Analysis of MTBE and BTEX by Direct Aqueous Injection GC/MS

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1. ABSTRACT

A direct aqueous injection (DAI) method was developed for the determination of the fuel oxygenate, methyl tert-butyl ether (MTBE), along with benzene, toluene, ethyl benzene, and xylene (BTEX) and several other alkylated benzenes. These compounds are commonly found in contaminated groundwater due to leaking underground gasoline storage tanks. Methanolic stock solutions of these compounds (plus nine other volatile components) were spiked into distilled water at the 20- to 20,000-ppb levels and analyzed by direct aqueous sample introduction into a fused-silica capillary column interfaced to a benchtop ion trap mass spectrometer (GC/MS). Using the method of external standardization, the response factors, retention times, concentration range, and method detection limits for the 14 compounds were determined. Replicate data (n=7) was collected at each concentration and precision data (%RSD) generated. For comparison, method detection limits (MDLs) were determined from the data by three commonly used methods.

Replicate injections by DAI of a 10-ppm solution over a 16 hour time period (n=24) were used to determine the concentration decay in water of the 14 constituents in an open container at room temperature.

2. INTRODUCTION

Methyl tert-butyl ether (MTBE) is a "fuel oxygenate", a chemical added to motor fuels primarily for the purpose of improving fuel combustion and reducing emissions such as carbon monoxide and other pollutants. MTBE can find its way into groundwater by a variety of means, often from leaking underground fuel tanks. Its toxicology is poorly understood. While volatile, MTBE is also miscible with water and therefore poorly purgeable. It is therefore not amenable to the Agency's normal chemical analysis methods. We have developed a method for the direct aqueous injection (DAI) analysis of poorly purgeable pollutants, as well as other volatile and semivolatile components present in gasoline-contaminated groundwater. This technique uses direct aqueous sample injection into a gas chromatograph/mass spectrometer for qualitative and quantitative analysis. DAI is rapid, sensitive, easily applied, and generates no waste solvent.

3. EXPERIMENTAL

Standard Solutions

Standard and stock solutions were prepared from 2 commercially available methanolic Supelco Standards, Methyl tert-Butyl Ether (catalog # 4-8483) and Volatile Organic Compounds Mix 2 (catalog # 4-8777). A 10-μL syringe was used to add the appropriate volume directly through the septum into an inverted 1.8-mL autosampler vial containing 1.0 mL of distilled water (see Table 1). The lower concentrations were prepared from a 1 to 100 dilution of the standards. Aqueous standards were run within 10 hours of preparation.

Conditions

After some initial experimentation, the following conditions were used to collect the data for method development.

GC Conditions

initial temperature	40 °C
initial time	1 min
temperature rate	10 °C/min
final temperature	240 °C
final hold time	0 min
total run time	21 min
transfer line	240 °C

SPI Injection

initial temperature	60 °C
initial time	0.1 min
temperature rate	150 °C/min
final temperature	280 °C
final hold time	18 min
total run time	19.56 min
injection volume	0.5 μL (delivered by autosampler)

Mass Spectrometer

scan range	40 to 300 amu
scan time	0.6 sec/scan
mass defect	0 mmu/100 amu
acquire time	20 min
solvent delay	2 min
background mass	45 m/z

Column

dimensions	25 m × 0.20 mm × 0.5 μm film
liquid phase	5% diphenyl-95% dimethyl polysiloxane
head pressure	10 psig helium
linear velocity	35 cm/sec at 40 °C

Table 1. Preparation of aqueos standards.

final concentration (ppb)	initial concentration (μg/mL)	volume added (μL)
20	20*	1
200	20*	10
2 000	2 000	1
10 000	2 000	5
20 000	2 000	10

* 1/100 dilution of initial standard solution.

4. CALCULATIONS

Method Detection Limit Calculation #1 (MDL1)

This EPA formulated MDL calculation is based on a statistical argument (1,2) and is defined as the minimum concentration of a substance greater than zero that can be measured with 99% confidence. It is calculated from the formula:

$$MDL = (\% \ rsd \times 3.143 \times concentration)$$

where % rsd is the relative standard deviation in per cent, and 3.143 Student's t value which, in this case, is for 7 replicate injections. The method stipulates that the concentration of the replicates must not be greater than 5 times the resulting calculated MDL.

Method Detection Limit Calculation #2 (MDL2)

This calculation (3) is a quick and simple estimate of the MDL based on the assumption that the minimum area count that is discernible from background is the same for any analyte. It uses the formula:

$$MDL = (area \ discernible \ from \ background \div \ response \ factor)$$

where the area discernible from background is defined as the area of a peak that is three times the noise level. Response factor is the average peak area over the linear range per amount (in this case in picograms injected on-column).

