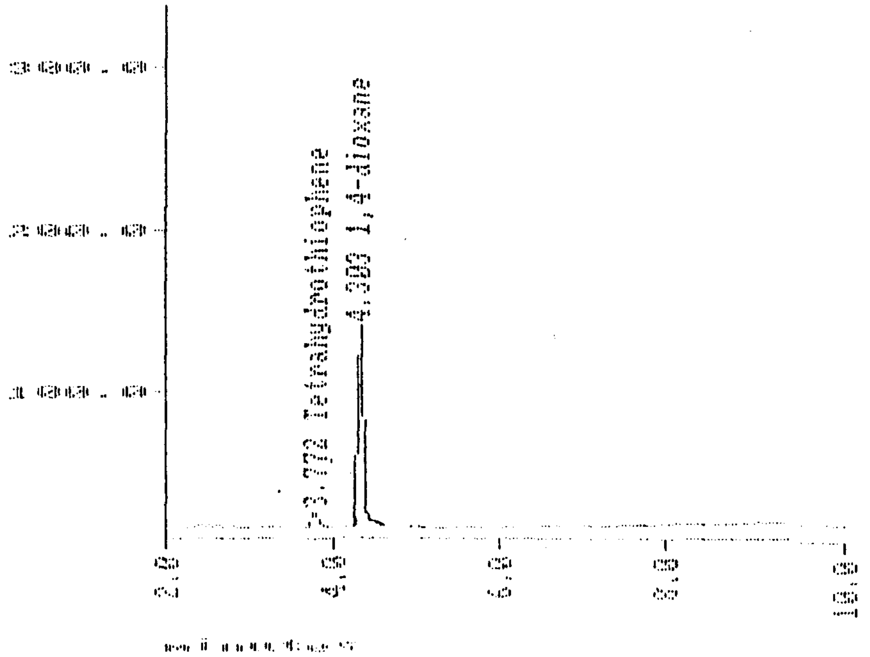

Fig. 2. Chromatogram of thiolane observed on soil sample

Table 4. Thiolane Concentrations observed in the Study Area

depth(m)	Thiolane((g/kg-dry soil)										
	Location No.										
	1	2	3	4	5	6	7	8	9	10	11
0.65	60										
0.65	59										
1.40	156	35	50	0	49	38	0	46	28	0	0
1.40	47										
2.75	87	59	66		0	42	37	98		0	0
3.50	59										
4.25	95	0			0		49	107	254	16	
5.20	78			93							
5.95		0	87			183	0	171	33	82	30
6.75				47							
7.45		54	28			30		47		38	14
8.25	90			0	46						
8.65	53									109	
9.00						34		48	35		
10.00					145					147	

variance of plume in the study area.

4. Conclusion

The specially designed purging vessel was successfully used in the analysis of thiolane from the soil matrix regardless of soil types such as clay and sand. It allowed same extent of recovery for both clay and sand in the analysis of 1 ppm of thiolane, whereas in higher concentration of 5 ppm, sand sample gave 5% higher recovery than clay. Based on the field study, the remediation action would be properly considered for the recovery of the site.

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