

Gas Chromatography

Author:

Kira. Yang

Angela LaCroix-Fralish

Lenny Pitts

Zhangjiang High-Tech Park
Shanghai, PRC

Determination of t-Butyl Methyl Ether (MTBE) in Water and Soil

Introduction

As an alternative to tetraethyl lead, t-Butyl methyl ether (MTBE) has been widely used as an octane enhancer for gasoline, added to increase the oxygen content and reduce

carbon monoxide in support of regulatory emissions requirements. Studies have found increasingly high levels of MTBE in groundwater, often a result of accidental spills or leaking underground storage tanks. In water, MTBE dissolves more rapidly than it volatilizes, and is slow to biodegrade in the environment. Water contaminated with MTBE has a pungent odor and unpleasant taste, even when contamination is present in low concentrations. Thus, small amounts of MTBE contamination can render a drinking water source unfit for human consumption.

The United States Environmental Protection Agency has listed MTBE as a “possible” carcinogen to human beings on the basis of inhalation cancer tests, but has not yet set a Maximum Contaminant Level (MCL) indicating the legal threshold limit for concentrations of the compound in public water supplies. Many US states, including California, Colorado, Massachusetts, New Jersey and Oregon, have established water quality standards ranging from 13 to 70 µg/L.

In this paper, a method for the determination of MTBE in water and soil was established using the PerkinElmer Clarus® 690 GC/FID with the TurboMatrix™ HS-40 Trap. The methodology offers a simple, sensitive and efficient means of detecting MTBE in a wide range of environmental matrices.

Experimental

Sample Preparation and Extraction

A t-Butyl methyl ether standard was obtained from ANPEL Laboratory Technologies (Shanghai) Inc., and the pure water utilized in the experiment was produced by Mini-Q.

A number of matrices were collected for use in the experiment: potable water taken from an office faucet, rainwater collected on the day of the experiment, and soil obtained from the office garden. The extraction procedure used is as follows:

1. Dilute 3.0 g soil sample in a bottle with 20 mL pure water.
2. Seal the bottle and stir for 2 hours.
3. Isolate 5 mL supernatant layer in a headspace vial.

Method precision was investigated with six injections of the level 5 standard. Method detection limits were determined by analyzing seven replicates of the level 1 standard. Method recovery was investigated by spiking 0.096 µg of standard in 5 mL water samples and supernatant of soil samples.

Instrumentation

The PerkinElmer Clarus 690 GC/FID and TurboMatrix HS-40 Trap were used to perform these experiments with the conditions presented in Table 1. A PerkinElmer Elite-624 column (60 m x 0.25 mm x 1.4 µm) was used to separate the eluting compounds. The Clarus 690 GC/FID, used in conjunction with the TurboMatrix HS-40, offers a turnkey solution for the determination of a variety of volatile and semi-volatile compounds, providing the performance and stability you need, without sacrificing sensitivity or versatility.

Calibration

The calibration curve was prepared by dissolving 25.0, 50.0 µL of 0.096 µg/mL MTBE, 10.0, 20.0, 50.0 µL of 0.96 µg/mL MTBE and 10.0, 20.0, 30.0, and 40.0 µL of 9.63 µg/mL MTBE, respectively, in 5 mL of pure water (Table 2). Each calibration standard was transferred to a separate headspace vial. All vials were sealed immediately with the PTFE side of the septum facing toward the sample.

Results and Discussion

The chromatogram of a calibration standard is shown in Figure 1. The calibration curves were plotted as the peak

Table 1. Analytical parameters.

HS Parameters	
Needle Temperature	95 °C
Transfer Line Temperature	105 °C
Oven Temperature	90 °C
Trap Low Temperature	40 °C
Trap High Temperature	280 °C
Dry Purge (Helium)	5 min
Trap Hold Time	8 min
Desorb Time	0.5 min
Thermostating Time	30 min
Pressurization Time	1 min
Decay Time	2 min
Outlet Split	OFF
Column Pressure	35 psi
Vial Pressure	35 psi
Desorb Pressure	10 psi
GC Parameters	
Headspace Connector	Universal Connector
Inlet Temp	150 °C
Carrier Gas	Helium
Initial Oven Temp	35 °C
Oven Hold	3 min
Ramp	10 °C/min to 105 °C
2nd Oven Temp	0 min
Ramp	20 °C/min to 180 °C
3rd Oven Temp	1 min
FID Temperature	200 °C
H ₂	40 mL/min
Air	400 mL/min
Attenuation	-6

area versus the amount of analyte. The determination coefficients (r^2) was over 0.9996, showing the reliability of the analysis in the range of 0.48 – 77.02 µg/L (Figure 2). Table 3 summarizes the results for method detection limit (MDL), repeatability and percent recovery. Area repeatability measured by the relative standard deviation (RSD) was found to be 4.01%. Retention time precision was calculated and found to be 0.07%. The recovery was 96.2% for tap water sample, 90.5% for rainwater sample, and 87.6% for soil sample. The method detection limit was 0.29 µg/L.