Method Detection Limit Calculation #3 (MDL3)

This method detection limit calculation (4) is determined from standard injections, in this case a 10-ppm standard. The S/N was determined for each analyte's quantitation ion using the GC/MS software and extrapolated down to a S/N of 10. This approach purportedly gives more realistic MDLs for the DAI-GC/MS than the MDL1 method above.

Concentration Decay in Water Calculation

A logarithmic half-life decay model did not fit the data sufficiently to determine a half-life so a linear model was used to calculate the rate of concentration decay with time. A least squares regression analysis was applied to the time (independent variable) and concentration (dependent variable) data and the slope used as a measure of decay reported in Table 2 as units of ppb/min.

Table 2. Compound number, quantitation ion, retention time, response factor, %RSD, MDLs, decay rate, and water solubility (5).

no.	compound	quan ion (m/z)	reten time (min)	resp factor (area/pg)	RSD (%)	MDL1 (ppb)	MDL2 (ppb)	MDL3 (ppb)	decay rate (ppb/min)	solubility (ppm)
1	Methyl-t-butyl ether	73	2:09	10.2	14	12	26	6	-11.46	51000
2	Benzene	78	3:09	15.2	10	21	11	11	-11.99	1800
3	Methylbenzene	91	4:46	22.7	11	6	8	20	-10.35	526
4	Ethylbenzene	91	6:29	21.0	13	7	10	20	-9.50	206
5	m-Xylene	91	6:37	20.8	13	9	8	76	-9.54	----
6	Styrene	104	7:02	10.9	12	18	17	40	-9.67	320
7	Bromobenzene	158	7:49	7.4	13	9	26	5	-9.19	----
8	1,3,5-Trimethylbenzene	105	8:28	19.3	11	6	9	42	-6.27	----
9	1,2,4-Trimethylbenzene	105	8:57	18.8	13	6	11	31	-6.40	----
10	p-Isopropyltoluene	119	9:29	15.8	11	6	10	20	-4.62	----
11	n-Butylbenzene	91	10:04	16.6	14	14	9	52	-4.02	----
12	1,2,4-Trichlorobenzene	180	12:14	8.4	13	11	18	127	-4.23	49
13	Naphthalene	128	12:24	33.7	9	8	5	64	-6.66	31
14	1,2,3-Trichlorobenzene	180	12:52	9.1	11	9	15	48	-4.46	----

Figure 4. MTBE response curve of average (n=7) response versus concentration.
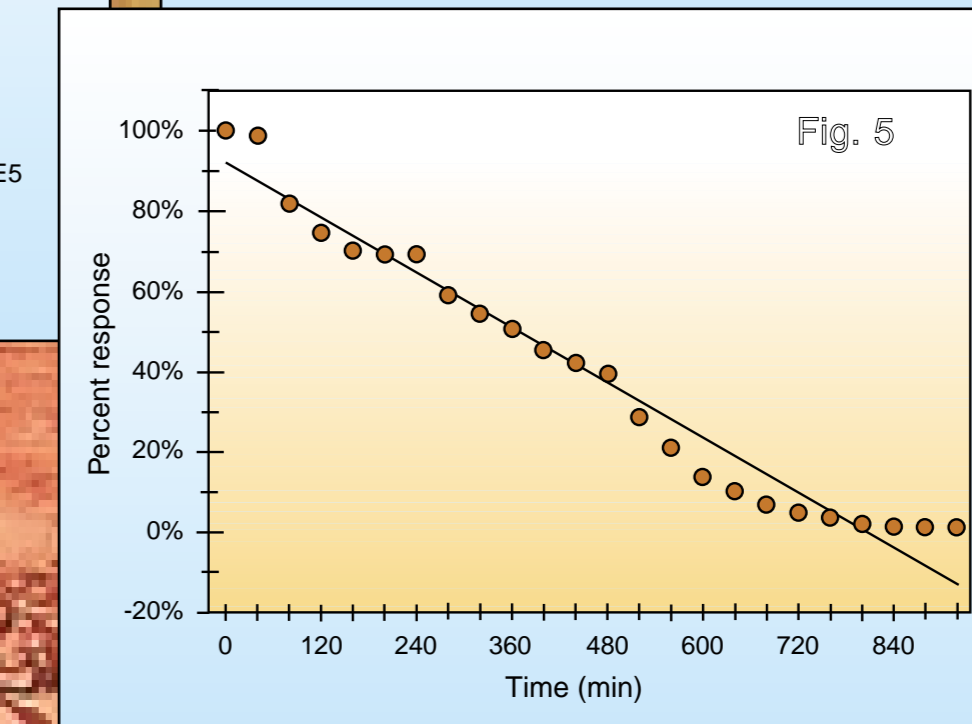
Figure 5. Concentration decay of MTBE with time.

Figure 3. Bar graph showing average response of all 14 analytes versus concentration.

Chromatogram Plot   C:\SATURN\DATA\TEST47   DATE: 01/25/00
Comment: 10PPM MTBE AND BTEX
Scan: 800 Seg: 1 Group: 0 Retention: 7.99 RIC: 2584 Masses: 51-284
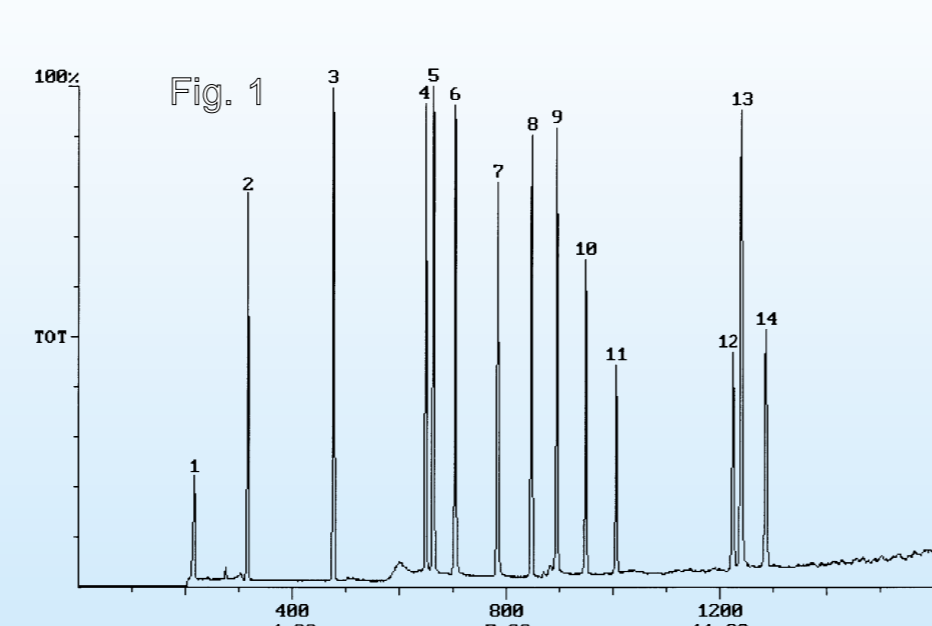Plotted: 1 to 1600   Range: 1 to 2000   100% = 117613