Table 2. Calibration points employed in this study.

Compound Name	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
MTBE (µg/L)	0.48	0.96	1.93	3.85	9.63	19.26	38.51	57.77	77.02

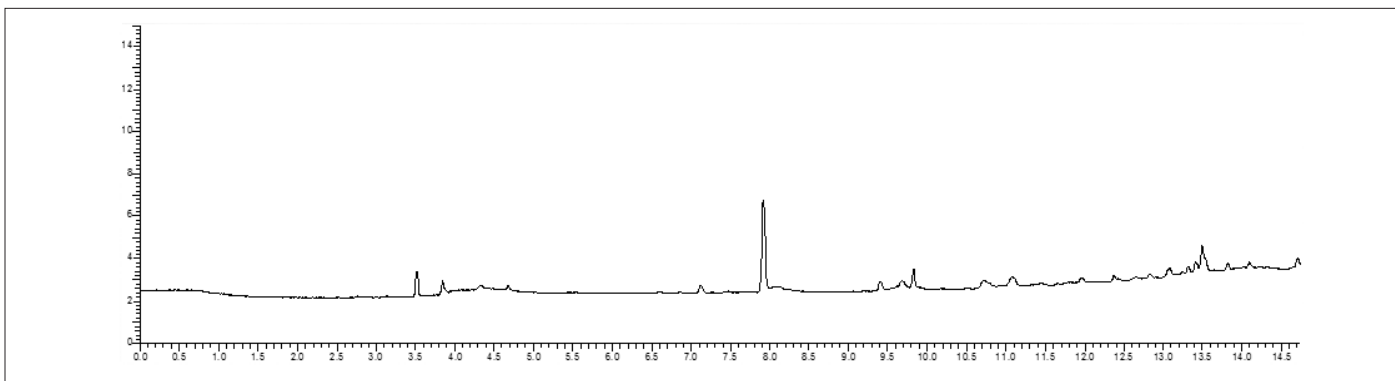


Figure 1. The chromatogram of a calibration standard (level 6).

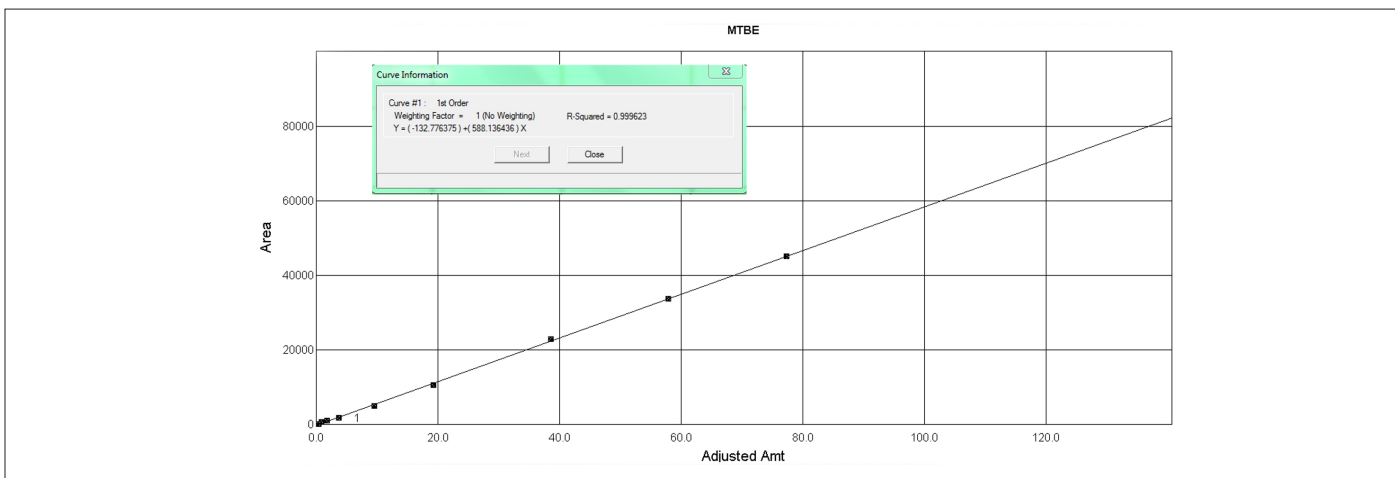


Figure 2. The MTBE calibration curve.

Table 3. Results for MDL, repeatability and recovery.

Compound Name	MDL (µg/L)	Repeatability (RSD%)		Recovery (%)		
		RT	Area	Tap Water	Rainwater	Soil
MTBE	0.29	0.07	4.01	96.2	90.5	87.6

Summary

The results obtained in this experiment demonstrate the ability of the PerkinElmer Clarus 690 GC/FID and the TurboMatrix HS-40 Trap to efficiently quantify fuel oxygenates in a variety of matrices. The precision, recovery and linearity achieved by the instrument ensure a reliable determination of MTBE at ultra-trace levels, enabling accurate monitoring of environmental samples.