Figure 1. Gas chromatogram of 14 analytes at 10-ppm level. Peak number cross-referenced to compounds listed in Table 2.
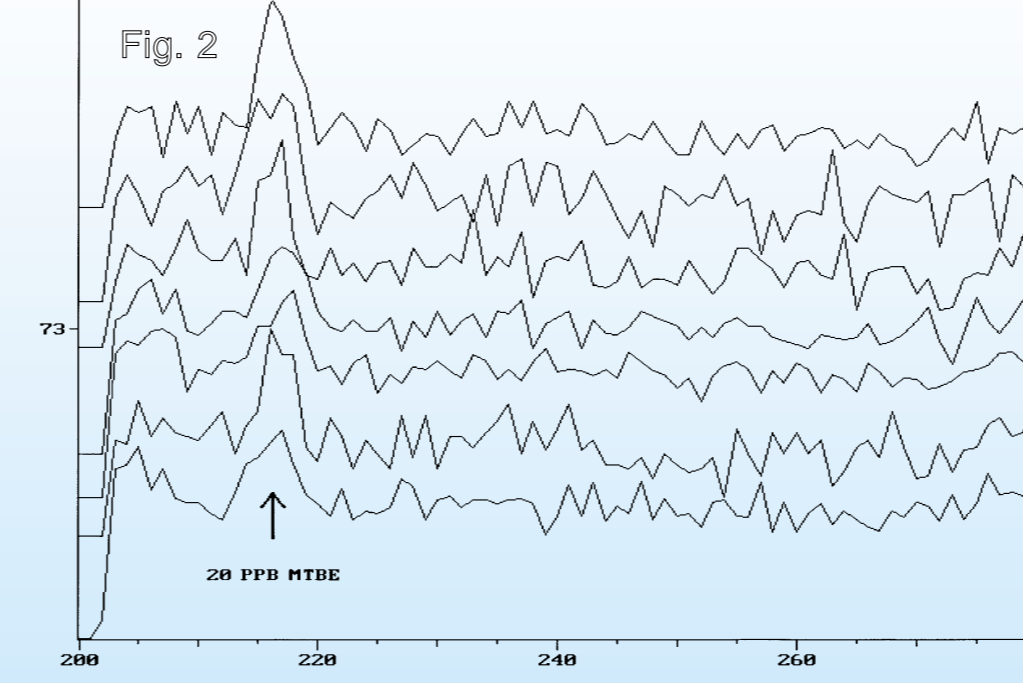
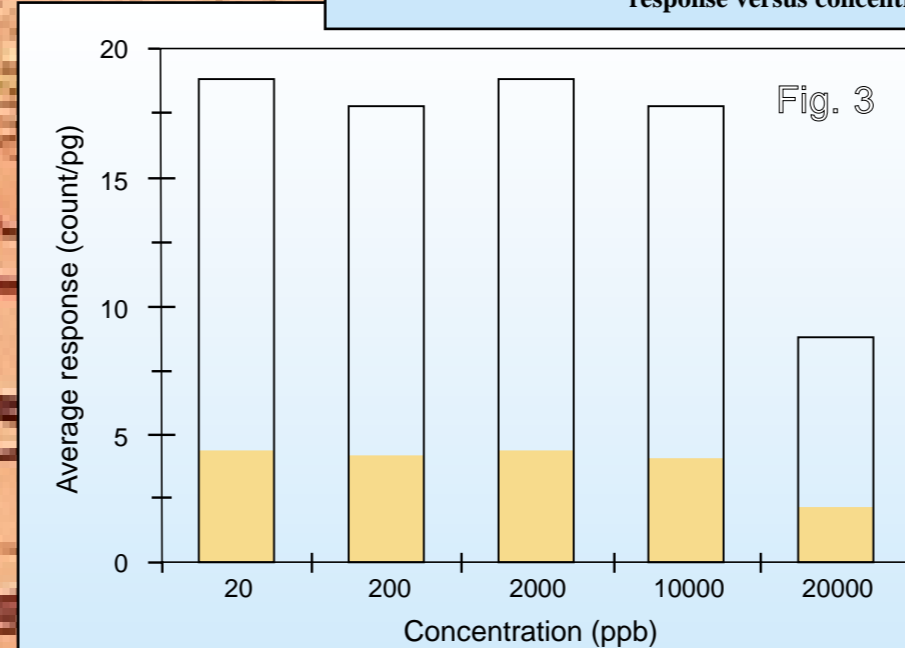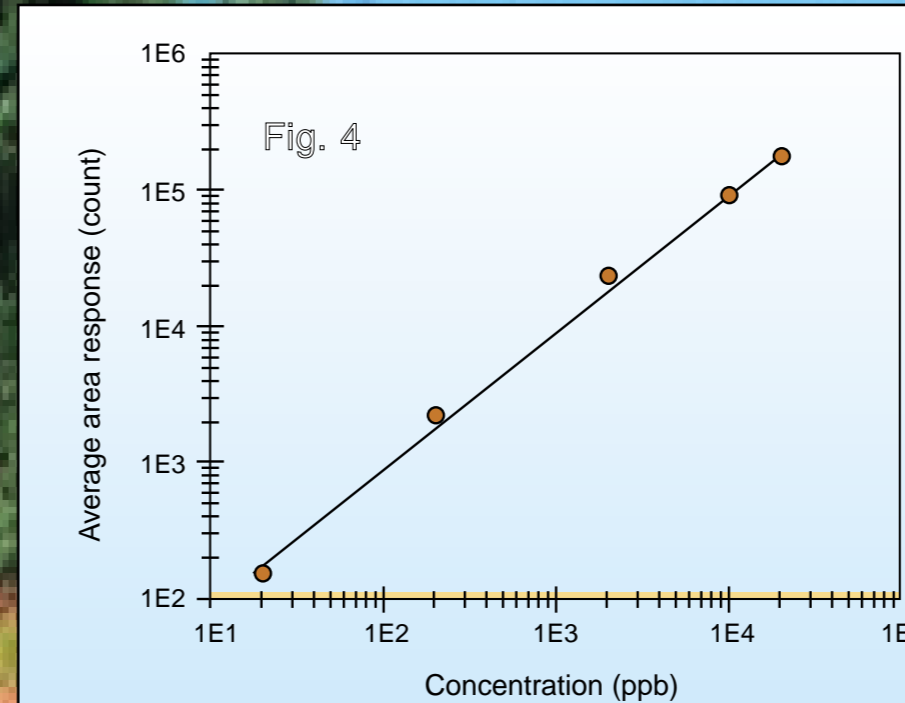Figure 2. Reconstructed ion chromatogram (m/z 73) of replicate (n=7) 20 ppb MTBE injections.

5. CONCLUSIONS

1) DAI analysis showed good chromatographic separation and peak shape.
2) Adequate sensitivity (20 ppb) and precision (average of 12% RSD at 200 ppb level) was obtained for MTBE and 13 other components.
3) DAI was applicable over a 3-decade concentration range.
4) DAI is rapid, easily applied, and generates no waste solvent.
5) Application of DAI to concentration versus time showed 50% of volatiles were lost in average of approximately 500 minutes under quiescent conditions.

6. References

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